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Post-synthesis annealing effects on SrGa₂Se₄:Eu²⁺ phosphors with peak emission wavelength in the green gap

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ABSTRACT

A high-quality white light source requires high luminous efficacy (lumens per input watt). Theoretically, in the “green-yellow” spectral region (with a peak wavelength at around 555 nm), the luminous efficiency (lumens per radiant watt) reaches a maximum based on the luminous efficiency function, $V(\lambda)$, and can potentially generate high luminous efficacy. Unfortunately, the light-emitting diode (LED) suffers from low external quantum efficiency in the “green-yellow” region, thereby lowering the luminous efficacy value. Researchers have sought solutions such as nonpolar or semipolar InGaN/GaN LEDs. An alternative to generating green light is to use phosphor down-conversion by exciting a green emission phosphor with a near-UV or blue LED of higher external quantum efficiency. In this study, a SrGa₂Se₄:Eu²⁺ phosphor with peak emission wavelength at 555 nm was initially synthesized and followed by a systematic study of the post-synthesis annealing. The purpose of this study was to investigate how post-synthesis annealing conditions, including annealing temperature, annealing duration, and annealing ambient atmosphere, can affect phosphor performance. The phosphor performance was characterized in terms of external quantum efficiency and emission properties. How the external quantum efficiency of the phosphor can be further improved is also discussed.

Keywords: light-emitting diode, LED, green gap, phosphor, thiogallate phosphor, annealing

1. INTRODUCTION

Solid-state lighting (SSL) technology is increasingly used in the lighting industry due to its promise of significant energy savings. The industry goal for one SSL technology—the light-emitting diode (LED)—is to achieve 200 lumens per watt (lm/W) with high color quality by the year 2020.^{1,2} Additionally, LED technology holds the promise for a potentially long lifetime of over 100,000 hours, and thus low maintenance. In early 2010, the U.S. Department of Energy (DOE) forecasted that converting to SSL would decrease lighting energy consumption by 25% in 2030 compared with that in 2010.³ Even though the efficacy and light output of white LEDs have been improving steadily, they still need to improve by twice as much and offer good color appearance and rendering properties before they achieve the target set by the SSL industry.^{1,2}

In general, there are two methods to create white light from LEDs: color mixing of monochromatic LEDs⁴, and phosphor down-conversion by using III-V emitters and one or more types of phosphor.⁵ For the mixed-color method, radiation at different wavelengths from three or more emitters (e.g., red, green, blue [RGB]) are mixed at appropriate intensity ratios to produce white light. However, the requirement of additional color-mixing optics and the poor efficiency of III-V green emitters make the monochromatic LED solution less efficient in reality compared with the phosphor-converted (PC) white LED solution. Most commercial PC white LEDs employ a III-V emitter and a broadband “yellow” phosphor (e.g., YAG:Ce). Some portion of the short-wavelength (blue) light is down-converted by the phosphor to longer wavelengths, and the combination of the residual blue light and down-converted yellow light creates white light. Improving the current state of PC white LED performance to the industry-set goal of 200 lm/W requires improvements to each subcomponent of the LED package, including the chip, encapsulant, phosphor and the entire package integration.

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It is important to understand the factors that affect the performance of the PC white LED, including both the light output (and the resulting luminous efficacy) and the color properties. The performance of the PC white LED is mainly affected by three factors: (1) the external quantum efficiency of the short-wavelength (i.e. blue) LED; (2) the absorption efficiency and quantum efficiency of the phosphor; and (3) the phosphor-converted photon extraction efficiency of the PC LED package. A white LED with superior performance in both efficacy and color properties requires a spectral power distribution (SPD) providing: (1) CIE chromaticity coordinates located on the blackbody locus in the white light source region; (2) high color-rendering values (CRI); and (3) high luminous efficacy. In terms of these requirements, the phosphor emission spectrum influences the overall performance of the white LED significantly.

