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Design of binder-free phosphor paste for warm white LEDs

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ABSTRACT

Cerium-doped yttrium aluminum garnet (YAG: Ce) is used to convert blue light which is emitted from InGaN-based LED chip for white light. In this study, the phosphor paste was prepared using monodispersed spherical YAG: Ce phosphor synthesized by co-precipitation based on one-pot synthesis. Also, orange-red emitting $Sr_2Si_5N_8$:Eu^{2+} (SSN: Eu) phosphor was added to confirm the change in optical characteristics. Alpha terpineol was used as a paste solvent because it enabled easy screen-printing. Phosphor paste films for optoelectronic devices were prepared by coating on a glass substrate using a doctor blade method. We compared the conversion efficacy, color rendering index (CRI), and correlated color temperature (CCT) of YAG: Ce which is added to various amounts of SSN: Eu. We measured scanning electron microscopy (SEM) images to confirm the difference of porosity between, depending on binder addition.

1. Introduction

Solid-state lighting based on phosphor converted white-emitting diodes (pc-WLEDs) has gained considerable attention as a replacement for conventional incandescent and fluorescent light sources due to their advantages compared with their conventional counterparts, such as luminous efficiency, lower energy consumption, diversity of packaging forms, long operating lifetime, and environmental safety [1,2]. For this reason, these pc-WLEDs have played an important role in wide applications of display backlighting, interior/exterior lighting, general illumination, and high-power automobile headlamps [3]. Currently, the most widely used type of commercial WLED is fabricated from InGaN-based blue chip with cerium doped yttrium aluminate garnet (YAG: Ce) yellow phosphor. The 5 d-4f parity-allowed transitions of cerium dopant [4–9], which has broad absorption bands and luminescence spectra compared with 4f-4f transitions of the majority of rare-earth ions [10]. Blue light from GaN-based blue chip excites the YAG: Ce phosphor to emit yellow light that combines with the blue light to make white light. The primary conversion phosphor material used in pc-WLEDs is YAG: Ce, due to its high absorption of the blue region (450 nm), quantum efficiency, higher thermal luminescence efficiencies, and chemical stability [11–13]. This phosphor requires Thermal Quenching which can endure a higher temperature (approximately 200° Celsius) for application to LEDs. However, the polymeric material composed of YAG: Ce phosphor and usually has low thermal conductivity caused by the accumulated heat on the InGaN chip [14–16], causing organic resin and silicone easily deteriorate and turn yellow due to the heat emitted when the blue light emitting diode (BLED) chip temperature increases with its output power [17,18]. Various studies, as described below, have been conducted to resolve a variety of degradation problems of the existing LEDs: controlling the concentration/thickness of Cerium and research to develop WLEDs with high CRI value using transparent YAG: Ce ceramic [19]; improving conversion loss by pressing YAG: Ce in the form of a plate [20]; and research on improving thermal stability by using phosphor in glass composed of single crystals. However, these processes are relatively complex and require high temperatures. In order to solve the problems of epoxy resin or silicone mentioned above, LED Packaging is required only with a phosphor without a binder. Therefore, we achieved ideal thermal stability and color stability by eliminating the binder, using Phosphor paste to control light scattering, thermal stability, and CRI value in accordance with the control of porosity/thickness based on whether or not the functional material is added [21]. Furthermore, we have adopted a co-precipitation method to synthesize monodispersed phosphor to increase the packing efficiency of the paste film. By taking advantage of remote phosphor and phosphor paste, we presented a study on high-power LED applied with the remote phosphor paste film, which can have ideal thermal stability and color stability.

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2. Experimental

2.1. Preparation of phosphors

Spherical shaped yellow emitting YAG: Ce powder prepared using co-precipitation method. All raw materials were purchased from sigma Aldrich without further purification. $Y(NO_3) \cdot 6H_2O$, $Al(NO_3)\cdot 9H_2O$, Ce $(NO_3)\cdot 6H_2O$ and (HPC) (MW > 100,000) were dissolved in a solvent mixture of water and n-propanol at a ratio of 1:4 according to the chemical formula. The solution was mixed at 25 °C for 2 h s. Then, urea was added as a precipitant and mixed continuously at 90 °C for 8 h. The precipitate formed by the reaction was aged for 1 h, centrifuged at 10,000 rpm for 10 min, and then washed with water and ethanol. It was then lyophilized to obtain a monodispersed precursor. Finally, the obtained precursor was annealed at 1200 °C for 4 h in air atmosphere.

2.2. Phosphor films

YAG: Ce and SSN: Eu were mixed with ethanol at a ratio of 10:0 and 7:3, respectively, for 10 min in a mortar. The mixture was placed in a glass vial bottle, dodecanoic acid was then added, and the mixture was then dispersed by ultrasonic treatment. The dispersed mixture was further dispersed by adding α-terpineol as a solvent, removing ethanol through 3-roll-milling, and finally obtaining phosphor paste. The prepared phosphor paste was coated on a glass substrate using the doctor-blade printing method and heat treated on a hot plate for 10 min to form a phosphor film.

