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Multilayer design of hybrid phosphor film for application in LEDs

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ABSTRACT

Crosslinked polydimethylsiloxane (PDMS) composite coatings containing luminescent micrometer-sized yellow $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) particles were prepared by spraying for potential applications in solid-state lighting. Blue light was down converted by phosphor particles to produce white light, yet poor color properties of $YAG:Ce^{3+}$ stemmed from a deficiency of red. When nitride-based red phosphor was simply blended into the system, the electrostatic interaction of negatively charged $YAG:Ce^{3+}$ and positively charged red phosphor particles caused remarkable clustering and heterogeneity in particle dispersion. Consequently, the light is dominantly blue and shifted to cold white. In other case, phosphor particles were sprayed onto the diffused polycarbonate substrate in stacked layers. Coatings with >80% inorganic content by mass with a thickness of 60 μm were subjected to thermal crosslinking, which the presence of the phosphor particles obstructed, presumably due to the hindrance of large phosphor particles in the diffusion of PDMS precursors. The coating of $YAG:Ce^{3+}$ first followed by red phosphor in stacked layers produced better light output and color properties than the coating obtained by spraying the mixture at once. Monte Carlo simulation validated the hypothesis.

1. Introduction

Since lighting is responsible for nearly 20% of electricity consumption worldwide [1], the invention of light-emitting diodes (LED) has been deemed a breakthrough in minimizing global energy consumption [2]. LED lighting has also prompted the production of a wide range of lighting applications, including in white light, as a promising alternative to incandescent and fluorescent lamps [3,4]. In that context, the combination of red, green, and blue LEDs has emerged as a straightforward solution for fabricating white light. However, given the different requirements of individual LEDs—for instance, their independent driving currents and the degradation-related characteristics of materials employed—mixing different colors in coherence necessarily involves a complex system of integration [2,3].

As an alternative, blue light can be down converted with yellow phosphor [2,3,5,6]. Polymer-based composite films containing yellow garnet particles provide flexible composite films for direct or remote applications with blue LEDs. A part of the incident light passes through the film with virtually no attenuation or backscattering, while some of the primary light is absorbed and converted by the phosphors to secondary light. The combination of incident light and secondary light passing through the film forms white light. To that end, various polymer–phosphor particle systems have been employed for down conversion [7–9], including $CeF_3:(Tb^{3+}, Dy^{3+}, Eu^{3+})$ [10], $YVO_4:(Eu^{3+})$ [11], GYAG [12], $YAG:(Ce^{+3}, Gd^{3+})$ [13], $YAG:(Ce^{+3})$ [8,14–16], $Zn_2SiO_4:(Mn^{2+}, Eu^{3+})$ [17], $BaIn_6Y_2O_{13}:(Yb^{3+}, Tm^{3+}, Er^{3+})$ [18] particles dispersed in poly(methyl methacrylate), Na_2SO_4 [19] and $BaAl_xO_y:(Eu^{2+}, Dy^{3+})$ [20] in low-density polyethylene, $YAG:Ce^{+3}$ in polydimethylsiloxane (PDMS) [21,22], and $YBO_3:(Eu^{2+})$ [23] and $YGG:(Tb^{3+})$ [24] in a polyvinylpyrrolidone matrix. In any case, the goal is a stable white light with a high color rendering index (CRI) and high luminous efficacy as well as a light color that is stable and almost independent of the charged current. However, that attractive optical feature is governed entirely by the quality of the material components and the internal microstructure of the composite coating [25,26].

Widely used for white-LED applications due to its high conversion efficiency, better energy-saving aspects than incandescent and fluorescent lighting, and low cost, cerium-doped yttrium aluminum garnet ($YAG:Ce^{3+}$) has been used as yellow phosphor

Abbreviations: PDMS, Polydimethylsiloxane; CIE, Commission Internationale de l'éclairage; CRI, Color Rendering Index; CCT, Correlated Color Temperature; FTIR, Fourier Transform Infrared Spectroscopy; $YAG:Ce^{+3}$, Cerium doped Yttrium Aluminum Garnet; $Sr_2Si_5N_8:Eu^{+2}$, Europium doped Strontium Silicon Nitride.

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[27]. However, YAG:Ce^{3+} possess serious shortcomings, including thermal quenching [28], a low CRI due to red emission deficiency [29]. Whereas remote phosphor setup has been used to prevent thermal quenching [30], additional red phosphor—that is, europium-doped strontium silicon nitride ($Sr_2Si_5N_8$:Eu^{2+})—has been used to improve overall CRI and the resulting color properties. By comparison, PDMS—a transparent binder and polymeric carrier employed in spraying—has a rotationally flexible Si–O bond that allows an unusually high degree of chain flexibility [31], as well as greater bonding energy (452 kJ/mol) than common vinyl polymers with C–C bonds (347 kJ/mol) [32]. Considering the sustained exposure of light-converting film to highly energetic blue light, PDMS also offers greater UV resistance than other vinyl polymers.

PDMS is an inexpensive hydrophobic polymer that can be coated as thin films on solid surfaces. Ability to wet nearly any substrate surface, appropriate viscoelastic behavior, and cross-linkable nature make PDMS suitable coating material for various processes. In the structural development of coating, the interaction of material components—for instance, the interaction of phosphor particles with polymer precursors and other ingredients—and the spatial arrangement of phosphor particles are critical parameters. In this study, the interaction of YAG:Ce^{3+} and PDMS precursors and red phosphor were examined in detail. YAG:Ce^{3+} and red phosphor particles were sprayed either as a random mixture in a single layer or consecutively as two distinct stacked layers from the PDMS and hexane solution, which achieved the multilayer buildup of coating. Crosslinking was monitored by vibrational spectroscopy, both in the absence and presence of phosphor particles, and the morphology of the coatings was examined by both optical and scanning electron microscopy techniques. The surface charge of the particles was studied in terms of the zeta potential of dynamic light scattering, whereas the optical performance of coatings prepared by the two strategies was compared in terms of correlated color temperature (CCT), CRI, and efficacy.

