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Luminescent Phosphor-in-Glass Composite for White Light-Emitting Diodes

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Abstract A luminescent composite material based on YAG:Ce^{3+}–doped silicate glass (Phosphor-in-Glass, PiG) was fabricated and studied. For the glass matrix, the $40SiO_2$–$25PbF_2$–$20PbO(Pb_3O_4)$–$15AlF_3$ material was used. PiG samples were sintered at the temperature 550°C with concentration of YAG:Ce^{3+} varying from 90% down to 50%. Luminescence spectra of the PiG samples were recorded and quantum efficiency of the experimental samples was measured with the use of an integrating optical sphere. A design of light-emitting diode (LED) modules with the sintered PiG was developed and the temperature of the surface of the modules was analyzed.

Keywords: *phosphor-in-glass, luminescence, LED*

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1. Introduction

Light-Emitting Diodes (LEDs) are presently considered to be the most promising sources of artificial light. The operation of LEDs is based on mixing blue light produced via electroluminescence of a semiconductor chip with yellow light produced via photoluminescence of phosphor particles embedded in a matrix, which also protects the LED chip. Currently, yttrium–aluminum garnet (YAG) doped with Ce^{3+} ions is the most popular phosphor material. In the present–generation LEDs, YAG:Ce^{3+} is commonly placed in an organic matrix made of silicone resin, as described, for example, by Chen *et al.* [1]. This design works well for low–power LEDs, but using organic matrix in high–power LEDs leads to rapid degradation, which is mainly caused by strong heat dissipation in the silicone matrix with low thermal conductivity. One of the ways of solving this problem is to use materials based on glass with nano–sized light–converting crystals (glass–ceramics), as was shown, for example, by Aseev *et al.* and Kim *et al.* [2,3]. Another alternative is to use glass ceramic materials as the matrix for phosphor particles (Phosphor–in–Glass, PIG), as discussed elsewhere [4-12]. Glasses possess higher thermal and chemical stability and mechanical durability as compared to silicone resins.

In this paper, we present a luminescent PiG composite for white LEDs and report on the properties of the material. We also present a LED module, which consists of blue LED chip and the material, and is designed with the “chip-on-board” technology. The optical properties and heat dissipation in the LED modules based on the new material are discussed.

2. Materials and Methods

PiG composites were sintered with various concentrations of YAG:Ce^{3+}, see Table 1.

Table 1. Chemical composition of PiG samples

Sample	Glass Composition	Weight fraction of YAG:Ce^{3+}, %
1	$SiO_2(40)$-$PbF_2(25)$-$PbO(Pb_3O_4)(20)$-$AlF_3(15)$	90
2		80
3		70
4		60
5		50

Uniform mixture of YAG:Ce^{3+} and glass ($40SiO_2$ – $25PbF_2$ – $20PbO(Pb_3O_4)$ – $15AlF_3$) was formed in square-shaped samples with the thickness of 500 µm. This type of glass was chosen because of high refraction index (n>1.7) and low sintering temperature (down to 350°C) [13].

On the basis of the results of preliminary experiments, which showed that synthesis temperatures lower than 600°C were needed to achieve reasonable homogeneity and optical transparency of the PiG system under study [14], the temperature of the synthesis was chosen as 550°C with the duration of the process 30 min. The morphology of the samples was studied with the use of electron microscope Leica DX RX. The optical properties of the material were examined using integrating optical sphere OrbOptronix SP-75. Also, a LED module system consisting of a blue semiconductor chip and the PiG material (for all PiG samples) was designed. The luminescence spectra were recorded and optical properties of the system were studied using integrating optical sphere Gamma Scientific and SpectralSuite 3.0 software. The temperature at the surface of the LED modules was measured with an infrared camera Optris PI450. For these measurements, the operating conditions of the modules were: working current, 1 A; voltage, 11 V; surrounding temperature, 23°C; working time before temperature measurement, 30 min.

