CHARACTERIZATION OF OPTICAL PARAMETERS AND EVALUATION OF THE QUANTUM YIELD OF THE LED PHOSPHOR LAYER

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This paper studies absolute photoluminescence as well as the quantum yield of phosphors (YAG: Ce) used in the manufacture of LEDs. The interactions between light and phosphor samples with and without silicone dispersion were investigated, since the optical properties of luminescent materials have a great influence on the efficiency of LEDs. From the calculations of the reflected, absorbed and transmitted radiation in the phosphor, the quantum yield of the phosphor was evaluated.

Keywords: LED, phosphor, luminescence spectrum, quantum yield
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INTRODUCTION

Phosphor conversion is the most common method for achieving white light using single LED chips. Among the mainstream and most commonly used phosphors is the yellow YAG: Ce phosphor (known to have high quantum efficiency), which is usually pumped by a blue (450 nm) light energy source. This simple and effective method produces a white LED with a color rendering index of 70-80. It is known that only a limited number of phosphors can be used as conversion materials due to the many requirements for the realization of the spectrum conversion process. These phosphors should have wide enough excitation and emission spectra and energy conversion to provide the required CRI and quantum efficiency. Phosphors must also provide a high fluorescence quantum yield and high thermal stability. They are expected to have a small particle size and a uniform spherical morphology to reduce scattering, improve quantum efficiency, and be easily mixed in matrices of silicones, epoxies, and other resins.

The precise characterization of phosphors used in LEDs for solid state lighting is important for understanding the extraction efficiency and light conversion in LED devices [1]. An accurate assessment of the photoluminescence (PL) efficiency of phosphors is a difficult task, mainly due to the difficulty of understanding the behavior of reflected and transmitted light (scattered and transmitted), as well as the need for accurate estimation of light losses in the optical range. When the light wave hits the silicone/phosphor layer, several things can occur. Light can reflect against the surface, be selectively absorbed by the phosphor, scattered by the phosphor particles (differently depending on the particle size), converted to different wavelengths, or transmit through the layer. That is why an accurate understanding and explanation of the processes describing the interaction of the particles of light with the phosphor is necessary [2,3]. The quantum yield of a luminescent material is defined as the ratio of the number of emitted photons and the number of photons absorbed by the irradiated sample; it characterizes the radiative transition in combination with the luminescence lifetime, the luminescence spectrum and the stability of the phosphor.

Quantum yield is a criterion for the selection of luminescent materials used in solid state lighting devices. Knowledge of the quantum efficiency provides important feedback in the development of new synthesis methods for the various luminescent materials in research. Despite the importance of an accurate assessment of the quantum yield of luminescent materials, there are very few studies in the literature devoted to the study of its absolute values [4,5]. In these references, the photoluminescence quantum yield value for the yellow phosphor YAG: Ce is often quoted as being greater than 90%.

The behavior of incident radiation interacting with samples of different absorption and diffusion properties cannot be thoroughly studied, since the reflected and transmitted light are not differentiated in the integrating sphere. Measuring the reflected and transmitted light separately will give more information about the interaction of light with the phosphor: the amount of reflected and transmitted converted light, the difference in the ratio of yellow and blue components between reflected and transmitted light. These effects are due to the physical properties of the phosphors (absorption, particle size and concentration). Thus, analyzing the properties of both reflected and transmitted light gives a deeper look at these phenomena, which is important for optimizing LEDs.

EXPERIMENTAL PART

To study the characteristics of the phosphor, an integrating sphere with a diameter of 30 cm was used. The setup is shown schematically on fig. 1. The sample was placed at the input slit on the wall of the sphere, so that one of the sides of the sample was facing the outside of the sphere. To register the photons reflected from the sample (blue and yellow), the source of exciting emission must illuminate the sample from the inside of the sphere, the reflection from which is measured by a spectrophotometer, optically connected to the sphere. For this purpose, an optical cable is inserted into the sphere, which has an optically non-

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absorbing coating, the exciting radiation of which is concentrated on the sample. To register the photons transmitted through the sample, the sample should be illuminated from outside of the sphere, with the light scattered and emitted by the phosphor being measured with a spectrophotometer. The integrating sphere and the applied measuring equipment used in the experiment were from Everfine (PMS-80 Spectrophotocalorimeter).

