Color-converted remote phosphor prototype of multiwavelength excitable borosilicate glass for white light-emitting diodes*

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We report a unique red light-emitting Eu-doped borosilicate glass to convert color for warm white light-emitting diodes. This glass can be excited by from 394 nm-peaked near ultraviolet light, 466 nm-peaked blue light, to 534 nm-peaked green light to emit desired red light with an excellent transmission in the wavelength range of 400–700 nm which makes this glass suitable for the color conversion without great cost of luminous power loss. In particular, assembling this glass to commercial white light-emitting diodes, the tested results show that the color rendering index is improved to 84 with a loss of luminous power by 12 percent at average, making this variety of glass promising for inorganic "remote-phosphor" color conversion.

Keywords: white light-emitting diodes (WLEDs), color rendering index, remote phosphor, borosilicate glass

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1. Introduction

Phosphor converted white light-emitting diodes (pc-WLEDs) have achieved wide applications particularly in the indoor lighting field, which is expected to replace the conventional incandescent and fluorescent lamps in the future.[1] Generally, the WLEDs are realized by the combination of a GaN-based blue LED chip and yellow phosphors.[2−4] For high power WLEDs, the temperature increase of p–n junctions of WLEDs in service leads to serious degradation of phosphor particles and packaging resin, and then decrease of luminous efficiency. Fortunately, a new variety of bulk phosphor, called the remote phosphor, appears in the form of silicon/phosphor particle composite very recently, providing a solution for the above-mentioned thermal threat to WLEDs and a means to convert lighting resource from point to plane.[5,6] Furthermore, the luminous efficiency can be effectively improved by the remote phosphor packaging. However, some serious drawbacks are need to be overcome, including high correlated color temperature (CCT) and low color rendering index (CRI) mainly owing to the deficiency of red emission. In order to compensate red emission, color mix with red light with AlInGaP red chip or red-emitting phosphors to YAG: Ce^{3+} yellow light has been adopted to generate warm white.[7−9] Moreover, all-inorganic remote phosphor such as glass, glassceramics, and transparent ceramics could be superior to those organic/phosphor composites particularly in chemical stability. Thus, the glass system of SiO_2–Al_2O_3–Na_2O–SrO doped with Eu^{3+} can be applied to color addition of red for white light emitting diodes to improve the quality of white light.[10] Meanwhile, the borosilicate glass as a bulk material might meet the requirements of high and stable transmission coefficient in the visible range. It

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is stable, inexpensive, and easy to be made into a large plate,[11] and has been widely investigated.[12,13] In this study, we synthesized a Eu-doped borosilicate glass and observed a unique photoluminescence of this luminous glass excitable with near ultraviolet light at the wavelength of 394 nm, blue light at 466 nm, and green light at 534 nm simultaneously, enabling a red addition to color mix for WLEDs.

2. Experimental

The compositions of all glass samples with different Eu-doping concentrations (mole percent) are listed in Table 1. Glass was melted in air using an alumina crucible at the temperature of 1500 °C for 2 h, followed by quickly pouring into a preheated stainless steel mold for quenching. To ensure the thermal and structure stability, the glass samples were annealed at temperature of 600 °C for 1 h and then cooled naturally to room temperature in a high temperature furnace. All the as-prepared glass samples were cut and then polished to pellets in a size of 10 mm in diameter and 3 mm in thickness.

Table 1. Nominal composition of all glass samples (%).

Sample	Composition/%
SBB0	$35SiO_2$–$35B_2O_3$–30BaO
SBB2	$35SiO_2$–$35B_2O_3$–30BaO–$2Eu_2O_3$
SBB4	$35SiO_2$–$35B_2O_3$–30BaO–$4Eu_2O_3$
SBB6	$35SiO_2$–$35B_2O_3$–30BaO–$6Eu_2O_3$
SBB8	$35SiO_2$–$35B_2O_3$–30BaO–$8Eu_2O_3$
SBB10	$35SiO_2$–$35B_2O_3$–30BaO–$10Eu_2O_3$
SBB12	$35SiO_2$–$35B_2O_3$–30BaO–$12Eu_2O_3$
SBB14	$35SiO_2$–$35B_2O_3$–30BaO–$14Eu_2O_3$

