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Preparation and luminescent properties of the coating of phosphor in lead-free glass by multilayer screen-printing

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ABSTRACT

The coating of phosphor in glass (PiG) for white light emitting diodes (WLEDs) has been prepared by multilayer screen-printing and low sintering-temperature. The lead-free and low-melting glass was synthesized, and the main compositions were P_2O_5-ZnO-B_2O_3 (PZB). The microstructure, luminescence spectra and lifetime behaviours of coating were investigated. The results of microstructure revealed that decreasing content of phosphor and increasing sintering temperatures were benefit for the coating because of better sintering. Based on the luminescence spectra, the suitable content of phosphor was 25% and sintering temperature was 600 °C. Under blue light (460 nm) exciting, the broad yellow band around 550 nm was obtained. It's indicated that the white light can be achieved. The coating showed longer lifetime with increasing content of phosphor and lower sintering temperature. The obtained coating of PiG is expected to be an excellent material instead of organic resin for high-power WLEDs packaging.

1. Introduction

In the last few decades, the white light emitting diodes (WLEDs) have been the indispensable light sources for illumination applications since they are mercury-free, low light attenuation, compact and energy-efficient [1–4]. They have gradually replaced the traditional lamps to be the essential lighting source of new generation [5]. The most commonly used WLEDs are formed by the two-color mixing method of the blue LED chip and yellow phosphor [6–9]. Combined with the blue InGaN chips, Ce-doped yttrium aluminum garnet (YAG:Ce) phosphor has been successfully applied in WLEDs [10]. The organic resins color converters are usually utilized for packaging phosphor because of its low cost, simple fabrication and mature processing [11,12]. However, this kind of WLEDs exhibits poor heat-resistance [13–15], low aging-resistance and weak humidity-resistance. It causes the degradation of luminous intensity and the change of emission color. The long-term reliability of WLEDs becomes more and more significant with increasing output power of blue or n-UV LED for general illumination.

To solve the problems, a new kind of WLEDs using glass-ceramic for packaging has been studied [16–20]. This inorganic material shows high-temperature resistance and easy formability compared with organic resins. Therefore, this new developed phosphor in glass (PiG) is expected to be a promising candidate to achieve WLEDs with high-temperature resistant, high-humidity resistant and long-life. The zinc phosphate glass has the advantages of lead-free, low-melting [21], inexpensive and good optical performances. After the addition of B_2O_3, the glass reveals better thermal stability and chemical durability [22,23]. Moreover, P_2O_5-ZnO-B_2O_3 (PZB) glass can keep the stability of rare ions because of its three dimensional rigid tetrahedral network structure [24]. Therefore, PZB glass shows great research value and application potential.

In this paper, PZB glass was chosen as the glass matrix due to its great properties, especially lead-free and low-melting, based on our previous work [25,26]. The PiG with commercially available YAG:Ce yellow phosphor were fabricated by multilayer screen-printing, which is a simple and usual method to fabricate the coating on the glass substrate [27]. The microstructure, photoluminescence properties and lifetime behaviors were analyzed by varying the ratios of phosphor to glass and sintering temperatures. The results show that the coating of PiG has unique advantages comparing

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with organic resins. Our work intend to illustrate the coating has the potential to use for packaging of high-power WLEDs.

2. Experiment and measurement

2.1. Preparation of coating of YAG:Ce phosphor in PZB glass

The fabrication process of coating of PiG is shown in Fig. 1. PZB glass used in this work was prepared with the following compositions in mol (%): (33–40) P_2O_5, (43–50) ZnO, (8–15) B_2O_3, (2–5) Al_2O_3, (3–6) Li_2O, (2–4) Na_2O, (1–3) K_2O, by employing the melt-quenching technique and using high purity $NH_4H_2PO_4$ (99.0%), Li_2CO_3 (98.0%), Na_2CO_3 (99.8%), H_3BO_3 (99.5%), K_2CO_3 (99%), ZnO (99.0%) and Al_2O_3 (98.5%) as raw materials. Each batch was mixed homogeneously and slowly heat up to 260 °C in high-purity alumina crucibles. It was holding at 260 °C for 4 h to prevent P_2O_5 from volatilizing and then melted up to 1200 °C, finally keeping the temperature for 2 h. The obtained melt was cast in graphite moulds followed by annealing for 1 h at about 400 °C and then slowly cooled down to the room temperature. Then the milling process was carried out to grind a wide variety of the glass powder into 200–300 mesh of size. The powder of PZB glass, YAG:Ce phosphor (the content is 10%, 15%, 20%, 25% and 30%), binder (ethyl cellulose) and solvent (alpha-terpineol) were stirred for 1 h to prepare the glass paste for multilayer screen-printing. The printed coating on the glass substrate was sintered at 550 °C, 600 °C, 650 °C and 700 °C [26] respectively and then cooled down. Finally, the phosphor particles were embedded in the coating.

