



Lu₃Al₅O₁₂:Ce@SiO₂ phosphor-in-glass: Its facile synthesis, reduced thermal/chemical degradation and application in high-power white LEDs



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ABSTRACT

Phosphor-in-glass (PiG) approach draws great attention because polymer encapsulants can be avoided during the wLEDs fabrication. However, phosphor degradation occurs, primarily in co-sintering process (with glass) which significantly reduces the emission intensity of the PiG. The aim of the present study is to develop a thermally/chemically robust color converter. Lu₃Al₅O₁₂:Ce@SiO₂ core-shell structure was proposed to reduce phosphor degradation during the PiG fabrication. Uniform SiO₂ shell with tunable thickness was obtained via a facile process. For the PiG samples sintered at 680 °C for 30 min, internal QE of the Lu₃Al₅O₁₂:Ce@SiO₂ based PiG retained 59% of the initial value which was obviously higher than that of the pristine Lu₃Al₅O₁₂:Ce based PiG (48%). A high-power wLED was constructed by coupling the PiG plate with a 440 nm InGaN blue chip. Under a driving current of 500 mA, the device showed a luminous efficacy of 129 lm/W.

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1. Introduction

In recent decades, lighting-emitting diodes (LED) have been receiving large attention as light sources because of their high-energy efficiency, long lifetime and environmental friendliness [1–5]. The LED is basically a *p-n* junction, composed of an InGaN dice that can emit wavelengths from near-UV to blue area. For general illumination purpose, phosphor-converted-white-LEDs (pc-wLEDs) have enormous potential to replace conventional lighting sources, such as incandescent, fluorescent and high intensity discharge lamps [4–8]. Phosphor has been found to have significant effects on the performance of pc-LEDs, and is thus, considered as a key material in such LEDs. Usually, phosphor is blended with organic resins (e.g., silicone) and pumped by a blue LED. However, considerable heat formation (~150 °C) from the chip usually detaches the methyl groups from the silicone, resulting in yellowing of the resin [9]. This result leads to significant deterioration of optical performance of the wLEDs, such as the lumen loss and chromaticity shift [9,10].

To overcome the weaknesses of the polymer binders, high thermally stable, transparent phosphor-in-glass (PiG) inorganic color converters have drawn extensive attention in recent years [3,11–17]. There are mainly two strategies to obtain PiG, one is glass crystallization, which is achieved through controllable crystallization after heating precursor glass at a suitable temperature, and the other is co-sintering of a simple mixture of phosphors and mother glass powders at temperature between 600–800 °C [3,14,17]. Compared with the glass crystallization, the co-sintering route has the advantages of low sintering temperature, wide applicability of phosphors and facile process, indicating its promising future in wLEDs device fabrication.

However, the commercialization prospect of PiG prepared by low-temperature co-sintering route still remains uncertain. Aside from the fabricating cost factor, significant phosphor degradation during the sintering process is an obvious drawback of this method [3,14,15,18]. For example, Zhang et al. reported that the internal quantum efficiency (QE) of a PiG sample (Y₃Al₅O₁₂:Ce phosphor in Sb₂O₃–B₂O₃–TeO₂–ZnO–Na₂O–La₂O₃–BaO glass) reduced to ~45% after sintering at 680 °C for 30 min [19]; Xie et al. reported that luminescence intensity of their PiG sample (β-SiAlON:Eu²⁺ in ZnO–B₂O₃–BaO–Al₂O₃ glass) significantly declined with increasing co-firing holding time [14]. Herrmann et al. reported that low *T_g* glass matrix can be chemically much more aggressive and dissolve the phosphor more easily under the same sintering conditions [20].

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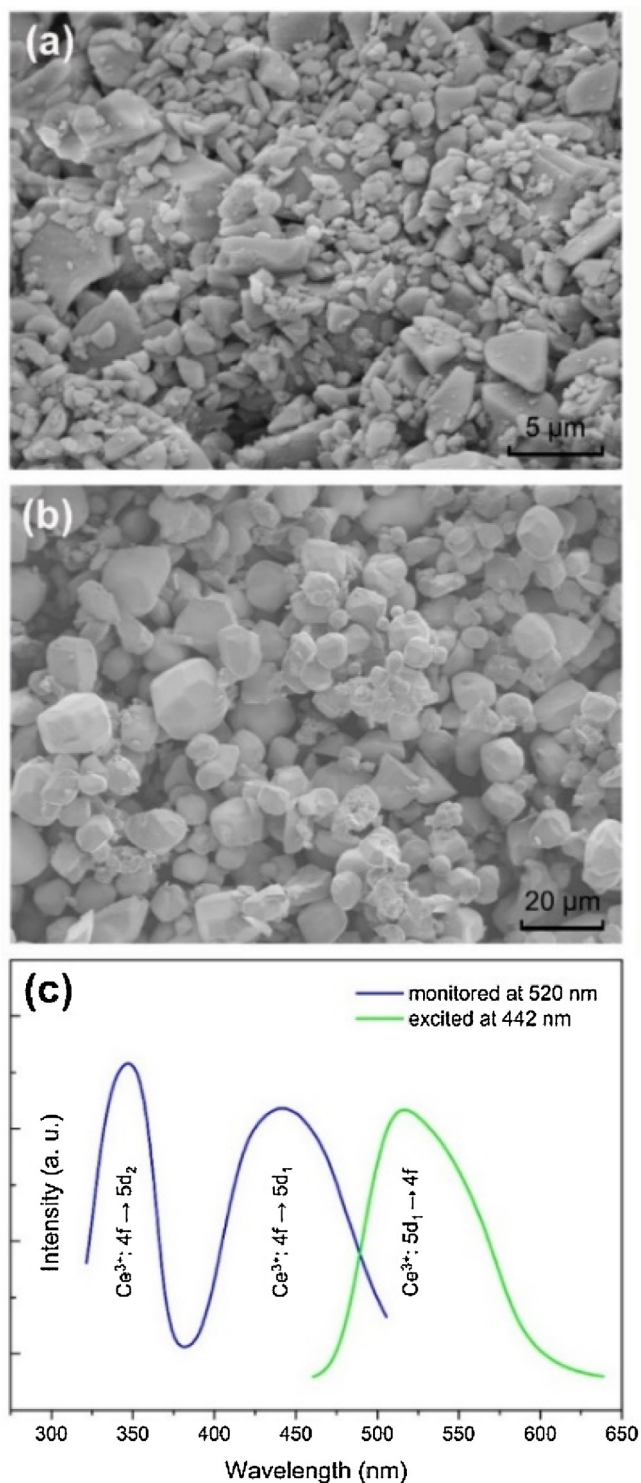