As the first step in this study, a simulation exercise was carried out to understand how luminous efficacy and CRI are affected by the SPD of the phosphor emission, namely, the peak wavelength and the full-width at half-maximum (FWHM). This analysis sets the requirement for an ideal emission SPD of a single phosphor that can be used in a white LED. Based on the simulation study findings, a $\text{SrGa}_2\text{Se}_4:\text{Eu}^{2+}$ phosphor with peak emission wavelength at 555 nm was initially synthesized and followed by a systematic study of the post-synthesis annealing. The purpose of this study was to investigate how the post-synthesis annealing conditions, including annealing temperature, annealing duration, and annealing ambient atmosphere, can affect phosphor performance. The phosphor performance was characterized in terms of external quantum efficiency and emission properties. How the external quantum efficiency of the phosphor can be further improved is also discussed.

2. SIMULATION

A simulation study was carried out to understand how the phosphor emission spectrum affects the PC white LED performance, including both luminous efficacy and color properties. In general, the properties of an ideal phosphor should include: (1) high absorption efficiency in the range from 440 to 470 nm to reduce the Stokes shift loss; (2) high quantum efficiency; and (3) tailored emission spectrum. Based on the findings of the simulation study, an ideal phosphor emission spectrum is proposed.

The peak wavelength of the luminous efficiency function, $V(\lambda)$, is 555 nm, at which each radiant watt output light is converted to a maximal value of 683 lm based on the human eye's sensitivity. Therefore, in this simulation 555 nm was selected as the peak wavelength of the phosphor emission spectrum, while the FWHM was changed incrementally from 1 nm to 100 nm. Both the luminous efficacy and the color properties were investigated and an optimal value of FWHM determined.

Each emission spectrum was simulated as a Gaussian beam. The spectrum of a PC white LED combines the short-wavelength "blue" emission from an LED and the long-wavelength emission from the phosphor down-conversion. The external quantum efficiency of the phosphor was assumed to be 90%. The FWHM of the phosphor emission changes from 1 nm to 100 nm while the peak wavelength is fixed at 555 nm and the peak wavelength of the short-wavelength "blue" emission is at 456 nm. It was found that the luminous efficacy (lumens per wall-plug watt) decreases while the CRI increases when the FWHM increases from 1 to 100 nm. This means a tradeoff exists between luminous efficacy and CRI values. Since all these phosphor emission spectra suffer from extremely high CCT values above 10,000K and low color rendering properties (especially for R9 [red color sample rendering] when combined with a short-wavelength blue LED), a second type of phosphor with an emission peak wavelength ranging from 600 nm to 640 nm is required. Based on the simulation results, when the FWHM changes from 1 nm to 60 nm, the luminous efficacy does not drop significantly, but a green-yellow phosphor with an emission FWHM at or beyond 60 nm is more practical to be synthesized. As a compromise between luminous efficacy and color rendering properties, a FWHM of 60 nm was selected as the interest of this study and investigated in the following step.

A second red phosphor was added to the previous one-phosphor PC white LED package to simulate its performance. The peak wavelength and FWHM of the simulated red phosphor are 640 nm and 70 nm, respectively, which is a combination that is commercially available. The peak wavelength and the FWHM of the green-yellow phosphor are selected at 555 nm and 60 nm, respectively, which were found earlier to be a good compromise between luminous efficacy and color properties. It was found that although the two-phosphor package yields slightly lower efficacy than the one-phosphor LED package, the two-phosphor package has much better color appearance with a lower CCT and satisfying color-rendering properties, especially with the R9 (red color sample) rendering. The two-phosphor PC white LED package solution can help achieve the industry goal of 200 lm/W with good color properties by the year 2020.

3. EXPERIMENT

Based on the previous simulation, to achieve a PC white LED package with high luminous efficacy, the ideal green-yellow phosphor requires a blue excitation in the range from 440 to 470 nm, a phosphor emission peak wavelength around 555 nm, an emission FWHM of 60 nm, and minimal wavelength overlap between the absorption and emission regions to avoid phosphor reabsorption.

Past studies show that most commonly used green-yellow phosphors include host materials of aluminates⁶, silicates⁷⁻⁹, nitridosilicates¹⁰, modified nitridosilicates¹¹⁻¹⁴, oxo-nitridosilicates¹⁰, thiogallates¹⁵⁻¹⁷, oxide¹⁸, sulfide^{19, 20} and oxysulfide²¹, and dopant materials of Eu²⁺ and Ce³⁺. Many of these phosphor candidates have been studied extensively while the thiogallate phosphors have not yet, although they have promising attributes. Some studies on SrGa₂S₄:Eu²⁺ and Sr_{1-x}Ca_xGa₂S₄:Eu²⁺ have been published, but there are only a very limited number of studies on SrGa₂Se₄:Eu²⁺. Therefore, in this study, SrGa₂Se₄:Eu²⁺ phosphor was selected for further analysis, primarily because it is easy to synthesize due to its simple compositions and relatively low synthesis temperature.

