ECMS 2018

Analysis and Reliability Study of Luminescent Materials for White Lighting

Nicola Trivellin *, Matteo Meneghini, Matteo Buffolo, Gaudenzio Meneghesso, Enrico Zanoni

Department of Information engineering, University of Padova, Via Gradenigo 6B, 35131 Padova (PD) Italy; nicola.trivellin@dei.unipd.it

* Correspondence: nicola.trivellin@dei.unipd.it @e-mail.com; Tel.: +390498277625

Received: 24 April 2018; Accepted: 13 May 2018; Published: 15 May 2018

Abstract: With this work we report on the characterization and reliability/stability study of phosphorescent materials for lighting applications. More specifically, we investigate: a) phosphors directly deposited over LED chip, b) remote phosphor solutions encapsulated in plastic medium for LED lighting, c) phosphors without binder for extreme high intensity Laser Diode white lighting. The optical and thermal properties of phosphors have been studied to develop solution based on mix compounds to achieve different Correlated Color Temperatures and high Color Rendering Index LEDs. Thermal properties of Cerium Doped YAG phosphors materials have been evaluated in order to study the thermal quenching. A maximum phosphor operating temperature of 190–200 °C has been found to cause a sensible efficiency degeneration. Reduced efficiency and Stokes shift, also cause a localized temperature increase in the photoluminescent materials. In the case of remote phosphors, heat does not find a low thermal resistance path to the heatsink (as occurs through the GaN LED chip, for direct phosphor converted devices), thermal analysis indicate that material temperature might therefore increase up to values in excess of 60°C when a radiation of 435 mW/cm^2 hits the sample template. Reliability has also been investigated for both plastic encapsulated materials and binder free depositions: pure thermal reliability study indicate that phosphors encapsulated in polycarbonate material are stable up to temperature of approximately 100 °C, while binder free phosphor do 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 has become in the last years the favorite method to achieve a good spectrum quality (in terms of Correlated Color Temperature, Color Rendering Index and white point accuracy) in blue pumped light sources.

Photoluminescent materials (phosphors) are a primary component of the white solid state lighting systems. Being based on rare earth doped Aluminate, Silicate, Garnets or Nitride compounds they offer green, yellow and red photoluminescence, when excited with a blue radiation (445–455 nm), typically emitted by a Gallium Nitride based 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.

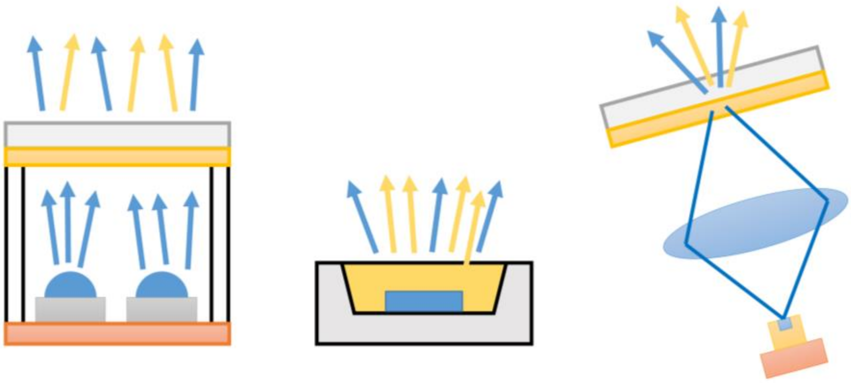


Figure 1. Remote phosphor for LED lighting application (left), Encapsulated Phosphor for mid power LED applications (center), and phosphor for laser lighting application.

2.1. Remote Phosphors for LED Application

The study remote phosphor performances and reliability carried out in this work is round plates (diameter = 61.5mm, thickness 2.1 mm) fabricated by a leading manufacturer; plates are based on a diffusive/transparent polymeric material of the polycarbonate family where a thin layer of phosphor has been deposited. When combined with a royal-blue light source (usually emitting around 455 nm), plates allow the emission of white light at a specific Correlated Color Temperature (CCT) [2]. The chromatic characteristic of choice for the experiment have a CCT of 4000 K and a Color Rendering Index (CRI) of 80.

