Phosphor in Glass based on High Refractive Index Glasses for LEDs

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Abstract: Composite “phosphor-in-glass” based on high refractive index lead-silicate glass and YAG:Ce and SiAlON powder has been developed and synthesized. Glass composition optimization in the order to reduce scattering at glass/phosphor interfaces has been performed. Samples of composite light-converting materials for white LEDs were prepared by sintering glass powders and phosphor at 600 °C. Spectral, luminescent and structural properties of the obtained composites have been investigated. White LEDs based on the composite glass phosphor materials obtained have been tested. The color temperature of the probe LED was found to be 4370 K with the luminous efficacy 58lm/W.

1 INTRODUCTION

White light-emitting diodes (LEDs) have attracted considerable attentions now due to promising features such as low energy consumption, long lifetime, small size, fast switching, as mercury free nonpolluting environment, so have a great perspective for applications in display backlights, transport and general lighting, advanced communication technique, etc. (S. Ye, F. Xiao et al, (2010), De Clercq et al. (2010)). There are two main approaches for producing white light with LEDs. In the first one, white light is generated by additively mixing of multiple primary color LEDs with a high luminous efficacy (LE) since there is no Stokes losses. But the color rendering index (CRI) depends on the number of selected primary color LEDs that leads to increase their cost. In the second approach, white light is generated by single or multiple phosphors using down-conversion of blue light pumped from InGaN chip into visible light. For example, the single yellow $Y_3Al_5O_{12}$:Ce phosphor has already commercially used with blue-emitting InGaN chip to fabrication low cost phosphor converted white LEDs (pc-WLEDs). For fixing powered phosphor on a chip usually use silicone resins. But these materials are unstable to UV exposure and temperatures above 150°C. Degradation of resins result to dramatically decreasing of WLED efficiency due to induced absorption (N. Narendran,Y.Gu, J et al. (2004), M.-H.Chang, et al (2012)).

Inorganic materials, like glasses and ceramics, are more stable as polymer binders. For instance, thin transparent ceramic plates based on $Y_3Al_5O_{12}$:Ce used as a phosphor for making WLED (S. Nishiura, et al. (2011)). But sintering process is difficult and therefore results in a high cost ceramics.

2 EXPERIMENTAL

Lead-silicate glasses with different amount of lead fluoride and aluminum fluoride have been synthesized ($40SiO_2$-20PbO-(40-x)PbF_2-xAlF_3, x = 25, 15, 10, 5, 0). Glass have been synthesized from high purity materials – National Standart 13867-68. All compounds have been weighted with a high accuracy (±0.01 g). Glass synthesis has been provided in electrical furnace with silit heaters at 900 °C for 30 min. Glass synthesis in opened corundum crucible in air atmosphere provided high glass quality (primarily, transparancy) and corresponded to oxidative conditions. Obviously, glass composition of synthesis has not been matched with final glass composition because of high fluoride losses in form of SiF_4. Effect of fluorides on some physical properties changing for lead-fluoride-silicate glasses has been analyzed. Substitution of

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lead oxide PbO with lead fluoride PbF_2 results in increasing of total content of fluorides in glass. Just after glass moulding, the glass has been quenched just at 320 °C in muffle furnace.

Introduction of lead fluoride into glass reduces the glass transition temperature, thereby reducing the sintering temperature of the samples to prevent thermal interaction between the components and experimental phosphor-glass samples sintering, because interaction between components can lead to structural failure of the phosphor, whereby it may lose luminescent properties, or they may be broken.

In the synthesis of the starting glass, a smooth variation in the refractive index has been produced by the substitution of lead fluoride to aluminum fluoride in a number of lead silicate glass matrix ($40SiO_2$-20PbO-(40-x)PbF_2-xAlF_3, x = 25, 15, 10, 5, 0). As mentioned, the character of the changes in refractive index demonstrated in Fig. 1. associated with a high specific refraction lead ions compared with aluminum ions.