Transmission spectra were measured by a UV-Vis spectrophotometer (Purkinje General, TU-1900, China). Photoluminescence (PL) spectra were recorded on a fluorescence spectrometer equipped with a xenon light source (Hitachi F-4500, Japan). CRI and the luminous power were measured on a plus UV-Vis-near IR spectrophotocolorimeter (Everfine PMS-50, China). All of these measurements were carried out at room temperature.

3. Results and discussion

Figure 1 shows the optical transmission spectra of the glass samples with different Eu-doping concentrations. In the visible range, the glass without doping does not exhibit any transition bands, while all Eu-doped samples exhibit a complete difference with high and stable transmission coefficients. The transmission spectra consist of several inhomogeneously broadened f–f transitions of the Eu^{3+} ions. The bands peaked at around 394, 466, and 534 nm correspond to $^7F_0$–$^5L_6$, $^7F_0$–$^5D_2$, and $^7F_1$–$^5D_1$ transitions of Eu^{3+} ions, respectively.[14,15] The intensities of those peaks at around 394, 466, and 534 nm increase gradually with the increase of Eu-doping concentrations due to the absorption enhancement of Eu^{3+} ions transition. In the ultraviolet range, the transmission coefficients of all samples drop dramatically to zero with the decrease of wavelength, which is most likely due to the electronic transitions in the glass. The band gap in inorganic glass depends mainly upon two factors: one is the atomic number of anions and cations, and the other is the proportion of non-bridging oxygen (NBO) in the glass.[16] Because of narrowed energy band gap with increasing NBO sites in borosilicate glass, the addition of Eu_2O_3 to borosilicate glass increases the number of NBO sites, leading to a red-shift of the UV transmission edge.

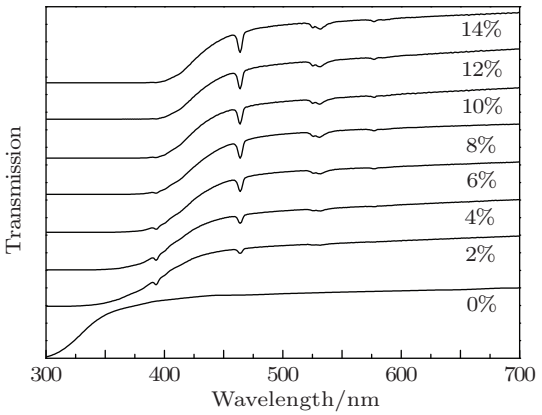


Fig. 1. The transmission spectra of Eu-doped borosilicate glass with different Eu-doping concentrations.

As shown in Fig. 2(a), Eu^{3+}-doped borosilicate glass could be excited effectively by near ultraviolet light at the wavelength of 394 nm, blue light at 466 nm and green light at 534 nm. Two strongest peaks of the excitation spectrum at 466 and 534 nm are found to correspond exactly to the emission from InGaN blue-chip and YAG: Ce^{3+} band respectively. In Fig. 2(b), several characteristic emission peaks are observed, the intensity of the emission for 466 nm ranks as the highest, for 394 nm as the lowest, and for 534 nm lies in between. The strongest emission of the sample is located at the wavelength of 617 nm, corresponding to $^5D_0$–$^7F_2$ transition of Eu^{3+} ions.[17]