To determine the absolute values of the reflected and transmitted radiation for commercial phosphors, firstly, the power of the initial blue radiation was measured in the integrating sphere. The spectrophotometer measures the spectral flux distribution (W/nm), which allows the direct calculation of power values for individual wavelengths as well as reflected and transmitted components of total optical power. YAG:Ce phosphor with a peak emission wavelength of 550 nm dispersed in silicone epoxy at a concentration of 0.5 g/cm^3 was used as a sample, and also the same phosphor compressed into a tablet without the epoxy. The density was maintained equal in both samples, so as to keep the same amount of phosphor across its thickness. The concentration of phosphor in the silicone was 10% because the density of the phosphor particles in a 10% sample (~9×104 particles/mm^3) is of the same order of magnitude as the density of the phosphor commonly found in LED packages.

To evaluate the influence of the clear encapsulating material on the transmittance of the luminescent layer, the transmission properties of the silicone epoxy were measured on a linear optical bench. By placing the sample between the light source and the detector, the light emitted by the control LED was transmitted through the silicone layer and compared to a measurement of the emission from just the light source. Resulting data was obtained by subtracting these two data sets.

RESULTS

Figure 2 shows the emission spectra of the excitation source and the phosphor. An important requirement for the measurement of the quantum yield of the phosphor is that the excitation spectra of the pump source and the phosphor do not intersect. It can be seen that the emission spectra do not overlap, which makes it possible to calculate the energy distribution of the two spectra.

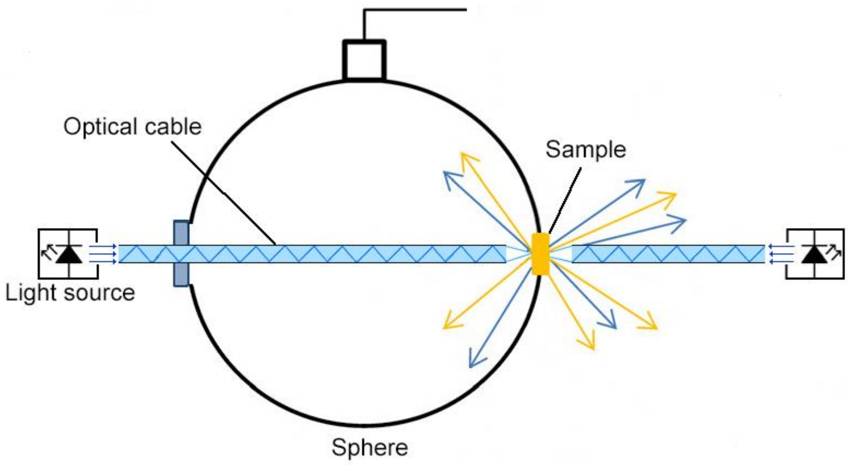

Fig. 1. Schematic representation of an integrating sphere for measuring the properties of a phosphor.

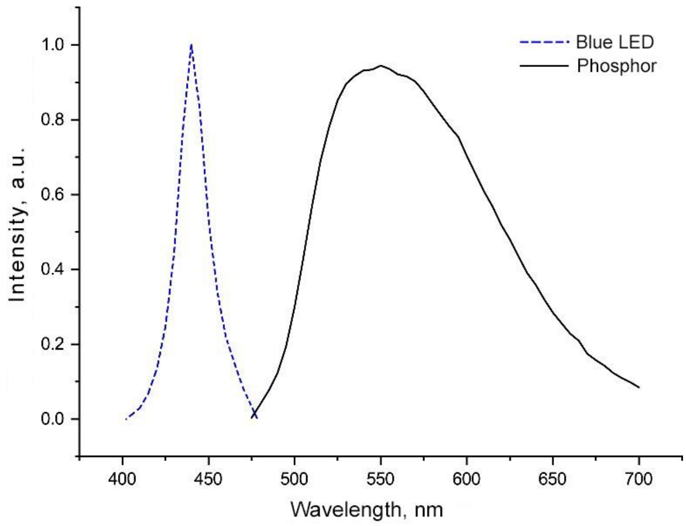

Fig. 2. Spectral distribution of the LED and phosphor.

