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Analysis and Reliability Study of Luminescent Materials for White Lighting †

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Abstract: In this work, we report on the characterization and reliability/stability study of phosphorescent materials for lighting applications. More specifically, we investigated (a) phosphors directly deposited over light-emitting diodes (LED) chip, (b) remote phosphor (RP) solutions encapsulated in plastic medium for LED lighting, and (c) phosphors without binder for extreme high-intensity laser diode white lighting. The optical and thermal properties of phosphors were studied to develop a sample based on a mix of phosphor compounds in order to achieve different correlated color temperatures (CCT) and high color rendering index (CRI) LEDs. Thermal properties of cerium-doped YAG (Yttrium Aluminum Garnet) phosphor materials were evaluated in order to study thermal quenching. A maximum phosphor operating temperature of 190–200 °C was found to cause a sensible efficiency degeneration. Reduced efficiency and Stokes shift also caused a localized temperature increase in the photoluminescent materials. In the case of remote phosphors, heat did not find a low thermal resistance path to the heatsink (as occurred through the GaN LED chip for direct phosphor-converted devices) and thermal analysis indicated that material temperature might therefore increase to values in excess of 60 °C when a radiation of 435 mW/cm^2 hit the sample template. Reliability was also investigated for both plastic-encapsulated materials and binder-free depositions. Pure thermal reliability study indicated that phosphors encapsulated in polycarbonate material were stable up to temperature of approximately 100 °C, while binder-free phosphor did not show any sensible degradation up to temperatures of 525 °C.

Keywords: phosphor; lighting; LED; laser

1. Introduction

The use of light conversion phosphors in solid-state lighting (SSL) has become the preferred method in recent years to achieve a good spectrum quality (in terms of correlated color temperature (CCT), color rendering index (CRI) and white point accuracy) in blue-pumped light sources.

Photoluminescent materials (phosphors) are a primary component of white solid-state lighting systems. Being based on rare-earth-doped aluminate, silicate, garnets, or nitride compounds, they offer green, yellow, and red photoluminescence (PL) when excited with a blue radiation (445–455 nm), typically emitted by a gallium nitride-based light-emitting diodes (LED). Phosphors are thus a key element for white light generation, and their performances and reliability require a specific analysis. Conversion efficiency, saturation, and operating temperature have a strong impact on the efficiency of the final system, while the stability of the emission over time has a crucial effect on LED color temperature and luminous flux stability [1]. Due to much higher incident power density and higher operating temperatures, phosphors also become the most critical element in laser-based white light system. With this work, we report on an accurate analysis of the performances and reliability of phosphor for SSL systems. The analysis is based on the optical characterization of different structures of photoluminescent materials, from remote phosphors to binder-free phosphors for laser lighting applications. Samples were submitted to stress at several temperatures, illumination, and humidity levels.

2. Methods

In this work, we report on phosphor in three different applications (sketch presented in Figure 1): (i) remote phosphor for LED application, (ii) silicone-encapsulated phosphors in mid-power LED applications, (iii) phosphors with and without binder for high intensity laser applications.

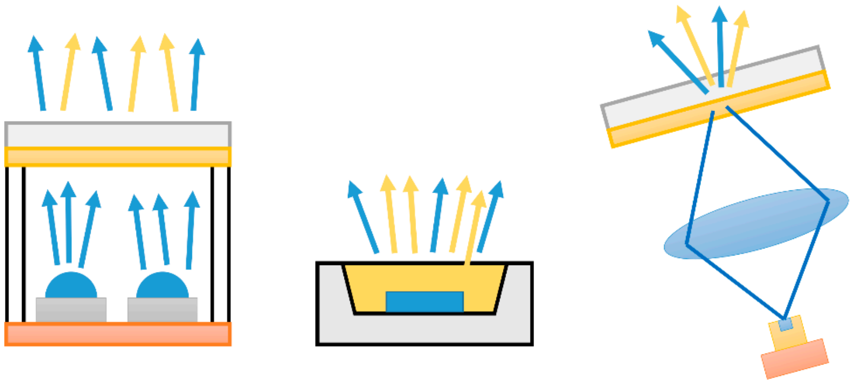


Figure 1. Remote phosphor for LED lighting application (**left**), encapsulated phosphor for mid-power LED applications (**center**), and phosphor for laser lighting application.