2. Experimental

2.1. Materials and methods

Phosphor powders YAG:Ce^{3+} and $Sr_2Si_5N_8$:Eu^{2+} (HB-4155H and HB-640, Zhuhai Hanbo Trading Co., Ltd., Guangdong, China) were used as received. PDMS (SYLGARD 184 Kit, Dow Corning, Midland, MI, USA) was used as a polymer matrix for film formation. Due to high viscosity of PDMS, hexane (>95%, Sigma–Aldrich, St. Louis, MO, USA) was used to thin the PDMS powder solutions. The diffraction pattern of the phosphor powders was recorded with an X-ray diffractometer (X'Pert Pro, Philips, Eindhoven, the Netherlands), and the photoluminescence (PL) spectrum was recorded on a fluorescence spectrophotometer (Cary Eclipse, Agilent, Palo Alto, CA, USA). Fourier transform infrared spectroscopy (FTIR; Spectrum 100, PerkinElmer, Shelton, CT, USA) was used to characterize and track changes in the kinetic behavior of bonds, and scanning electron microscopy (SEM; Quanta 250, FEI, Hillsboro, OR, USA) was used to determine particle morphology. The dispersion of powders in PDMS was observed with an optical microscope (BX 53, Olympus, Tokyo, Japan), while spectra of the resulting emissions were recorded by spectrometer (USB2000+, Ocean Optics Inc., Dunedin, FL, USA). Color coordinates and flux were obtained by an integrating sphere (ISP-50-80-R, Ocean Optics Inc.) connected with the USB2000 + spectrometer via premium fiber cable.

2.2. Preparing the phosphor composite film

Spraying is a coating technique used to make homogeneous films on a given substrate. By atomizing a solution or dispersion using high air pressure, the process is uniquely suited for dispersions consisting of heavy, large guest particles in host polymer solutions. In this study, phosphor particles with a density of approximately 4.6 g cm^{-3} were sprayed in the form of PDMS–phosphor dispersion thinned by hexane to polycarbonate (PC) diffuser substrates (Scheme 1). Following the standard process, powder was added into a test tube, and the composition of YAG:Ce^{3+} and red phosphor was fixed to 5:1 by mass ratio. PDMS precursors, i.e. a vinyl-ended PDMS oligomers and the curing agent were dropped in a 10:1 mixing ratio with respect to mass into a test tube. Next, hexane was added to reduce viscosity, the dispersion was mixed in a magnetic stirrer and poured into the hopper of a spray gun (400 W, 1–2 bar pressure), and spray coating was performed onto a set of PC substrate 7–10 s. The resulting composite coatings were approximately 60 μm thick; one side of the substrate was smooth and reflective, whereas another surface—the diffuser side—was rough. Phosphor was sprayed onto the diffuser side because rough surfaces can hold the phosphor coating. The samples were left in open air overnight so that the hexane could fully evaporate, after which they were cured at 100 °C for 2 h in an oven.

2.3. Optical measurement

With a diode emitting a monochromatic blue light at 478 nm, two types of measurement techniques were applied: direct and remote measurements. In the former, the PDMS–phosphor coating on the PC substrate was placed directly onto the blue LED chip so that the composite coating were placed directly over the chip. In the latter, a fixed distance (3 cm) was maintained between the film and LED surface in a black chamber (Scheme 2). Altogether, the system was run with a 0.35 mA input current.

The quality of color is crucial in determining color rendition. One measure of color rendition is the ability of a light source to produce the colors of various objects, which can be quantified by CRI. The best possible rendition shows a CRI of 100, whereas the poorest shows a CRI of 0. Typically, a CRI >80 is preferred in various applications. Another parameter that describes the quality of light is CCT, or the measure of the blackbody temperature needed to radiate a hue comparable to that of the related light source. In general, CCT >5000 K is called bluish white (cool) and 2500 < CCT < 5000 K yellowish white. Since white light is perceived by the human eye with particular precision, luminous efficacy (LEF) is used to define whether the efficiency of an overall spectrum falls within the region matching eye sensitivity [33]. LEF is

$$LEF = 683lm/W\frac{\int \nu(\lambda)\varnothing(\lambda)d\lambda}{\int \varnothing(\lambda)d\lambda} \quad (1)$$

in which $\nu(\lambda)$ is the luminosity function representing human perception normalized to unity at a wavelength of 555 nm due to eye sensitivity and $\varnothing(\lambda)$ is the spectral power distribution per wavelength. Given the definition of $\nu(\lambda)$, the inner product between the luminosity function and spectral power distribution should be 380–780 nm with 5-nm intervals.

3. Results and discussion

3.1. YAG:Ce^{3+} and red phosphor particles

Fig. 1 shows the morphological and structural characterization of the phosphor particles. Fig. 1a and 1b presents SEM images of the YAG:Ce^{3+} and red phosphor powders, respectively; YAG:Ce^{3+} had a nearly monodisperse polyhedral shape, whereas $Sr_2Si_5N_8$:Eu^{2+}