The main difficulty in synthesizing a ternary compound such as the thiogallate phosphor is control of the stoichiometry because of the different vapor pressures of each element.²² In SrGa₂S₄:Eu²⁺ thin film synthesis, depletions of S and Ga are observed.²² To compensate for the depletions, excessive S and Ga are introduced to the starting blends.²² On the other hand, the as-synthesized thiogallate phosphor is usually amorphous, weakly crystallized and not luminescent.^{22, 23} To improve the crystallinity of the thiogallate phosphor, a common solution is to increase the synthesis temperature and synthesis time. However, higher synthesis temperature and longer synthesis time result in phosphor agglomerations or sometimes formation as “sintered cake,” which requires grinding to break the phosphor into smaller particles.²⁴ Mechanical grinding causes lattice defects, which in turn reduces the external quantum efficiency of the phosphor.²⁴ Post-synthesis annealing is therefore used to improve the crystalline perfection, the surface morphology and stoichiometry in order to improve the phosphor external quantum efficiency.^{22, 23}

Based on literature reviews, it appears that to improve the performance of the PC white LED, it is essential to improve the external quantum efficiency of the phosphors used in PC white LED packages. In this investigation, the post-synthesis annealing method to improve the external quantum efficiency of a model material (green phosphor SrGa₂Se₄:Eu²⁺) was attempted. Past studies have shown that post-synthesis annealing can improve the phosphor crystalline perfection, surface morphology and phosphor quantum efficiencies.²⁴⁻²⁹ The post-synthesis annealing includes three parameters: annealing temperature, annealing time, and annealing ambient atmosphere. In this study, after the initial SrGa₂Se₄:Eu²⁺ green phosphor was synthesized, three groups of post-synthesis annealing experiments were conducted by changing either the annealing temperature, annealing time or annealing ambient atmosphere while maintaining the other two parameters in each group of experiments:

- Annealing time: 0.5, 1, 2 or 4 hours (with constant ramp rate of 350°C/hr)
- Annealing ambient atmosphere: nitrogen, hydrogen or vacuum
- Annealing temperature: 750°C, 850°C, 900°C, 1000°C, 1100°C or 1200°C

In phosphor efficiency analysis, each phosphor end-product was characterized in an SPE (scattered photon extraction) configuration³⁰ and the excitation light source was a commercial blue LED ($\lambda_{\text{peak}}=451$ nm). Each SPE package was characterized in a calibrated integrating sphere with a calibrated spectroradiometer, so that the SPD signals could be recorded. Therefore, the light output in radiant power can be calculated by:

$$P = \sum P(\lambda)\Delta\lambda \quad (1)$$

where $P(\lambda)$ is the radiant power in the wavelength interval $\Delta\lambda$. Similarly, the light output in lumens can be calculated by:

$$\Phi = K_m \sum P(\lambda)V_\lambda(\lambda)\Delta\lambda \quad (2)$$

where K_m is a constant, V_λ is the relative photopic luminous efficiency function, and $\Delta\lambda$ is the wavelength interval. Since the input voltage (V_{in}) and current (I_{in}) through the blue LED were also measured, the luminous efficacy can be calculated following:

$$Efficacy = \frac{\Phi}{P_{in}} = \frac{\Phi}{V_{in} \cdot I_{in}} \quad (3)$$

4. RESULTS

Table 1: Experimental results of the SPE PC green-phosphor LED luminous efficacy values with phosphors annealed under different time, ambient atmosphere, and temperature.

Annealing time (hour)*	0	0.5	1	2	4
Efficacy (lm/W)	17.0	79.5	76.7	76.7	59.0

* Annealing atmosphere remains in H_2 and annealing temperature remains at $850^\circ C$.

Annealing atmosphere*	N_2	H_2	Vacuum
Efficacy (lm/W)	40.1	76.7	62.8

* Annealing time remains for 2 hours and annealing temperature remains at $850^\circ C$.

