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Recent development in rare earth doped phosphors for white light emitting diodes

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Abstract: As new light sources for next-generation illumination, white light-emitting diodes (WLEDs) have been extensively developed and are commercially available due to their excellent advantages, such as high efficiency, energy-saving, compactness, long operational lifetime and environmental friendliness. Currently, WLEDs with high color rendering are mainly based on wavelength conversion by one or more phosphor materials. In this review, the recent developments of phosphors for WLEDs were introduced combined with the relative work of our group. The common methods for generating white light for blue/ultraviolet (UV) WLEDs were summarized, including: (1) optimizing the commercially used phosphors; (2) developing some new phosphors based on UV LEDs chips; (3) realizing white light emission based on single host. Moreover, some typical new developed phosphors and their luminescence properties were introduced.

Keywords: rare earths; phosphors; white LEDs; development

Phosphor-converted white light emitting diodes (pc-WLEDs)-based, solid-state lighting has been highly focused on due to the characteristics of high efficiency, low applied voltage and high power efficiency in the past decades[1,2]. By virtue of these advantages, WLEDs are currently widely used not only in point light sources but also in wide-illumination equipment, back-lighting of liquid-crystal TVs and high-power automotive headlights[3]. In phosphor converted WLEDs, phosphors are an important material in lighting technology and have been widely investigated. The most common commercial WLEDs are a combined blue-emitting InGaN chip and a yellow $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) phosphor, whose efficacy can be greater than 80 lm/W for 1 W devices, higher than compact fluorescent lamps (CFLs) and comparable to linear fluorescent lamps[4]. However, they have low color rendering index (CRI; usually less than 75) and high correlated color temperatures (CCT; usually lower than 6000 K) due to the lack of the red component. To solve this problem, the red component together with the yellow emission based on YAG:Ce^{3+} or some red emission phosphors which can be efficiently excited by blue light are required based on nitride or oxynitride. However, most nitride-type phosphors require critical preparation conditions, such as high temperature, high pressure and expensive raw materials[5]. To obtain higher efficiency WLEDs with appropriate CCT and higher CRI, more scientific efforts have been therefore focused on using near-ultraviolet (n-UV) or ultraviolet (UV) LED chips coated with blue/green/red tricolor phosphors or the single phased full color emission phosphors[6–8]. As a result, new phosphors with high efficiency and good thermal stability are desperately needed. In this review article, we highlighted the current methods to optimize the white light emission for blue/UV LEDs and the structure was as follows: (1) optimizing the commercially used phosphors, both by blue or UV LED chips excitation; (2) developing some new phosphors based on UV LEDs chips; (3) realizing white light emission based on single luminescent center or energy transfer between Eu^{2+}/Ce^{3+} and Mn^{2+} ions in a single phase.

1 Synthesis methods

The synthesis method of phosphors has played a significant role in determining the microstructure, luminescence properties, and quantum efficiency of phosphors. The common methods to synthesize powder phosphors for WLEDs can be summarized as follows: (a) the conventional solid-state reaction method[9,10]. This method is

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available for most oxide or oxynitride phosphors. The most significant advantage of this method is simple and efficient, which is suitable for industrial production. The stoichiometric raw materials were mixed and ground in an agate mortar in ethanol and then the mixture was pre-heated in an alumina crucible at high temperature for some hours under reducing atmosphere (5%H_2:95%N_2 or 40%NH_3:60%N_2). (b) The gas pressed sintering method[11,12]. Unlike the conventional solid-state reaction method, this method needs severe experimental conditions, such as high temperature (usually above 1700 ºC) and pressure (usually 1.0 MPa), causing a high cost. The gas pressed sintering method is usually applied for preparing pure nitride phosphors and the sintering process can be summarized as follows: stoichiometric amounts of raw materials were ground in an agate mortar in a glove box to form a homogeneous mixture. The concentrations of both moisture and oxygen in the glove box were <1 ppm. Thereafter, the powder mixture was transferred into a BN crucible and heated at high temperature for some hours under high-purity nitrogen (99.9995%) atmosphere at a pressure of 1.0 MPa.