The operating temperature of the samples during operation has been 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 has also been evaluated by means of pulsed measurements inside an integrating sphere (LabSphere LMS-650) at increasing excitation power, up to 25 W. The optical power is delivered by and array of 455 nm LEDs power by means of a Keithley 2614B SourceMeter instrument.

To test the 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, 145 °C. The atmosphere inside the chamber was air. The substrate material of the RP plates is of the polycarbonate family, thus has a glass transition temperature of approximately 150 °C, the substrate alone has also been tested to differentiate the degradation kinetics of two elements. At the 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 have been selected to study the reliability of phosphors encapsulated in a silicone based matrix. Reliability test have been performed at 80 mA nominal current at different ambient temperatures. The ambient temperature has been 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 has been 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 is commercially available YAG:Ce^{3+} in powder form it is deposited onto a substrate in order to have a mechanical support. Selected phosphor has a peak emission of 550 nm, the chromatic diagram coordinates x = 0.426 and y = 0.548 and an average particle size of 8.5 µm. The typical excitation wavelength is 450 nm.

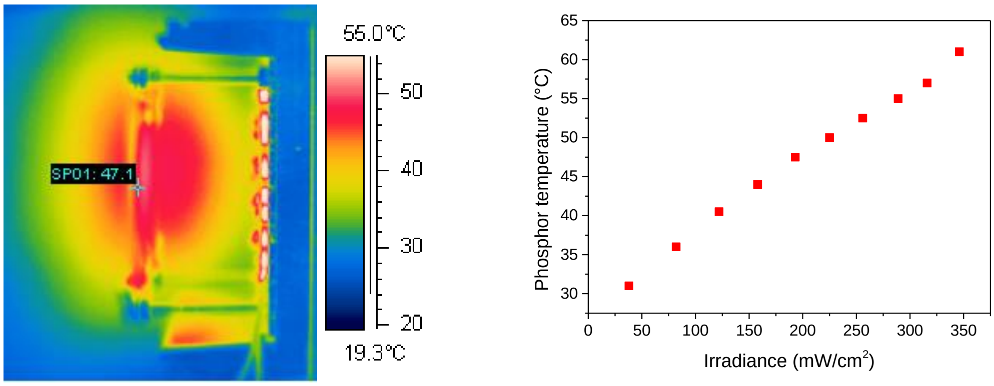
Phosphor powder has been deposited by drop casting without binder on a sapphire substrate with a diameter of 12.7 mm, and a thickness of 3 mm.

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

3. Results and Discussion

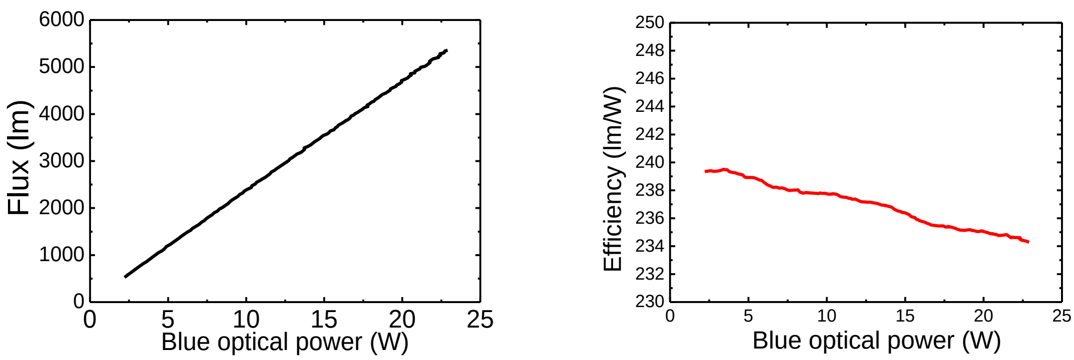
3.1. Remote Phosphors for LED Application