2.1. Remote Phosphors for LED Application

To study remote phosphor performances and reliability, round plates (diameter = 61.5 mm, thickness 2.1 mm) fabricated by a leading manufacturer was used. The plates were based on a diffusive/transparent polymeric material of the polycarbonate family where a thin layer of phosphor had been deposited. When combined with a royal blue light source (usually emitting around 455 nm), plates allowed the emission of white light at a specific correlated color temperature [2]. The chromatic characteristic of choice for the experiment was a CCT of 4000 K and a CRI of 80.

The operating temperature of the samples during operation were measured by means of an IR camera (FLIR A320s) and a Cr–Al thermocouple placed inside the phosphor plate when excited with increasing irradiance intensity (from 38 mW/cm^2 up to 346 mW/cm^2). The conversion efficiency was also evaluated by means of pulsed measurements inside an integrating sphere (LabSphere LMS-650) at increasing excitation power up to 25 W. The optical power was delivered by an array of 455 nm LED power by means of a Keithley 2614B SourceMeter instrument.

To test reliability, phosphor templates were submitted to thermal stress tests in climatic chambers at the following six temperatures: 85 °C, 105 °C, 115 °C, 125 °C, 135 °C, and 145 °C. The atmosphere inside the chamber was air. The substrate material of the RP plates was of the polycarbonate family and thus had a glass transition temperature of approximately 150 °C. The substrate alone was also tested to differentiate the degradation kinetics of the two elements. At different stages of the stress tests, the plates were removed from the thermal chambers and placed in an appropriate test fixture equipped with royal blue LEDs to measure the converted spectra and efficiency variation.

2.2. Silicone-Encapsulated Phosphors in Mid-Power LEDs

Mid-power chip scale package (2.0 × 0.8 mm) LEDs were selected to study the reliability of phosphors encapsulated in a silicone-based matrix. Reliability tests were performed at 80 mA nominal current at different ambient temperatures. The ambient temperature was controlled by means of a Binder FD56 heating chamber varying from 45 °C to 105 °C. At constant intervals during the test, the spectrum from the samples was characterized by means of an integrating sphere equipped with a spectrometer.

2.3. Phosphors for Laser Applications

The phosphor studied in this part of the work was a commercially off the shelf YAG:Ce^{3+} material which is provided in powder form. It was deposited onto a substrate in order to have mechanical support. Selected phosphor had a peak emission of 550 nm, chromatic diagram coordinates x = 0.426 and y = 0.548, and an average particle size of 8.5 µm. The typical excitation wavelength was 450 nm.

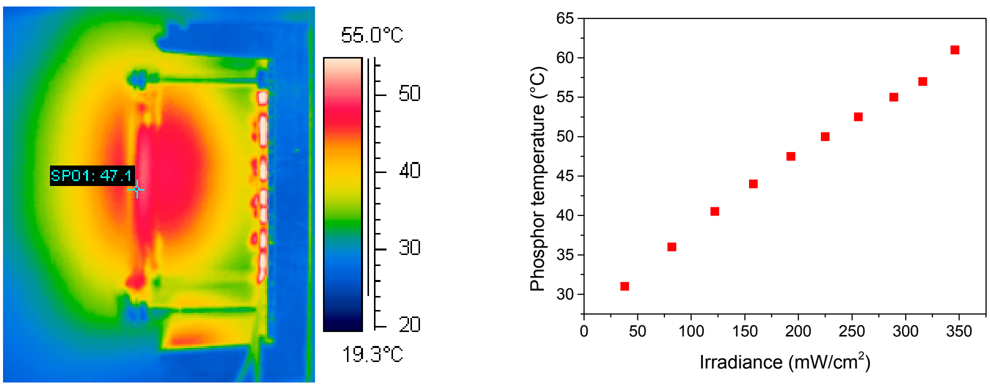
Phosphor powder was deposited by drop casting without binder on a sapphire substrate with a diameter of 12.7 mm and thickness of 3 mm.

The PL properties of drop-casted YAG phosphor samples were measured as a function of the temperature and laser irradiance; reliability study was performed as a pure high-temperature storage test. During the stress test, the transmitted and reflected photoluminescence were measured by means of a specific setup based on a 450 nm high-power LED.

3. Results and Discussion

3.1. Remote Phosphors for LED Application

Remote phosphor thermal characterization showed the effect of Stokes shift and reduced efficiency on the tested plates (Figure 2). The temperature on the plate surface gradually increased during the test and reached a value in excess of 60 °C at thermal equilibrium (T_a = 25 °C) when excited by a 455 nm radiation of 346 mW/cm^2.