YAG:Ce phosphor properties

Table 1

Emission	Initial, W	Reflected, W	Transmitted, W	Loss, %
Free phosphor				
Yellow	10	2.8	4.2	11
Blue		0.6	1.3	
Dispersed phosphor				
Yellow	10	2.7	4.1	13
Blue		0.6	1.3	

The measurement results shown in Table 1 showed that 34% of the initial light energy is lost just as a result of reflection at the phosphor particles. Another 11% of the optical power is wasted on the non-radiative absorption of blue photons by the phosphor. These losses are due to the Stokes shift and the quantum efficiency of the phosphor. As a result, the power of the initial irradiation not involved in the output emission is equal to:

$$Fe_{loss}=Fe_{total}-(Fe_{ref}+Fe_{tr}) \quad (1)$$

By converting the luminous power values into photon count values, the quantum yield of the phosphor can be calculated using the following expression [6]:

$$\eta_l=\frac{N_e}{N_b}=\frac{N_e}{N_b^{total}-(N_b^{ref}+N_b^{tr})} \quad (2)$$

where N_e is the number of photons emitted by the phosphor, N_b is the number of photons emitted by the blue LED, N_b^{ref} and N_b^{trans} are the reflected and transmitted blue photons, respectively.

The quantum yield in case of the phosphor dispersed in silicone epoxy was 93.2% ± 0.5%, while the quantum yield of the free phosphor was 91.2% ± 0.5%. Errors in quantum efficiency values were estimated by calculating the standard deviation from experimentally measured averaged quantum efficiency values from 10 different measurements.

Emission transmission in the silicon epoxy was within the 99% range for visible wavelengths, although there will always be a small shift of this value in the 380 nm to 780 nm range. Multiple reflections within the silicone layer result in only small transmission losses, which are wavelength dependent. This effect explains the shift in color coordinates to a slightly more reddish wavelength when the phosphor is mixed with transparent polymers or silicones.

Considering all the above, it can be stated that the traditional method of dispersing phosphor particles in silicones is not ideal for efficient photon extraction. To fully extract the reflected photons, it would be necessary to redirect them back using a 100% reflector placed on the die substrate surface. However, this approach does not solve the problem of yellow reflected photons, which will not excite the phosphor even if redirected backward. In phosphor converted white LEDs, low efficiency to a certain extent is an inherent property of the phosphor, which can only be improved by increasing the quantum efficiency. However, the isotropic nature of the emission of the phosphor converted light leads to the fact that approximately half of the converted light must undergo multiple reflections between the phosphor layer and the LED chip on the substrate, which will also lead to a certain decrease in efficiency.

CONCLUSION

Thus, using the transmission method in the integrating sphere, the optical parameters of the YAG:Ce phosphor were measured, as a result, the factors influencing the optical characteristics of white LEDs associated with the phosphor were revealed. Accurate measurements of the absorption of the incident blue light, together with the absolute values of reflected and transmitted light, are valuable optical constants of the tested phosphor samples. The quantum yield values obtained in this paper are in good agreement with the values reported by other authors in literature. It was concluded that the method of mixing the phosphor with silicone epoxy results in an increase in the intensity of the outgoing light, which is associated with the refractive parameters of the light in the layer.

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[1] *R. Cees.* Luminescence: From Theory to Applications, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (2008) 276 p.

[2] *H. Shi, C. Zhu, J. Huang, J. Chen, W. Wang, Y. Cao, X. Yuan.* Luminescence properties of YAG:Ce, Gd phosphors synthesized under vacuum condition and their white LED performances, Optical Materials Express. Vol. 4, No. 4 (2014) pp. 649-655.

[3] *L. Arunachalam & Ranganathan, S. Kumar, V. Sivakumar, T. Preema M.T. Jose.* Synthesis, photoluminescence and thermal quenching of YAG:Ce phosphor for white light emitting diodes,

Indian Journal of Pure and Applied Physics. Vol. 49, No. 5 (2011) pp. 303-307.

[4] *Lei, Chen & Chun-Che, Lin & Chiao-Wen, Yeh & Liu, Ru-Shi*. Light Converting Inorganic Phosphors for White Light-Emitting Diodes, Materials. Vol. 3, No. 3 (2010) pp. 2172–2195.

[5] *A. Keppens, Y. Zong, Y. Ohno, G. Deconinck, P. Hanselaer*, Determining Phosphors' Effective Quantum Efficiency For Remote Phosphor Type Of Led Modules, CIE Expert Symposium on Spectral and Imaging Methods for Photometry and Radiometry (2010).

[6] *S. Philippe, A.B. Parmentier, D. Poelman.* Journal of Electrochemical Society, Vol. 158, No. 6, (2011) pp. R37-R54.

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