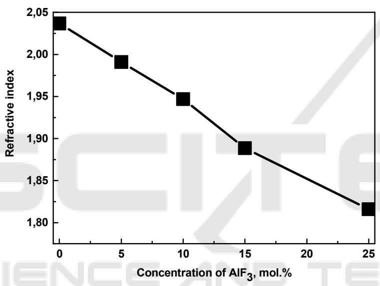

Figure 1: The dependence of the refractive index of the glass on the aluminium concentration in the system ($40SiO_2$-20PbO- (40-x)PbF_2-xAlF_3), x = 25, 15, 10, 5, 0.

Fig.1 shows that increasing of the aluminium fluoride results in increasing of the refractive index from 1.82 to 2.08. By varying the ratio of aluminium it's possible to achieve full match of the refractive indices of the crystalline phosphor YAG:Ce^{3+} and the glass matrix. In this case, a refractive index of 1.83 of glass, which coincides with the refractive index of the YAG:Ce^{3+}, is achieved when the content of aluminium fluoride is about 5 mol. %. One of the requirements for glass frit is the lack of interaction with the crystalline phosphor powder of YAG:Ce^{3+} during sintering. This is due to the fact that the broad band luminescence of cerium in the yellow-green region of the transition member 5d - 4f, and its intensity depends strongly on the surrounding structure. Cerium, which is in the structure of garnet ($Y_3Al_5O_{12}$) has one of the most efficient luminescence bands and garnet structure modification results in decreasing of the luminescence intensity. The "phosphor in the glass" sample has been investigated by X-ray analysis to find out, has the interaction of the crystal structure of garnet composite been broken not. For comparison, the spectrum of the starting YAG:Ce^{3+} powder is added (Fig. 2).

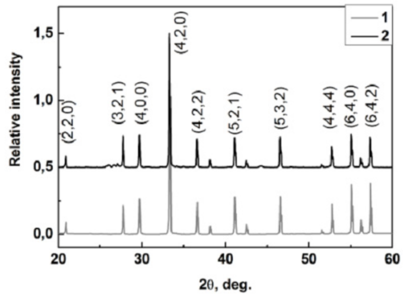

Figure 2: The powder XRD pattern of the crystal $Y_3Al_5O_{12}$:Ce (1) and composite "phosphor in glass" (2).

The XRD-curve shows that the peak position coincides in any matrix that indicates the presence of the same crystal phase $Y_3Al_5O_{12}$. The difference in the intensity of the peaks indicates a different volume of the crystalline phase in the samples.

To show that the crystal structure of the garnet has not broken, when added red phosphor powder based on the oxynitride into the "phosphor in glass" sample – the sample was investigated by X-ray analysis. Figure 3 shows the X-ray diffraction for the "phosphor in glass" with SiAlON and heat-treated sample of the same composition.

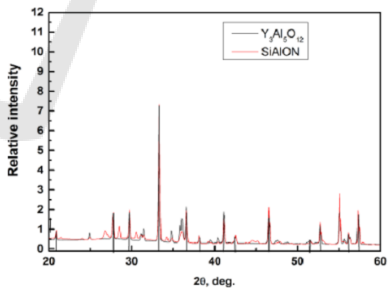

Figure 3: The powder XRD pattern of the pure crystal $Y_3Al_5O_{12}$:Ce powder (black) and composite "phosphor in glass" with SiAlON (red).

XRD-curve shows that the peak position coincides in any matrix that indicates the presence of the same crystal phase of $Y_3Al_5O_{12}$. Adding in the SiAlON composition does not affect on the structure of the $Y_3Al_5O_{12}$ under heat treatment.

3 RESULT AND DISCUSSION

Let us compare the excitation spectra (Fig. 4a) and luminescence spectra (Fig. 4b) of origin crystal powder of YAG: Ce^{3+} with the spectra of YAG: Ce^{3+} in different matrices: commercial silicone and developed PiG.