(**a**) (**b**)

Figure 2. (**a**) Remote phosphor plate subjected to irradiation from 455 nm LEDs with a radiation of 225 mW/cm^2; (**b**) heating transients of the phosphor plate at increasing irradiance.

Luminous conversion efficiency was carried out under pulsed operation at 25 °C (Figure 3). Analysis results showed an optimal uniformity of operation of the phosphor at different excitation values, indicating that saturation was not reached at these relatively low excitation power densities.

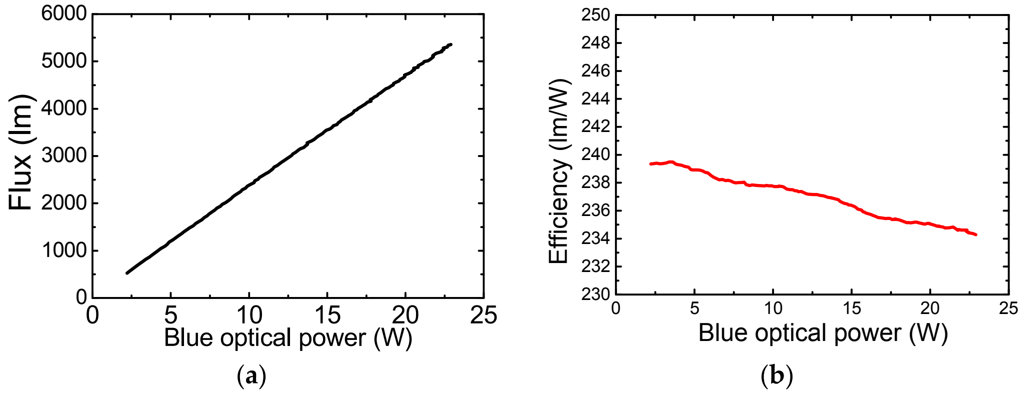


Figure 3. (**a**) Remote phosphor plate emitted flux at different excitation power; (**b**) relative luminous conversion efficiency.

Results from thermal reliability tests reported in Figures 4 and 5a indicated that temperature had an important role in remote phosphor reliability. At 85 °C, only 5% degradation was detected after 5000 h, but as the temperature increased, the degradation kinetic was much faster. The thermal degradation process was analyzed, resulting in an activation energy of TTF80% (Time To Failure at 80% of the initial flux) of 1.33 eV. Comparing the degradation kinetics of phosphor plates and the bare polycarbonate substrate (Figure 5b), it was possible to appreciate that although most of the degradation was related to the decrease in transparency of the substrate, the initial exponential decay was still related to the phosphor material [3].

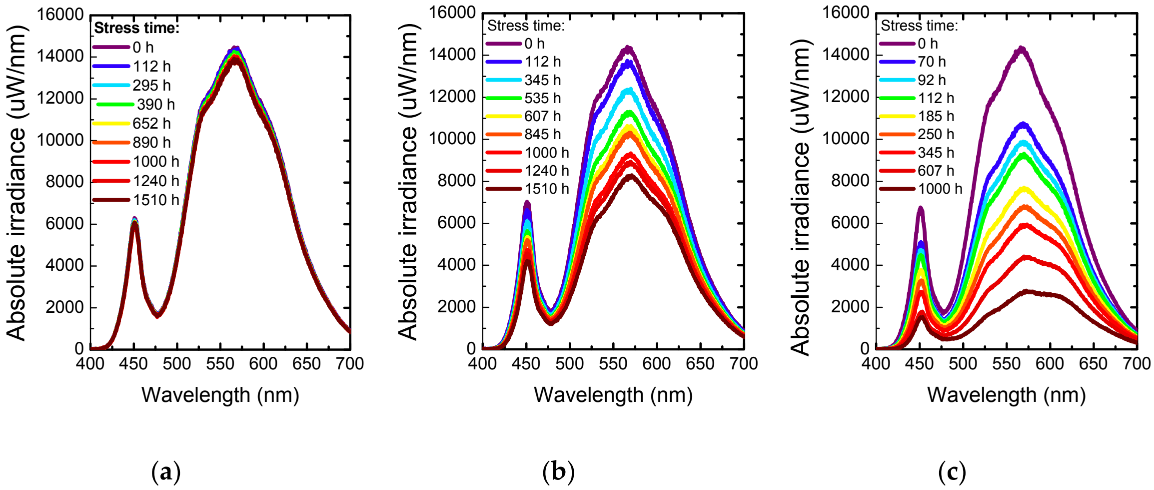
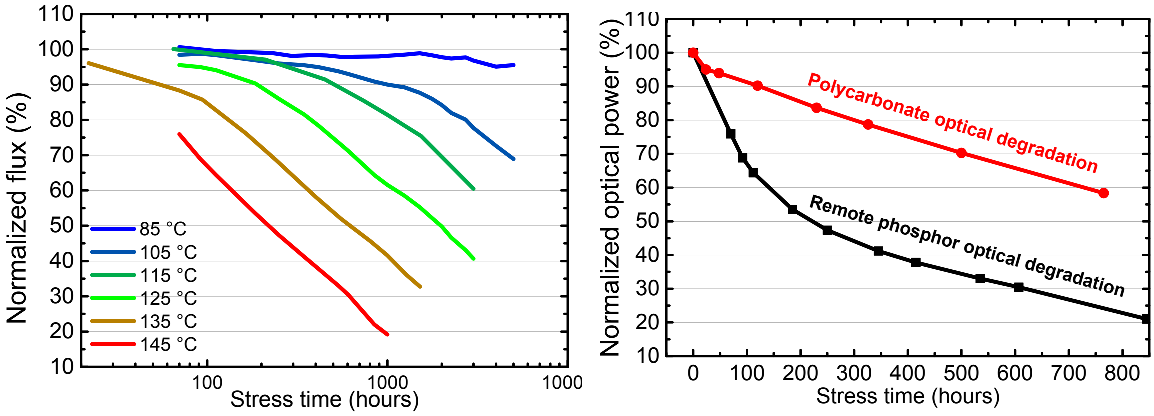