Remote phosphor thermal characterization show the effect of Stokes Shift and reduced efficiency on the tested plates (Figure 2), the temperature on the plate surface gradually increases during the test and reaches 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**)

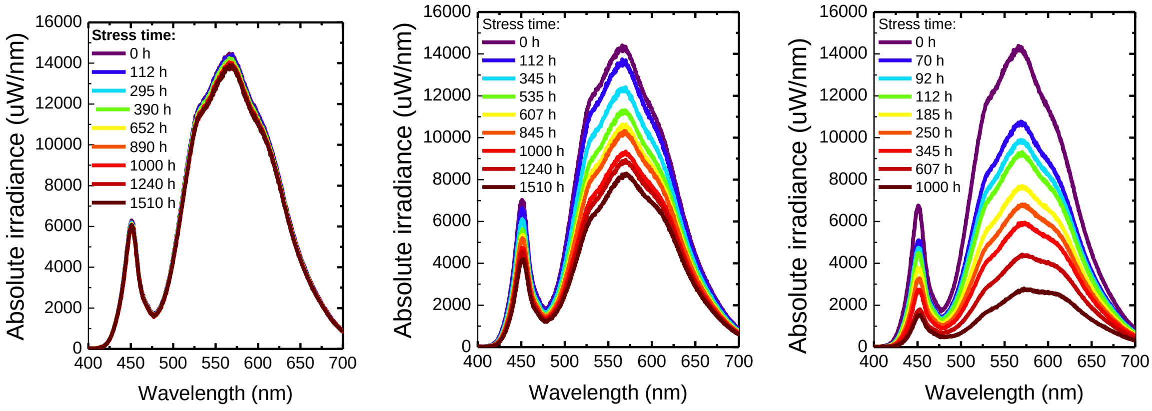
Figure 2. (**a**) Remote phosphor plate subjected to irradiation from 455 nm LEDs with a radiation of 225 mW/cm^2; (**b**) heating transients of the phosphor plate at increasing irradiance.



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

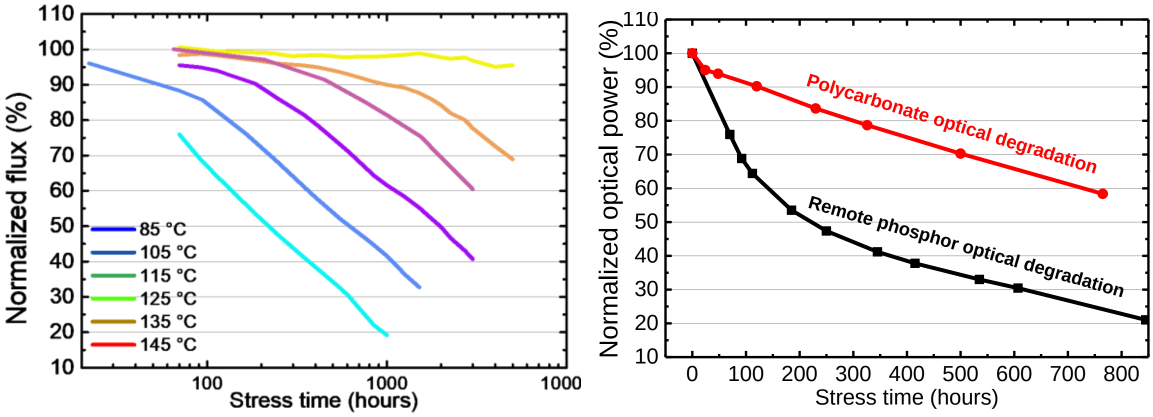
Figure 3. (**a**) Remote phosphor plate emitted flux at different excitation power and (**b**) relative luminous conversion efficiency.

Luminous conversion efficiency carried out at pulsed operation at 25 °C (Figure 3) analysis results show an optimal uniformity of operation of the phosphor at different excitation values indicating that saturation is not reached at this relatively low excitation power densities.