The method of preparing solution and film is detailed in Scheme 1. For comparison of porosity formation rates, a paste with organic binder was prepared and added to the above composition.

3. Results and discussion

3.1. Monodispersed spherical YAG: Ce

In the synthesis of YAG: Ce using one-pot synthesis, the raw materials are precipitated into a spherical form due to the decomposition of urea. Spherical particles are formed depending on the colloidal stability of the mixture solvent (n-propanol and D.I. water). As the ratio of N-propanol increases, the dielectric constant and the zeta potential of the solution decrease, and the uniformity and dispersion of the spherical particles improve [22]. The HPC used as a dispersant decreases the aggregation when up to 0.5 g/L HPC is added, and the uniformity decreases when more than 0.5 g/L HPC is added [23]. The SEM images of YAG: Ce phosphor powders synthesized by one-pot synthesis method are shown in Fig. 1. It was confirmed that the monodispersed spherical particles were synthesized, and the particle size was about 500–600 nm.

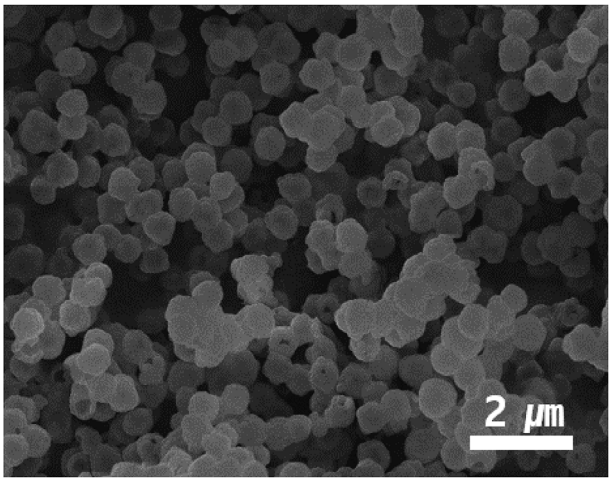
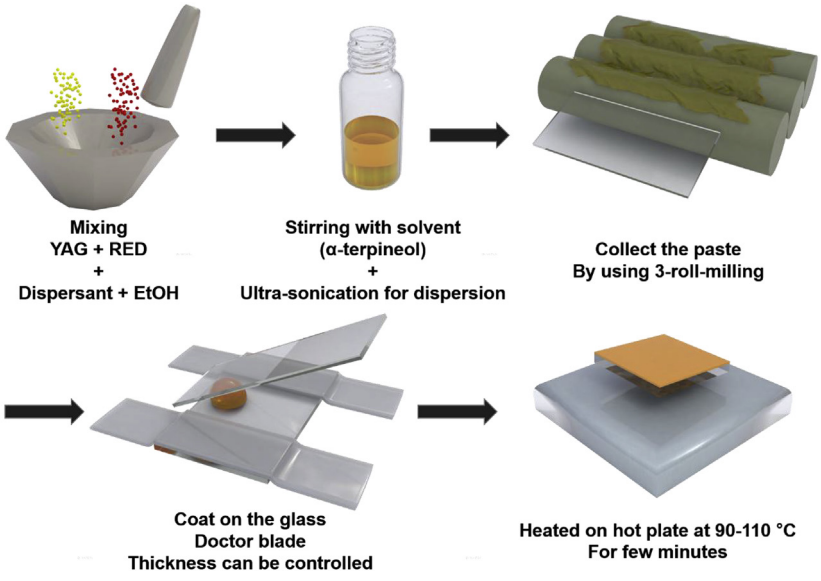


Fig. 1. SEM images of YAG: Ce prepared by one-pot synthesis.

3.2. Photoluminescence of YAG: Ce and SSN: Eu phosphors

Fig. 2 shows the PL and PLE spectra of powder YAG: Ce and SSN: Eu at room temperature. Fig. 2(a) shows the PL spectra of YAG: Ce synthesized by co-precipitation. The excitation spectrum shows two excitation peaks centered at about 340 nm and 460 nm between the 300 nm and 500 nm wavelength regions, respectively. The absorption in the range of 300–500 nm is assigned to the transition of Ce^{3+} ions ($4f^1 \rightarrow 5\,d^1\,(T_{2g})$ and $5\,d^1\,(T_{2g}) \rightarrow 4f^1$) [29]. The synthesized YAG: Ce showed an emission peak centered at 520 nm in the range from 475 to 650 nm. The photoluminescence spectra of SSN: Eu purchased by ~ co is shown in Fig. 2(b). The SSN: Eu phosphor exhibits a strong absorption spectrum in the range of about from 375 to 500 nm centered at 420 and 470, due to the $4f^7 \rightarrow 4f^6\,5\,d$ transitions of Eu^{2+}, and shows an emission spectrum in the range of from 500 to 750 centered 605 nm [24]. In addition, both YAG: Ce and SSN: Eu show strong absorbance at 450 nm,



Scheme 1. Prepared phosphor paste using YAG: Ce and SSN: Eu phosphors.