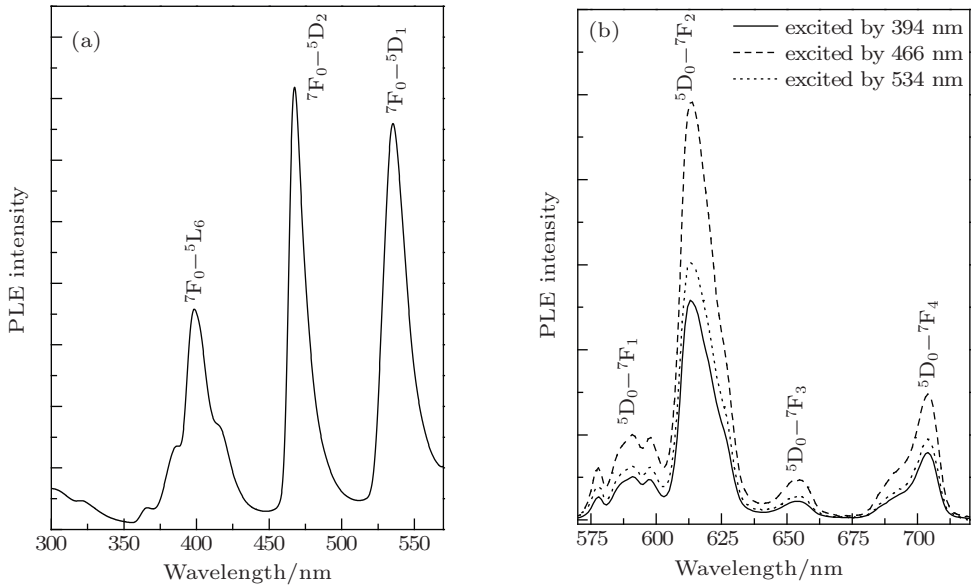


Fig. 2. (a) Photoluminescence excitation (PLE) spectrum of borosilicate glass (SBB8) sample with emission wavelength 617 nm, (b) emission spectra excited by near ultraviolet light at the wavelength of 394 nm, blue light at 466 nm, and green light at 534 nm.

Figure 3(a) shows the emission spectra of all samples excited by blue light at the wavelength of 466 nm, while Fig. 3(b) shows the relationship of intensity and doping concentration. As the doping concentration varies from 2% to 14%, the emission intensity increases until the doping concentration of Eu^{3+} is up to 8%, and then decreases for higher concentrations. Together with the absorption proportion in Fig. 1, this decrease of emission intensity for higher concentrations is attributed to the concentration quenching.

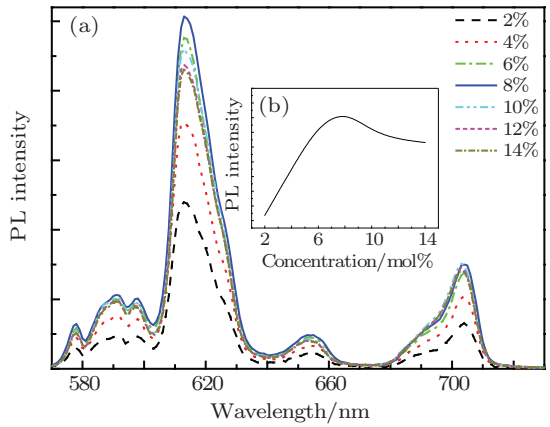


Fig. 3. (colour online) Emission spectra of borosilicate glass with different Eu-doping concentrations excited by blue light at the wavelength of 466 nm. The inset shows the relationship of intensity and doping concentration.

To examine the conversion effect with this glass, a prototype was fabricated by combining this fluorescence glass with a commerical WLED. Figure 4 shows the emission spectra of the prototype with the WLEDs of InGaN/YAG:Ce. It is observed that by covering the glass on WLEDs, the red component is added to the white light while the luminous efficiency tends to be reduced. Without fluorescence-converted glass, only two emission bands exist while the red emission bands are also observed upon applying the glass. In this way, the red component was mixed to improve the color quality.