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

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

Results from thermal reliability tests reported in Figure 4 and Figure 5 (a) indicate that temperature has an important role in remote phosphor reliability, while at 85 °C only a 5% degradation is detected after 5000 h, as temperature increases the degradation kinetic is much faster. The thermal degradation process has been analyzed, resulting in an activation energy of the TTF80% of 1.33 eV. Comparing the degradation kinetics of phosphor plates and the bare Polycarbonate substrate (Figure 5 (b)) it is possible to appreciate that although most of the degradation is related to the transparency decrease of the substrate an initial exponential decay is still related to the phosphor material.

3.2. Silicone Encapsulated Phosphors in Mid Power LEDs

Results from reliability test carried out on mid power LEDs with silicon encapsulated phosphors indicate a decrease both in the blue peak and in the yellow peak as presented in Figure 6, when LEDs are operated at 80 mA, and T_a of 105 °C. Analyzing the degradation kinetics of samples tested at different temperatures it is possible to observe a clear correlation between the operating temperature and the degradation intensity, where increasing the operating temperature has a negative impact on the device stability, and induces a faster degradation on the tested devices. By separating the contribution of the different luminescence peaks on the device spectrum we have analyzed the relative decrease of the blue LED chip and the phosphor luminescence. In Figure 7 it is reported the ratio between yellow and blue emission indicating a fast degradation mechanism that saturates after few operating hours.

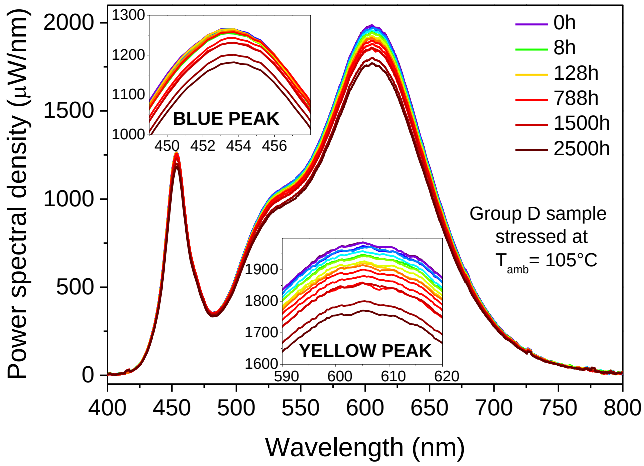
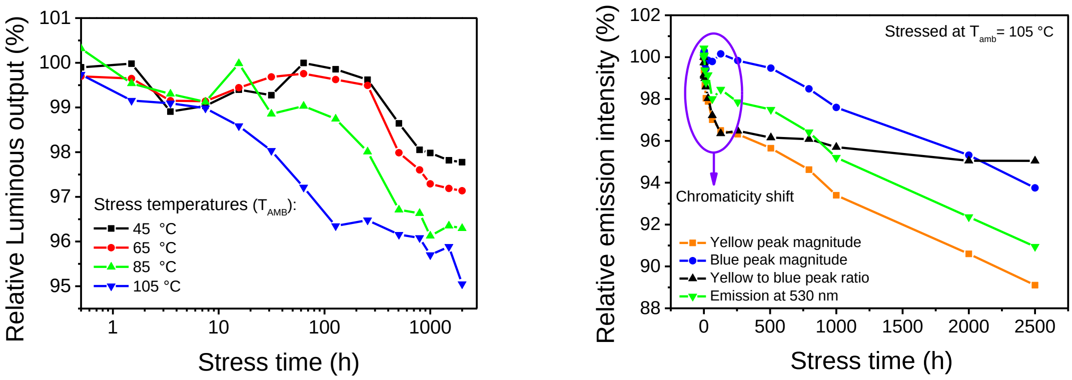


Figure 6. Mid power LED spectrum variation during ageing at 80 mA, 105 °C.