Fig. 1. Properties of the starting materials: SEM images of (a) the commercial glass frits, and (b) LuAG:Ce; (c) photoluminescence excitation (monitored by 520 nm) and photoluminescence (excited by 442 nm) spectra of the LuAG:Ce.

Their PiG (YAG:Ce/LuAG:Ce in Na_2O -CaO- SiO_2) was prepared by a high T_g glass frits, the phosphor degradation was low which showed great potential for the preparation of high quality PiG. However, the transmittance of the PiG was low, which might be caused by the relatively high viscosity of the glass at co-firing temperature. It was found that there are two main reasons that caused phosphor deterioration in the above examples: one is the oxidation of low-valence luminescence center (e.g., $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$) by oxygen, and the other is

the occurrence of interfacial reaction between phosphor and glass matrix [3,14,15,19,21].

Lutetium aluminum garnet (LuAG) crystal is known as an important host material for laser scintillators and luminescent materials due its high shock resistivity and outstanding chemical/thermal stability [6,22–25]. When LuAG crystal is doped with Ce^{3+} , it allows the 5d-4f transitions of Ce^{3+} , which makes the LuAG:Ce an efficient yellow-green color converter for pc-wLEDs. Moreover, the internal QE of commercial LuAG:Ce can reach up to ~90% at room temperature and the luminescence intensity is ~90% of the initial value even at 200 °C [6,22]. Garnet (e.g., YAG:Ce, LuAG:Ce) ceramics or single crystals have superior performance in terms of thermal stability and thermal conductivity [25,26]. At 20 °C, e.g., thermal conductivity of the single crystals YAG:Ce is $\sim 14 \text{ W (m K)}^{-1}$, which is more than 10 times greater than that of the PiG sample (0.9–1.2 W (m K)^{-1}) [26]. However, excessively high fabricating costs and processing difficulty (i.e., Czochralski method or vacuum hot-pressing sintering) are significant obstacles for its application in the field general illumination [23–25]. The PiG route can be seen as a compromise between manufacturing costs and thermal properties.

Because the PiG fabrication requires co-firing of phosphor powders and glass frits at a relatively high temperature (600–800 °C), LuAG:Ce with high thermal/chemical stability can be of great interest. One promising technique to improve the thermal/chemical stability and reduce degradation of phosphors is to encapsulate the phosphor surface with an inert oxide coating (e.g., TiO_2 , Al_2O_3 , Y_2O_3 , and SiO_2) [27–31]. However, to the best of our knowledge, there are no reports to-date on using oxide coating to reduce phosphor degradation of LuAG:Ce during preparation of PiG.

A survey of materials conducted with these features in mind led us to focus on using oxide coating to reduce phosphor degradation during co-sintering and ultimately design a LuAG@ SiO_2 core-shell structure. SiO_2 was chosen as the shell material which is commonly adopted to improve dispersion and thermal stability of phosphors. A thin, uniform, nanometer-thick SiO_2 layer was coated on the surfaces of LuAG:Ce particles. Tunable morphologies of the SiO_2 layer can be obtained by simply adjusting the concentration of the SiO_2 source (colloidal silica). A yellow-green-emitting PiG luminescent material was prepared by co-firing the LuAG:Ce phosphor powder and a Na_2O -CaO- SiO_2 - Al_2O_3 glass frit. The microstructure, transmittance, luminescence property, and thermal stability of the PiG material were further investigated.

2. Experimental procedure

2.1. Coating processing

The LuAG:Ce phosphor (with Ce concentration of 0.7 mol%) was commercially available from Parkathings (Xiamen) Corporation. Colloidal Silica (SiO_2 , 8.4 wt.%, Beijingsaide Co, Ltd.) was used as SiO_2 source and dispersed in deionized water in various mass fractions (10–90 wt.%), then placed in an Erlenmeyer flask with the LuAG:Ce phosphor and stirred vigorously for 30 min. After filtration, washing the precipitate in ethanol and drying at 300 °C for 10 min, SiO_2 -coated LuAG:Ce was obtained.

2.2. Co-firing of PiG

The glass frit with molar composition of 28.3 $\text{Na}_2\text{O}/5.5 \text{ CaO}/8.2 \text{ Al}_2\text{O}_3/58 \text{ SiO}_2$ was obtained from Honghai (Shanxi) Glass Corporation. It had a glass transition temperature of $T_g = 579 \text{ }^\circ\text{C}$ and a softening temperature of $T_s = 685 \text{ }^\circ\text{C}$. The concentration of the LuAG:Ce was 8 wt.%. The glass frits and phosphor were mixed and ground (for 30 min) in an agate mortar, then the powder mixture was compressed into a pellet with a diameter of 20 mm

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