Effect of temperature and moisture on the luminescence properties of silicone filled with YAG phosphor*

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Abstract: In order to determine the environmental effects on the luminescence properties of a phosphor layer for high-power light emitting diodes, a high humidity and temperature test (85 ℃/85%RH) and a thermal aging test (85 ℃) were performed on silicone/YAG phosphor composites. The luminescence properties of silicone/phosphor composites are monitored by a fluorescence spectrometer. The results show that high temperature could result in an increase in conversion efficiency of composites during the early aging stage and red shift of YAG phosphor; and high humidity could result in a significant decrease in conversion efficiency of composites while having a small influence upon the optimal excitation wavelength of the YAG phosphor.

Key words: high power light emitting diodes; phosphor layer; $Y_3Al_5O_{12}$; high humidity and temperature test; thermal aging test

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1. Introduction

High power LEDs (HP-LEDs), owing to their low energy consumption and long life, etc, are considered to be the fourth generation light source. There are three kinds of method to achieve white HP-LEDs, but not all are mature enough. Among them, the blue LED chip with a yellow/green phosphor excitation recombination, which was developed first and is now widely applied, is the most mature. As one of the key technologies, the coating and reliability of the phosphor layer in LED has attracted wide attention. The performance of the phosphor layer has a dramatic impact on the performance of white HP-LEDs. For example, the emission spectra of phosphor will have a mismatch with the chips after phosphor decay, which may lead to a blue-shift of the LED light, resulting in a serious impact on lighting applications.

The stresses resulting in phosphor layer decay might be induced by temperature, moisture, mechanical loading and so on. Zhang *et al*. studied the temperature dependence of the luminescence and decay time of YAG:Ce nanophosphor[1]. The effects of temperature or humidity on phosphor layer in the white LED device have been investigated by several researchers[2–5]. However, the phosphor layer in the white LED device is subjected to many complicated factors and the excitation spectrum of the phosphor layer on the full light wavelength range cannot be obtained. To investigate the effect of temperature and humidity on the luminescence properties of the phosphor layer, silicone/phosphor composites are prepared for aging under high temperature and high humidity conditions.

2. Experimental procedures

2.1. Materials

A two-part high optical transparency silicone was used as the matrix, and Ce^{3+} doped yttrium aluminum garnet ($Y_3Al_5O_{12}$) powder was used as the filled phosphor particles. The silicone/phosphor composites were prepared by mixing uncured silicone and phosphor in a 1 to 2 weight ratio. To remove air bubbles, the mixture was placed in the vacuum pressure chamber until no bubbles emerged. Then, composite samples (diameter 10 mm, thickness 0.8 mm) were obtained by curing at 150 ℃ for 1 h.

2.2. Test condition

In order to determine the effect of temperature on the silicone/phosphor composites, the composites were subjected to thermal storage: three samples were aged at 85 ℃ for 1000 h. Another three samples were aged in a constant temperature and humidity chamber with 85 ℃ and 85% relative humidity for 880 h to investigate the effects of the stress induced by moisture. The composites' luminescence properties were measured every 110 h with a fluorescence spectrometer.

2.3. Measurement

Fluorescence spectroscopy was used to measure the luminescence properties of the composites. A schematic diagram of the test method is given in Fig. 1. To obtain the emission

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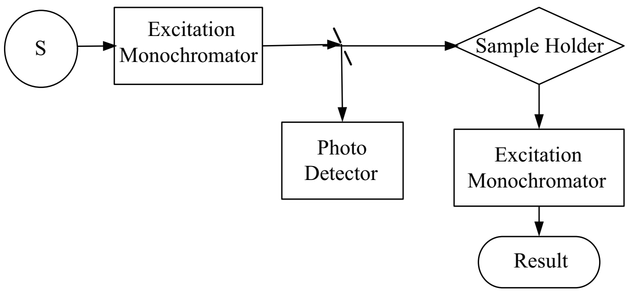

Fig. 1. Schematic diagram of fluorescence spectroscopy method to measure luminescence properties.