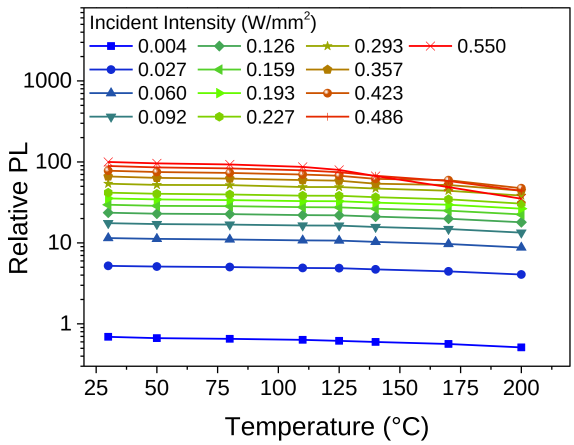


(**a**) (**b**)

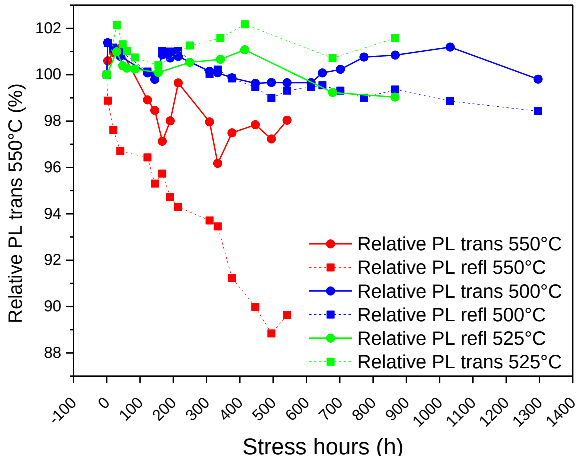
Figure 7. (**a**) Mid power LED luminous output decrease during ageing at different stress temperatures; (**b**) degradation kinetics of different emission peaks and yellow to blue ratio.

3.3. Phosphors for Laser Applications

Thermal characterization of phosphors excited with laser radiation reports a relative PL increase as the incident intensity increases. While the temperature alone has a small effect on photoluminescence performances at low excitation, the sample excited at higher radiative density shows a thermal rollover as temperature increases, this sudden drop indicates thermal quenching [4]. Since the combined effect of the carrier temperature and phosphor self-heating increases the temperature of the phosphor layer, thermal quenching is 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 indicate that up to 525 °C no sensible degradation can be noticed neither in reflected nor transmitted photoluminescence, while at 550 °C a gradual degradation in the Photoluminescence emission can be observed. Reflected PL signal shows a more intense degradation; this behavior is 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 where photoluminescent materials are crucial to achieve broadband white lighting. Results in particular indicate that temperature plays a fundamental role in performances and reliability of phosphors, but while for systems with binders temperature has a strong effect also at low values (in the order of 100 °C), in systems where no binders are involved temperature is only involved in the phosphor degradation at values above 500 °C.

References

1. Trevisanello, L.; De Zuani, F.; Meneghini, M.; Trivellin, N.; Zanoni, E.; Meneghesso G. Thermally activated degradation and package instabilities of low flux LEDS. *IEEE International Reliability Physics Symposium* **2009**, 98–103, doi:10.1109/IRPS.2009.5173231.
2. Kim, J.K.; Luo, H.; Schubert, E.F.; Cho, J.; Sone, C.; Park, Y. Strongly Enhanced Phosphor Efficiency in GaInN White Light-Emitting Diodes Using Remote Phosphor Configuration and Diffuse Reflector Cup. *Jpn. J. Appl. Phys.* **2005**, *44*, L649.
3. Dal Lago, M.; Meneghini, M.; Trivellin, N.; Mura, G.; Vanzi, M.; Meneghesso, M.; Zanoni, E., Phosphors for LED-based light sources: Thermal properties and reliability issues, Microelectronics Reliability **2012**, *52*, 2164–2167, doi:10.1016/j.microrel.2012.06.036.
4. Bachmann, V.; Ronda, C.; Meijerink, A. Temperature Quenching of Yellow Ce^{3+} Luminescence in YAG:Ce. *Chem. Mater.* **2009**, *21*, 2077–2084, doi:10.1021/cm8030768.