Figure 4. Remote phosphor plate-emitted spectrum measured during pure thermal stress at different temperatures: (**a**) stress at 85 °C; (**b**) stress at 125 °C; (**c**) stress at 145 °C.



(**a**) (**b**)

Figure 5. (**a**) Remote phosphor degradation kinetics at different stress temperatures; (**b**) comparison of the optical degradation kinetic at 145 °C of a bare polycarbonate substrate and the phosphor plate.

3.2. Silicone-Encapsulated Phosphors in Mid-Power LEDs

Results from the reliability test carried out on mid-power LEDs with silicon-encapsulated phosphors indicated a decrease in both the blue peak and the yellow peak, as presented in Figure 6, when LEDs were operated at 80 mA and T_a of 105 °C. Analyzing the degradation kinetics of samples tested at different temperatures, it was possible to observe a clear correlation between the operating temperature and the degradation intensity. Increasing the operating temperature had a negative impact on the device stability and induced a faster degradation on the tested devices. By separating the contribution of the different luminescence peaks on the device spectrum, we analyzed the relative decrease in the blue LED chip and the phosphor luminescence. The ratio between yellow and blue emission, as shown in Figure 7, indicated a fast degradation mechanism that saturated after few operating hours.

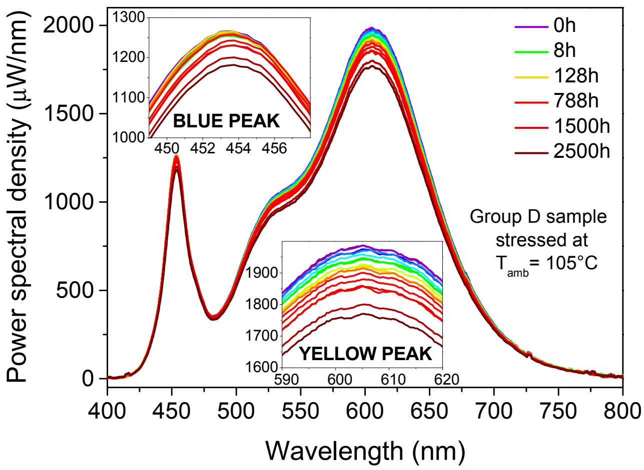
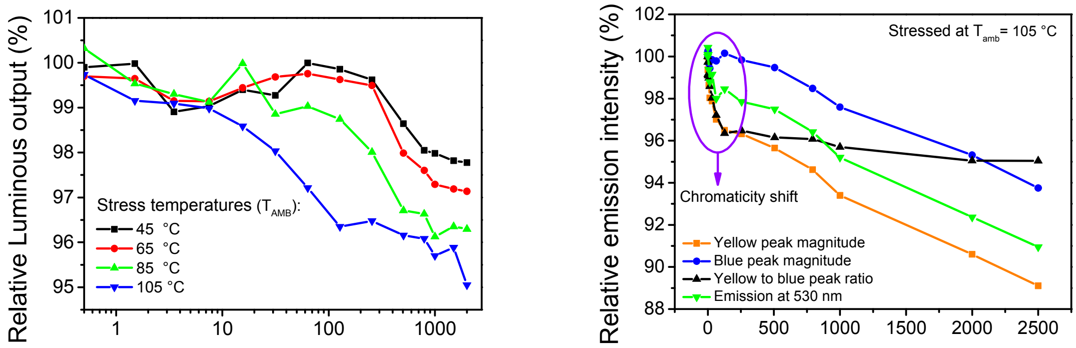