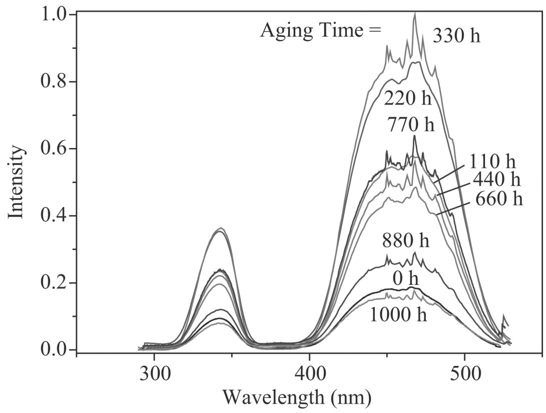

Fig. 2. Photoluminescent excitation spectra of silicone/phosphor composites during the 85 ℃ stress.

spectrum, a monochromator was used to hold the excitation light at a constant wavelength. In that way, the different wavelengths of fluorescent light emitted by the sample holder could be measured. An emission monochromator was used to hold the emission light at a constant wavelength. Then the excitation light was scanned through various wavelengths and an excitation spectrum was obtained. The measurement parameters remained unchanged during 85 ℃ and 85 ℃ /85%RH stresses.

3. Results and discussions

3.1. Excitation spectrum

The photoluminescent excitation spectra during the 85 ℃ stress and the 85 ℃/85%RH stress are shown in Figs. 2 and 3, respectively. Note that the excitation spectrum is the average of three samples and the results are normalized. The figures show that there are two excitation peaks (about 343 and 457 nm) in the wavelength range from 290 to 525 nm, which can be attributed to the Ce^{3+} transitions from the 4f ground state to the 5d field splitting excited states[6]. The excitation spectra changed with aging time under both 85 ℃ and 85 ℃/85%RH stresses. We are interested in the relation of the aging time to the optical power under blue LED chip irradiation and the optimal excitation wavelength of the main excitation peak. These relations are presented in Sections 3.1 and 3.2.

3.2. Intensity under blue LED chip irradiation

Since the radiation flux of the blue chip, P_{chip}, and the radiation flux of the phosphors, P_{phosphor}, are both the function of

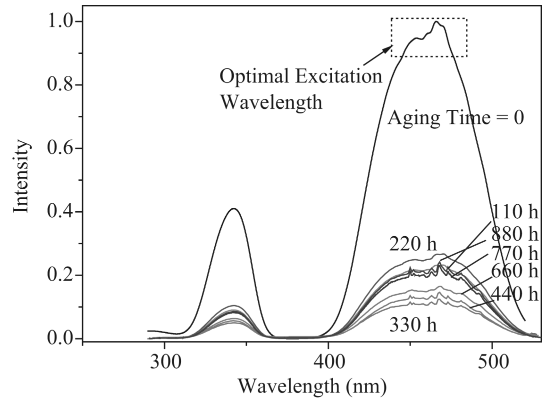

Fig. 3. Photoluminescent excitation spectra of silicone/phosphor composites during the 85 ℃/85%RH stress.

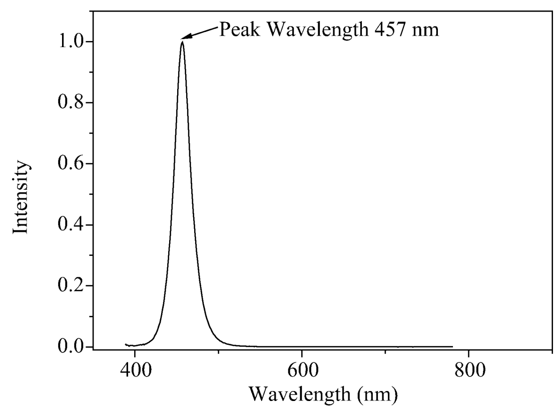

Fig. 4. Typical emission spectrum of blue LED chip.

the wavelength, the optical power of silicone/phosphor composites under blue LED chip irradiation are derived from integrating the excitation spectrum of the composite and the emission spectrum of the blue chip by the following equation,

$$P = \int_{\lambda_1}^{\lambda_2} P_{\text{chip}} P_{\text{phosphor}}, \tag{1}$$

where λ_1 is 290 nm and λ_2 is 525 nm. A typical emission spectrum of the blue chip (as shown in Fig. 4) is used to integrate, where the peak wavelength is at 457 nm and the half wavelength is about 20 nm.