3. Experimental Results and Discussion

Figure 1 shows morphology of PiG samples #1 and #5. The morphology of both samples was heterogeneous, yet the morphology of sample #5 was more uniform than that of sample #1. Using information from the two images in Figure 1, one can conclude that during the synthesis, the reaction of interaction between particles of glass and phosphor was not sufficiently strong to form a homogeneous structure, and as a result one co see big conglomerations of the particles. For the real LED, it would mean that the distribution of light would be different at the different parts of the sample. Note that all the sintered samples with the mass concentration of $YAG:Ce^{3+}$ varying from 90% down to 50 % with the step of 10%. were heterogeneous. The only conclusion that could have been made from these experiments was that reducing mass concentration of the $YAG:Ce^{3+}$ in the glass led to the improvement in the homogeneity of the samples. This can be possibly achieved via introduction of an additional step of vacuum stirring or through lowering the temperature of the synthesis while increasing the duration of the process.

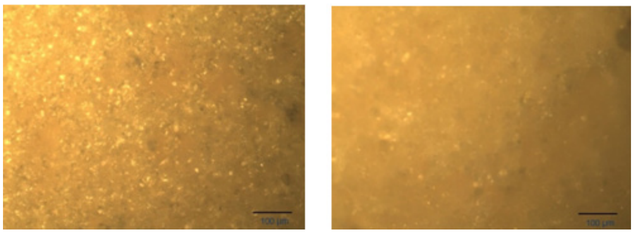

Figure 1. (Color online) Surface morphology of PiG samples #1 (left image) and #5 (right image)

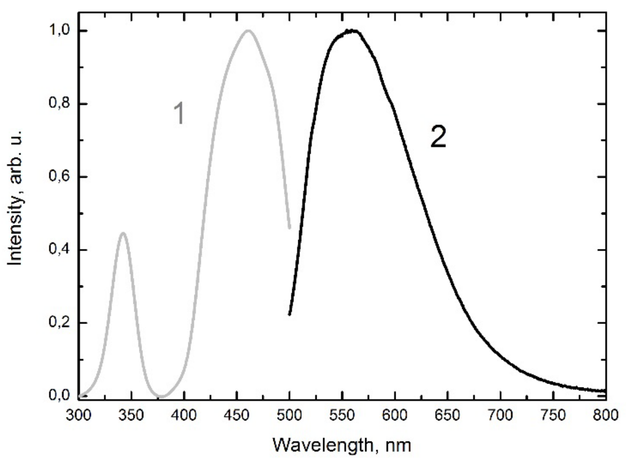

Figure 2. Excitation (curve *1*) and luminescence (curve *2*) spectra of PiG sample #1

Figure 2 shows excitation and luminescence spectra of PiG sample #1. In the excitation spectrum, peak at 348 nm corresponds to the F–F transition in Ce^{3+}, while peak at 470 nm corresponds to the F–D transition in Ce^{3+}.

In the luminescence spectrum, one can see a broad line with the peak at 535 nm, as can be expected from a phosphor for white LEDs. The obtained results show the absence of significant effect of replacing silicone resin with glass matrix on the emissivity of the phosphor. The variations in chemical composition of the glass matrix led to an insignificant displacement of the luminescence and excitation peak as was shown in the previous study [14].

In Figure 3, the design of a LED module consisting of a blue semiconductor chip and the sintered PiG sample is shown. A layer of silicone resin was used for attaching the PiG samples to the LED chips.

In Figure 4, luminescence spectra of the LED modules are shown for all PiG compositions. It can be seen that the highest intensity is observed for modules with PiG samples #3 and #5. However, the 'color' of the light produced by these modules was more bluish rather than warm white, which is needed for real LEDs. Closer examination of the spectrum of sample #3 shows that the intensity of yellow light from this module was very low. Such situation could happen because of shortcomings in the design of sample #3, with blue light being emitted from the sides of the LED module. In Figure 4 it is seen that in samples ##1, 2 and 4, the intensities of blue and yellow light were very similar. Such LED modules, therefore, could be used in real LEDs for producing warm white light. In Table 2, the luminescence efficiency of the LED modules is presented.