The process of multilayer screen-printing is shown in Fig. 2 [28]. The glass paste was transferred onto the glass substrate through open areas of patterned screen by a squeegee. Then the coating was dried and the organic solvent was out. The second layer was printed on the first layer. The final thickness of coating mainly depends on the screen-substrate distance, the viscosity of glass paste and the emulsion thickness on the screen [28,29], so we controlled these parameters strictly in the process.

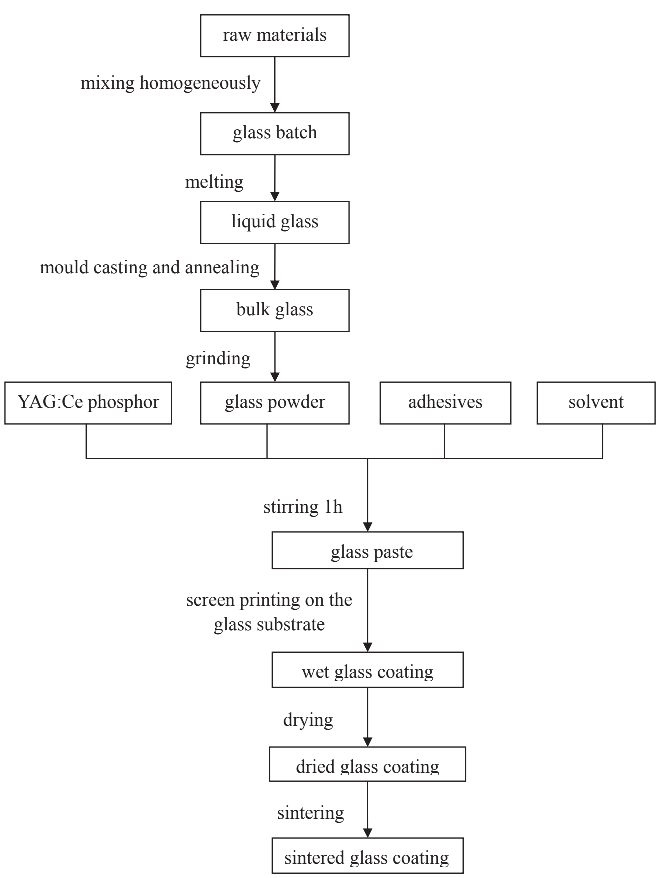

Fig. 1. Fabrication process of coating of PiG.

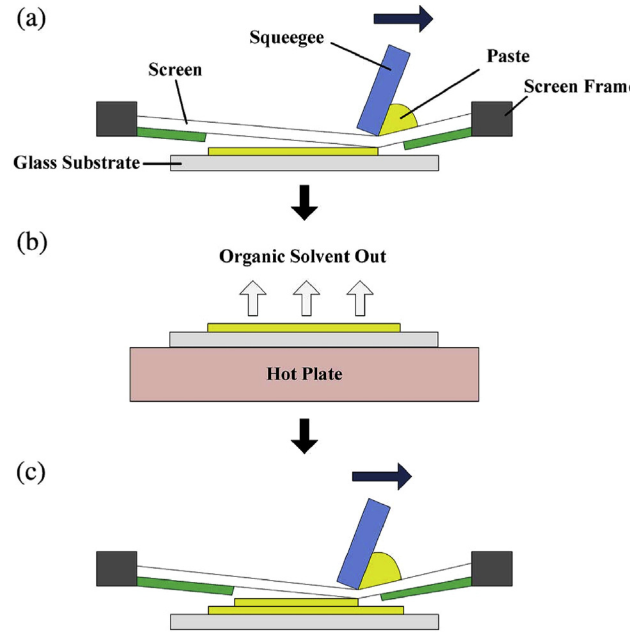

Fig. 2. Schematic diagram of multilayer screen-printing. (a) Printing the first layer. (b) Drying. (c) Printing the second layer and more.

2.2. Measurement

The surface images of coating was characterized by Keyence VHX-600 super depth of field microscope from 100 to 5000 magnifications. The crystallization behavior of coating was analyzed by the D/MX-IIIA XRD system with Cu Kα radiation. The luminescence excitation and emission spectra were measured with Jasco FP-6500 spectrofluorometer using a 150 W xenon lamp as excitation source. The luminescence decay curves were recorded by Edinburgh FLS920 spectrofluorometer with a microsecond pulsed xenon flashlamp μF920.

3. Results and discussion

3.1. Microstructure of coating of YAG:Ce phosphor in glass

3.1.1. Different amount of YAG:Ce phosphor

From 10% to 30%, four samples are chosen to investigate the influence of content of phosphor on the sintering. The content of phosphor and photographs of coating are shown in Table 1. The sintering temperature is 700 °C. In Fig. 3, when the content of

Table 1
Prepared samples of different content of YAG:Ce phosphor.

Sample	a	b	c	d
Content	15%	20%	25%	30%