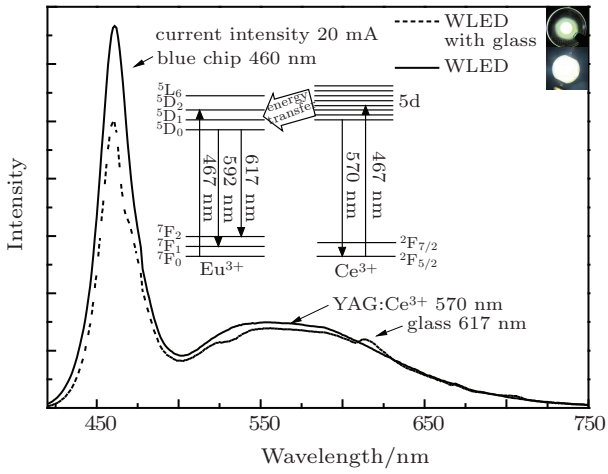


Fig. 4. The emission spectra of a WLED with and without Eu-doped borosilicate glass converter.

The CRI of a combination of the WLEDs with the Eu-doping glass slices drived by varied current intensity are measured, and for comparision, CRI of WLEDs are aslo included. As shown in Fig. 5, it is observed that the CRIs of the WLEDs covered by the Eu-doping glass are improved to 82.7, 83.4, 83.2, 83.9

and 84 compared with those of WLEDs, drived by 10, 15, 20, 25, and 30 mA, respectively. The results obtained from the experiments indicate, to some extent, an improvement of CRI vlaues for the WLEDs covered by luminous glass.

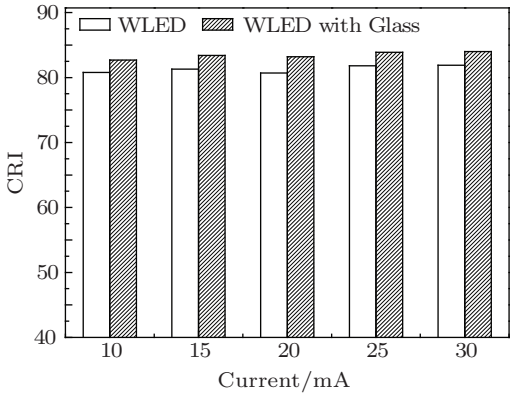


Fig. 5. The change of CRI of WLEDs with and withut luminous glass converter drived by varied bias current density.

As shown in Fig. 6, the luminous power of the combinational prototype are also evaluated. Preliminary experimental results show that the loss ratio of luminous power of the WLED covered by the fluorescence-converted glass is less than 12%, indicating a feasibility of applying this borosilicate glass as an excellent red-added material to improve the color quality of the present WLEDs.

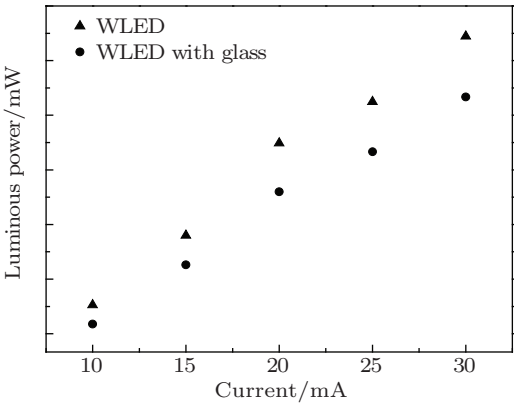


Fig. 6. The increase of luminous power of WLED with light conversion glass.

4. Conclusions

In summary, Eu-doped borosilicate glass is prepared with high-purity grade oxides or salts as the starting materials via melt quenching method in air. In the visible light range, the Eu^{3+}-doped borosilicate glass exhibits a high and stable transmission coefficient. The glass could be excited efficiently by near ultraviolet light at the wavelength of 394 nm, by blue light at 466 nm, and by green light at 534 nm. The emission intensity increases with the increase of Eu^{3+} concentration up to 8%, and then quenches for higher concentrations. To some extent, CRI has been improved by covering this converting glass to WLEDs with a loss ratio of the luminous power less than 12%. Through further optimization of the composition, structure and combination, the Eu-doped borosilicate glass is a promising red flourescent material to enhance the red emission. A trade-off for this luminous glass has to be made by taking into account of CCT, CRI, the luminous efficiency and the uniformity of light extraction upon light/color conversion from "point" to "plane" light with this all-inorganic remote phosphor.

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