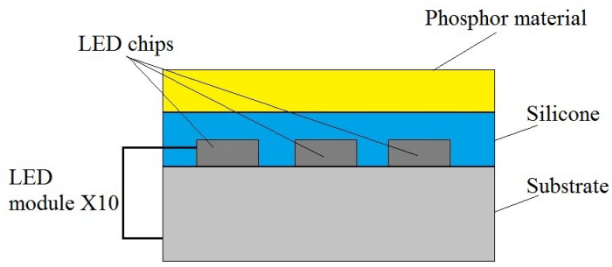

Figure 3. (Color online) Schematic view of the experimental LED module consisting of a blue LED chip and a PiG sample

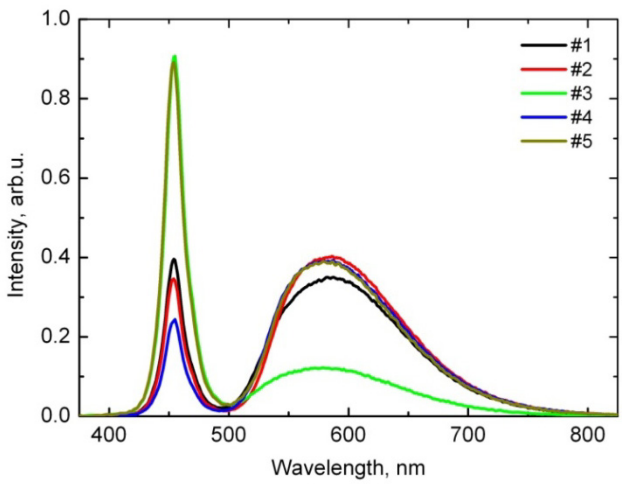

Figure 4. (Color online) Luminescence spectra of the LED modules consisting of blue LED chips and 5 PiG samples

Table 2. Luminous efficiency of LED modules

PiG sample used	Luminous efficiency, Lm/W
1	17.99
2	19.45
3	19.60
4	19.75
5	20.04

From samples ##1, 2 and 4, the best luminescence efficiency of 19.75 Lm/W was shown by sample #4 because of. However, all the studied samples had rather low luminescence efficiency as compared to that of real LEDs employing similar LED chips and silicone resin as the matrix for the phosphor (~110 Lm/W). This could be due to oxygen inclusions and cracks, which formed in the silicone interlayer during the cooling of the LED modules after PiG plate was deposited on the chips.

Figure 5 illustrates the image of the surface of the LED modules, where PiG samples #1 and #5, respectively, are used. As can be seen that the peak temperature at the center of the sample #1 is 185.1°C. The temperature is distributed over the surface of this sample non-uniformly. The maximum overheating is seen at the center of the module. Where PiG sample #5 is used, the maximum temperature is 186.7°C, and the peak of heating is again observed at the center of the sample. From this result, it can be concluded that the reduction of the concentration of YAG:Ce^{3+} in the sample can insignificantly increase the temperature of the module. A typical temperature at the surface of the LED module with similar chips and a silicone layer containing YAG:Ce^{3+} was around 110°C. The higher temperature of our samples can be related to cracks and oxygen inclusions in the silicone interlayer, which form during the cooling process after PiG is deposited on the chips. Such defects would lead to stronger heat dissipation in the layer, and eventually, to overheating of the system. Obviously, more research is required to optimize the design of the modules and to find optimal phosphor concentration, yet it is clear that thermally and chemically stable PiGs are promising materials for high-power LED technology.

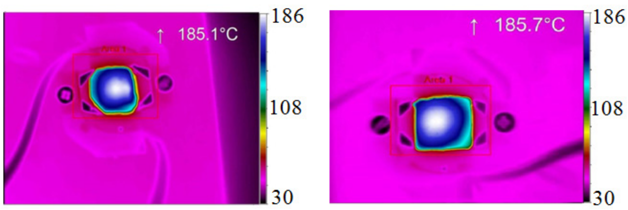

Figure 5. (Color online) Infrared images of the surface of the experimental LED modules with PiG samples #1 (left image) and #5 (right image). Temperature scale (in°C) is shown on the right of each image

4. Conclusions

A new Phosphor-in-Glass (PiG) material for white LEDs has been developed. The optical and thermal properties of specially designed LED modules, which utilized the PiG material, were explored. The results obtained during the research proved that the sintered PiG material was promising in meeting the main challenges of LED technology, yet required the development of the proper technology of integrating PiG material into LED structure. Additional studies are needed to explore the full potential of PiG in LED technology.

Acknowledgements

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