The relative changes in integrated optical power over all of the tests are given by a graph of normalized relative intensity versus aging time (Fig. 5). The results indicate that at 85 ℃, the conversion efficiency of silicone/phosphor composites increases with aging time first, and then decreases after 330 h. The conversion efficiency increase may result from a transmittance efficiency improvement of the silicone. This may be because the curing reaction of the silicone is not complete before the stress, and the cure degree of the silicone increases with aging time at 85 ℃. In contrast, in the 85 ℃/85%RH, the conversion efficiency of the composites decreases significantly in the early stage of aging, and then slightly increases with aging time after 330 h. The moisture absorbed by the silicone may be responsible for the significant decay during the early stage because water molecules may result in a decrease in the refractive

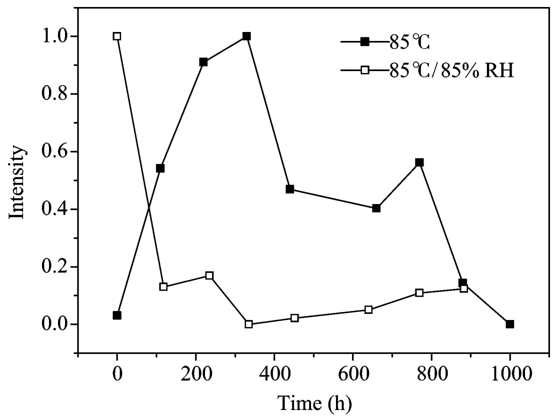

Fig. 5. Integrated optical power under blue LED chip irradiation during stress.

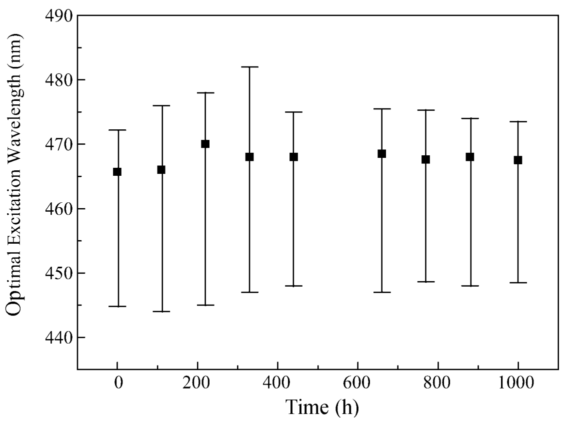

Fig. 6. Optimal excitation wavelength (■) and optimal excitation wavelength range (— represents upper and lower bounds) during stress at 85 ℃.

index of the silicone.

3.3. Optimal excitation wavelength

Optimal excitation wavelength versus aging time under 85 ℃ and 85 ℃/85%RH are shown in Figs. 6 and 7. Curves for the optimal excitation wavelength range, as shown in Fig. 3, versus aging time are also are plotted in the figures. The results show that at 85 ℃, the optimal excitation wavelength is slightly red shifted, and the optimal excitation wavelength range broadens with aging time and then narrows after a few hundred hours. The same phenomenon can be observed in 85 ℃/85%RH. This indicates that temperature has a great impact on the luminescence properties of phosphor, but humidity has little influence upon it.

4. Conclusion

A high humidity and temperature test and a thermal aging

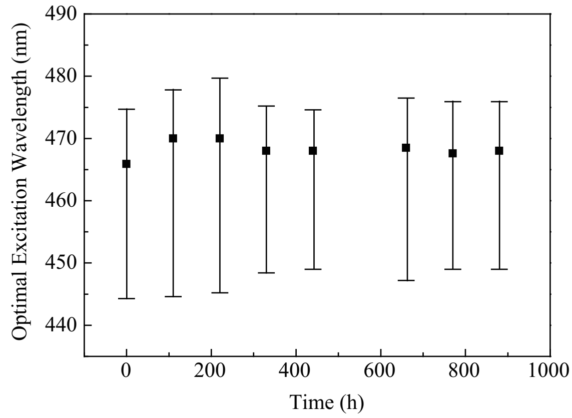

Fig. 7. Optimal excitation wavelength (■) and optimal excitation wavelength range (— represents upper bounds and lower bounds) during stress at 85 ℃/85%RH.

test were performed on silicone/YAG phosphor composites to determine the temperature and moisture effects on the luminescence properties of the phosphor layer for high-power light emitting diodes. Based on the experimental results, the following conclusions can be drawn:

(a) High temperature could result in an increase in conversion efficiency of composites during the early aging stage. This may be due to the high temperature improving the cure degree of the silicone.

(b) High humidity could result in a significant decrease in the conversion efficiency of the composites. This may be due to the moisture absorbed by the silicone decreasing the refractive index of the silicone significantly.

(c) High temperature could result in a red shift of the YAG phosphor; but humidity has little influence upon the optimal excitation wavelength of phosphor.

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