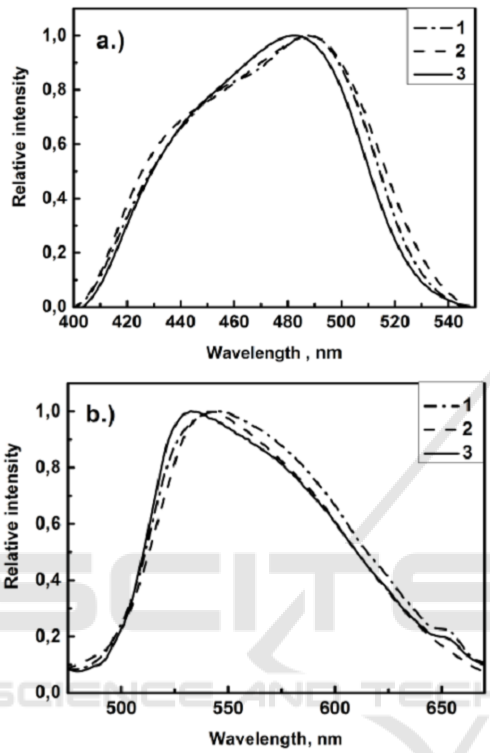

Figure 4: The excitation spectrum (a) and luminescence spectrum (b) of origin powder of YAG: Ce^{3+} (1), the composite "phosphor in glass" (2) "phosphor in the polymer" (3).

Fig. 4 shows that the shape of the spectrums is almost constant from the buffer composition of the binder material. These results also indicate that significant interaction between glass and crystalline phases does not occur during all period of sintering. The spectral-luminescent analysis of sintered samples "phosphor in glass" with two phosphors in its composition was held.

Figure 5 shows the results of spectrum's measurements of composites with varying contents of phosphors. The curves of luminescence and excitation for samples with two phosphors in their composition represent the cumulative spectrums of radiation from two phosphors, which are yellow and red.

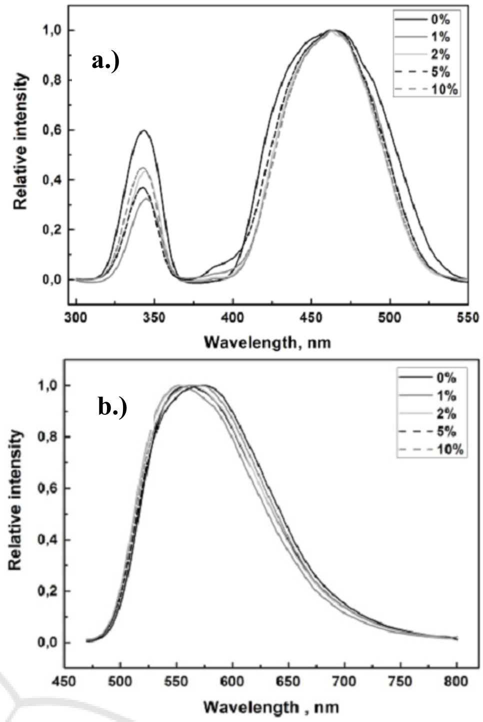

Figure 5: The excitation spectrum (a) and luminescence spectrum (b) of "phosphor in glass" with the different content of SiAlON 10%, 5%, 2%, 1% and 0%.

According to figure 5, it is clear that the shape of spectrums does not practically change in dependence on the composition of buffer binder material. This fact proves that significant interaction between glass and crystalline phases does not occur during sintering. In addition, figure 5 shows the possibility of modifying the spectral composition of radiation, by changing the ratio in YAG:Ce /SiAlON - glass composites. By picking up the required ratio, it is possible to get different values of color temperatures and color rendering indexes of white light, that corresponding to high-quality requirements. To find out how the radiation intensity of the LED is altering in dependence on different excitation wavelengths, the dependence of values of quantum yields on excitation wavelength for samples "phosphor in silicone" and "phosphor in glass" were measured. The resulting dependencies are presented in figure 6. That graph is illustrated that the variety of quantum yield's positions in the measured range of wavelengths, which include wavelengths from 440 to 470 nm for samples based on silicone and glass are the same and amounts to 1.5%.

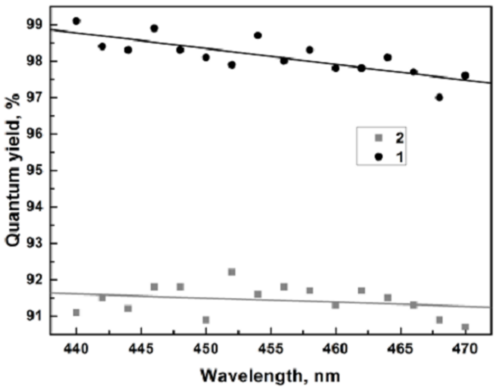

Figure 6: The comparison between the dependencies quantum yields from the excitation wavelengths for samples "phosphor in silicone" (1) and "phosphor in the glass" (2).