Figure 6. Mid-power LED spectrum variation during ageing at 80 mA, 105 °C.

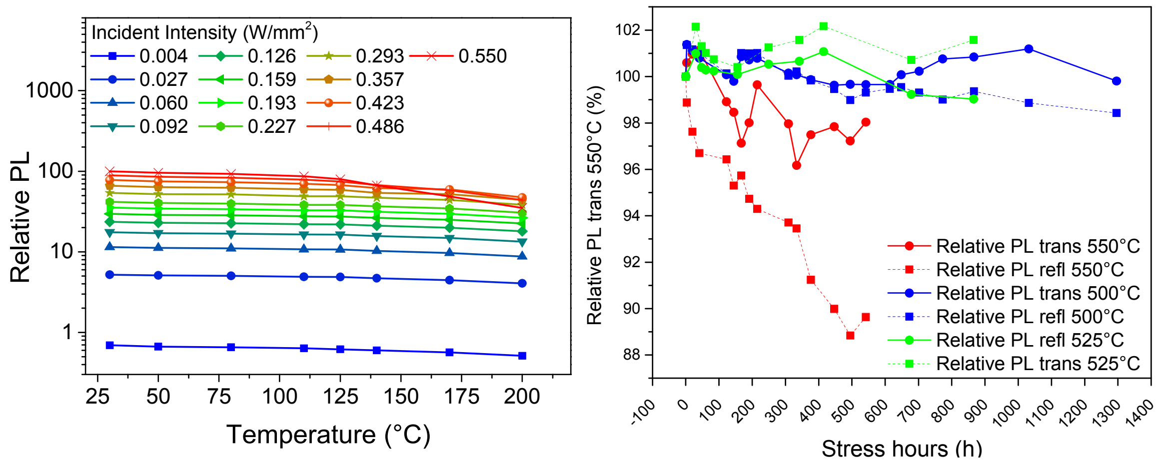


(**a**) (**b**)

Figure 7. (**a**) Mid-power LED luminous output decrease during ageing at different stress temperatures; (**b**) degradation kinetics of different emission peaks and yellow to blue ratio.

3.3. Phosphors for Laser Applications

Thermal characterization of phosphors excited with laser radiation reported a relative PL increase as the incident intensity increased. While the temperature alone had a small effect on photoluminescence performances at low excitation, the sample excited at higher radiative density showed a thermal rollover as temperature increased; this sudden drop indicated thermal quenching [4]. Since the combined effect of the carrier temperature and phosphor self-heating increased the temperature of the phosphor layer, thermal quenching was only visible for higher incident irradiance. Figure 8 also reports on the degradation kinetics of phosphors without binders subjected to pure thermal stress to simulate the operating temperature during high intensity laser excitation. Results indicated that up to 525 °C, no sensible degradation could be noticed in the reflected or the transmitted photoluminescence; however, at 550 °C, a gradual degradation in the photoluminescence emission could be observed. Reflected PL signal showed a more intense degradation. This behavior was probably related to the reduced conversion efficiency of the first layers of the phosphors.



(**a**) (**b**)

Figure 8. (**a**) Remote phosphor without binder photoluminescence signal measured at different ambient temperatures and different incident radiant intensity; (**b**) transmitted and reflected photoluminescence degradation of binder-free phosphors at temperatures between 500 °C and 550 °C.

4. Conclusions

This work reports on the characterization of phosphors for solid-state lighting applications in which photoluminescent materials are crucial to achieve broadband white lighting. In particular, our results indicated that temperature played a fundamental role in the performance and reliability of phosphors. However, while temperature had a strong effect for systems with binders even at low values (in the order of 100 °C), in systems where no binders were involved, temperature was only involved in phosphor degradation at values above 500 °C.

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