Annealing temperature ($^\circ C$)*	750	850	900	1000	1100	1200
Efficacy (lm/W)	71.3	76.7	77.5	43.7	dissociated	dissociated

* Annealing atmosphere remains in H_2 and annealing time remains for 2 hours.

Table 1 shows the experimental results of the SPE PC green-phosphor LED luminous efficacy values with phosphors annealed for 0.5, 1, 2 and 4 hours at the same annealing temperature of $850^\circ C$ and in the same ambient atmosphere of hydrogen. The as-synthesized phosphor (shown as 0 hour) yields 17 lm/W. Annealing for 0.5 hour significantly increases the luminous efficacy to 79.5 lm/W. However, there is no significant difference from annealing for 0.5 hour to 2 hours. When the annealing time extends to 4 hours, the luminous efficacy drops to 59 lm/W. This means that continuous annealing does not necessarily improve the phosphor performance further; instead, a longer annealing time can cause the disintegration of the phosphor crystals, and therefore the phosphor efficiency decreases. Since a 2-hour annealing is sufficient to improve the phosphor performance to a maximum, a 2-hour duration was adopted as the annealing time in later annealing experiments at other conditions. The peak wavelength and the FWHM of the as-synthesized phosphor are at 557 nm and 66 nm; after post-synthesis annealing, the peak wavelength shifted to 553 nm and the FWHM slightly narrowed to 60 nm for the phosphor annealed at $850^\circ C$ in H_2 for 2 hours.

Table 1 also shows the experimental results of the luminous efficacy values of the SPE PC green-phosphor LEDs with phosphors annealed under different annealing ambient atmospheres of N_2 , H_2 and vacuum, at the same annealing temperature of $850^\circ C$ and the same annealing time of 2 hours. For the annealing in N_2 , H_2 and vacuum, the ambient atmosphere was kept constant throughout the whole annealing process. As a reference, the as-synthesized phosphor yields 17 lm/W. Annealing under all three tested ambient atmospheres improves the phosphor performance significantly.

Table 1 also shows the luminous efficacy values of the phosphor samples annealed in H_2 for 2 hours at $750^\circ C$, $850^\circ C$, $900^\circ C$, $1000^\circ C$, $1100^\circ C$ and $1200^\circ C$. When the temperature increases from $750^\circ C$ to $900^\circ C$, the phosphor performance does not change significantly. When the temperature reaches $1000^\circ C$, the phosphor performance drops significantly. Once the temperature goes beyond $1100^\circ C$, the phosphor is dissociated.

5. SUMMARY

A simulation study showed that the phosphor emission with the peak wavelength and FWHM at 555 nm and 60 nm is a good compromise between luminous efficacy and color properties. This green-yellow phosphor and a blue LED can form a one-phosphor LED package. A second red phosphor with an emission peak wavelength and FWHM at 640 nm and 70 nm, respectively, can be added to form a two-phosphor LED package. It was found that although the two-

phosphor package yields slightly lower efficacy than the one-phosphor LED package, the two-phosphor package has much better color appearance with a lower CCT and satisfying color-rendering properties, especially with the R9 (red color sample) rendering. The two-phosphor PC white LED package solution can help achieve the industry goal of 200 lm/W with good color properties by the year 2020.

A $\text{SrGa}_2\text{Se}_4:\text{Eu}^{2+}$ phosphor was selected in this study because it can achieve the targeted emission peak wavelength of 555 nm and a FWHM of 60 nm, and it is relatively easy to synthesize due to its simple compositions and relatively low synthesis temperature. Experimental results have proved that post-synthesis annealing can improve the performance of $\text{SrGa}_2\text{Se}_4:\text{Eu}^{2+}$ phosphor when the annealing time, atmosphere, and temperature are carefully controlled. An optimal annealing condition for the phosphor synthesized is drawn from this study:

- Annealing duration = 2 hrs
- Annealing ambient = H_2
- Annealing temperature = 850°C

In this study, the highest achieved external quantum efficiency of the $\text{SrGa}_2\text{Se}_4:\text{Eu}^{2+}$ phosphor is approximately 58%. Therefore, there is still room for improvement to achieve the goal of 90%, as assumed in the simulation study. To achieve 90% external quantum efficiency, the phosphor absorption in the long-wavelength range needs to be cutoff to avoid self-absorption.

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