2 Recent development in phosphors for WLEDs

2.1 Development in optimizing commercially used phosphors

YAG:Ce is a famous yellow phosphor that has been commercially used for blue light pumped WLEDs. However, YAG:Ce has a deficient red emission, leading to its bluish-cold light, as mentioned in the introduction section, which cannot meet for many sophisticated applications such as light sources in offices, schools, medicals, hospitals and hotels. To enrich the red emission in YAG:Ce, some researchers attempted to co-dope some ions (Cr^{3+}, Pr^{3+} and Sm^{3+}) which can emit red emission into YAG:Ce[13–16]. However, the red emission cannot be greatly enhanced due to weak absorption in blue region, meanwhile the emission intensity of Ce^{3+} is decreased greatly. The other attempt is to replace Y^{3+} or Al^{3+} by other cations (i.e. Tb^{3+} , Gd^{3+}, Mg^{2+}-Si^{4+}) to change the crystalline field around Ce^{3+} and shift the emission spectrum to longer wavelength[13,17,18]. This method also causes the emission intensity of Ce^{3+} to decrease, while the shift of Ce^{3+} emission is limited. In our recent work, we introduced Mn^{2+} into YAG:Ce^{3+} [19]. The emission spectra of Mn^{2+} singly doped YAG samples show three bands, and the orange band is the strongest one, which means Mn^{2+} ions not only occupy two kinds of Al^{3+} sites, but also occupy Y^{3+} sites in YAG host, and the most inclined sites are Al^{3+} (I) sites. Quadrivalence ions including Zr^{4+}, Ge^{4+} and Si^{4+} are introduced to balance the charge difference between Mn^{2+} and Al^{3+}. Among them, Si^{4+} as charge compensator exhibits the best tunable effect on controlling the Mn^{2+} emissions in YAG:Ce^{3+}, $x$$Mn^{2+}$, the reason is due to its suitable ionic radius of Si^{4+}. For $Y_3Al_5O_{12}$:0.06Ce^{3+},0.04Mn^{2+},0.04Si^{4+} sample, the integral emission intensity is 101% that of com-YAG:Ce (P46-Y3) and it has better thermal quenching characteristics than com-YAG:Ce phosphor. The Commission International de L'Eclairage (CIE) chromaticity coordinates are (0.453, 0.526), which is redder than that of YAG:0.06Ce^{3+} phosphor (0.436, 0.540), as shown in Fig. 1.

The yellow phosphor Sr_3SiO_5:Eu^{2+} has attracted a lot of attention due to the application in UV pumped WLEDs. The combination of the UV LEDs, Sr_3SiO_5:Eu^{2+}, and other color-emitting phosphors yields superior luminous efficiency as well as high color stability. However, the color rendering of as-prepared Sr_3SiO_5:Eu^{2+} is not perfectly satisfactory for WLED applications because its

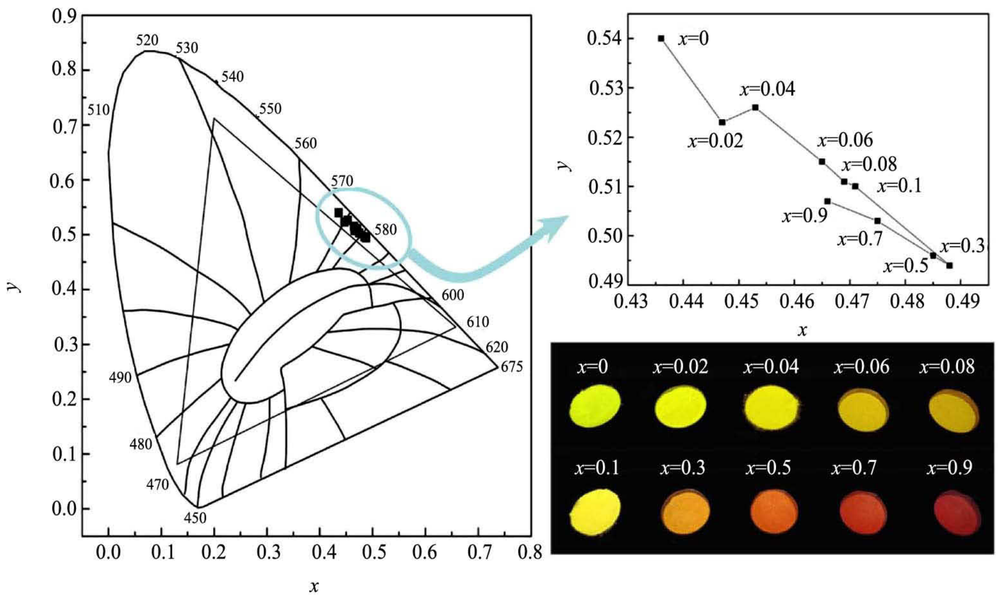

Fig. 1 CIE chromaticity diagram and photograph of YAG:0.06Ce,xMn,xSi ($0\leq x\leq 0.9$) samples (reproduced with the permission from Ref. [19], copyright ©2012 Optical Society of America)