The value of the quantum yields varies accordingly in the range of 97.3 - 98.9% for the silicon sample, and 90.7 - 92.2% for the sample of the phosphor in the glass. The difference in the magnitude of values may be associated with defects of production technology. The resulting composite contains inclusions that make additional acquisitions that may reduce the value of quantum yield.

To see possible values of quantum yield for composites with red phosphor in their composition, the dependence of quantum yield of the radiation from the composition of samples was measured. The results of measurement are presented in figure 7.

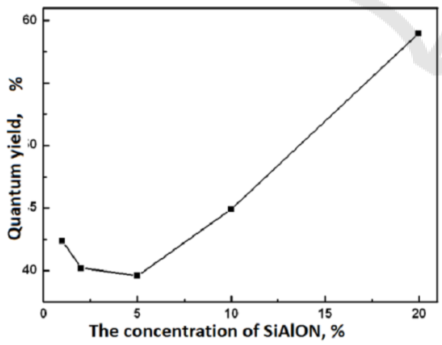

Figure 7: The dependence of the values of quantum yield from composition of samples "phosphor in glass" with different content of the SiAlON phosphor.

The highest value of quantum yield (59%) refers to the synthesizing sample with the content of SiAlON 20%. The standard silicone composite used in the manufacture of white LEDs has a higher value of quantum yield - about 96%. Such a reduction in the quantum yield’s value associated with the molecular interaction between the components of glass charge and phosphor’s powder, because the brightness and the chromaticity does not change significantly in the process of temperature impact due to thermal stability of their crystal structure. That happens through the some components of charge during sintering destroy the structure of oxynitride and forms compounds, which strongly absorbs excitation radiation. The light sources used for household lighting should have a warm white light, characterized by a color temperature in the range of 3500 K and 6,000 K. For radiation, given by the model of white LED, which includes samples of "phosphor in glass", the color temperatures (calculated by the program using the obtained spectrums) were measured. The results of the calculations are presented in figure 8.

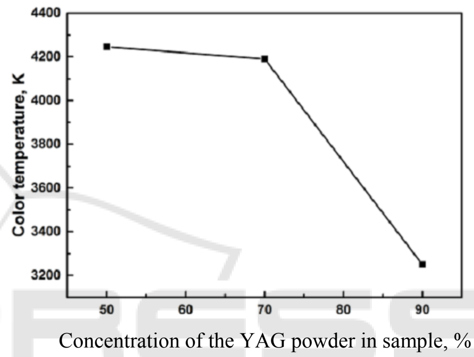

Figure 8: The dependence of color temperature from the phosphor’s concentration.

According to the research results, presented in figure 8 it is clear that the type of dependence of color temperatures from the phosphor concentration in mixture is of exponential nature. Next, the effectiveness of the obtained layout of the led with the ratio of the phosphor powder to glass 70:30 was measured. The resulting layout of the led emits radiation of white light with a color temperature of 4200 K. Luminous efficacy of radiation amounted to 58 lumens/watt. Values for traditional LEDs with silicone are about 85 Lm/W at a comparable color temperature. Also, simultaneously with the calculation of the color temperatures the color rendering indexes of phosphors emission were calculated. For samples consisting of one type of the phosphor the values lie in the range of 62 – 65 %. For samples with two phosphors index value increases in comparison with previous sample and lies in the range of 75-78 %. This confirms that the addition of the red phosphor in the composition allows improving the color characteristics.

4 CONCLUSIONS

The spectral and luminescent properties of PiG (phosphor-in-glass) samples have been investigated to define the relationships between light conversion efficiency, composition and structures. Optical properties of the phosphor have been investigated. It was shown that the optical properties of WLED based of such material can be easily adjusted by changing thickness of phosphor, ratio of glass to phosphor.

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