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Optical and Thermal Properties of Phosphors Based on Lead-Silicate Glass for High-Power White LEDs

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Abstract—A study is reported of the properties of a new phosphor material based on a highly refractive lead-silicate glass and microparticles of yttrium-aluminum garnet doped with cerium ions (YAG : Ce^{3+}). The mass percentage fraction of YAG : Ce^{3+} microparticles in the material was varied from 50 to 90%. The optical properties of the phosphor were examined, as well as its thermal properties when used as a primary optical material in high-power light-emitting diode (LED) units. The results obtained reveal problems of excess heat removal from an LED structure, which appear on passing from phosphor binders based on silicone elastomers to glasses, and demonstrate that the phosphor developed in the study is promising for obtaining warm white light.

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The introduction of light-emitting-diode (LED) lighting is an important factor in the development of energy conservation. The most topical tasks in the current stage of development of LED technologies are to improve the extraction of light and raise the color rendering index and the efficiency of LEDs. With increasing power of LEDs, the excess heat removal from an LED unit becomes the most important problem.

One possible way to solve these problems is by using a phosphor material based on glasses and glass ceramics, rather than on the conventional binders in the form of silicone elastomers. In particular, glasses are being developed in which quantum dots (QDs) serving as phosphor particles and converting the wavelength of light emitted by semiconductor chips are formed directly in the course of synthesis [1–3]. However, QDs still demonstrate a poor emission efficiency, and, therefore, alternative solutions have also been suggested in which microparticles of the conventional phosphor for white LEDs, yttrium-aluminum garnet doped with cerium ions (YAG : Ce^{3+}), are introduced in some way into the glass-ceramic matrix [4–7]. The present communication reports the results obtained in a study of the optical properties and quantum efficiency of a new composite material with inclusions based on a highly refractive lead-silicate glass and YAG : Ce^{3+} microparticles, as well as the results of an analysis of the thermal and optical properties of high-power LED units in which phosphor is used as a primary optical material.

YAG : Ce^{3+} microparticles were introduced into the $40SiO_2–25PbF_2–20PbO(Pb_3O_4)–15AlF_3$ glass chosen due to its high refractive index (~1.8), which will make it possible in the long run to diminish the loss of light in an LED structure, caused by the total internal reflection effect. This glass also has a comparatively low glass-transition point (~400°C) [8], which hinders the thermal disintegration of garnet particles and the mutual diffusion of the glass and garnet components and cerium atoms in synthesis of the phosphor material. The chemical compositions of the samples synthesized in the study are listed in Table 1.

Our synthesis technology consisted in the following: the glass ground into a homogeneous powder with a characteristic microparticle size of 15–25 μm was

Table 1. Chemical composition and quantum efficiency of the developed phosphor materials

No.	Mass fraction of YAG : Ce^{3+}, %	Mass fraction of glass, %	Quantum efficiency, %
1	90	10	85
2	80	20	91.5
3	70	30	80.3
4	60	40	92.6
5	50	50	82.0

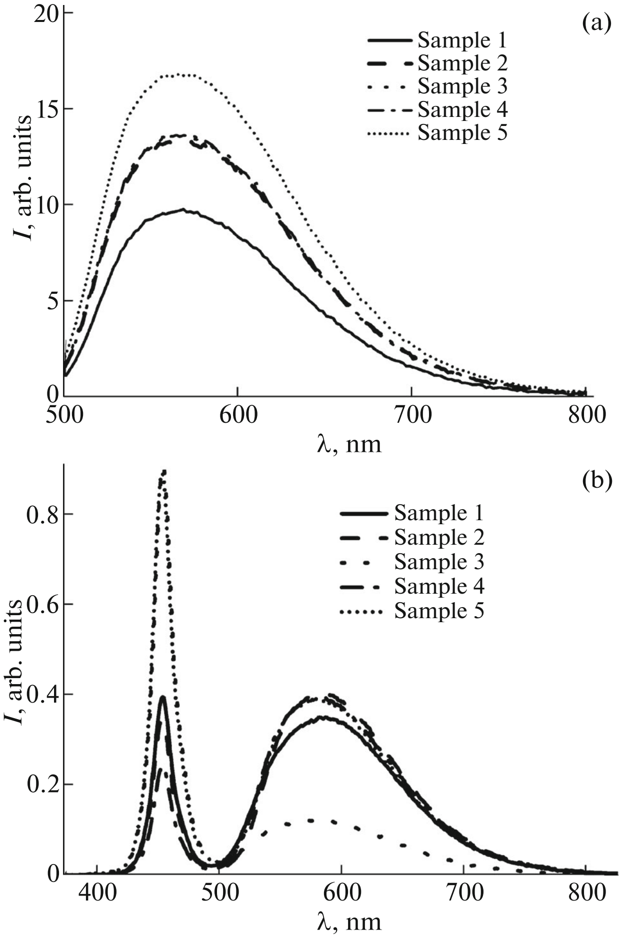

Fig. 1. (a) PL spectra of phosphor samples nos. 1–5 and (b) overall luminescence spectra of LED units with samples nos. 1–5.

mixed with YAG : Ce^{3+} microparticles in required proportions (Table 1). The resulting powder was used to produce square glass-ceramic samples with a side length of 5 mm and thickness of 300 μm with a press and special die mold under a pressure of 4000 bar. The samples were sintered at a temperature of 550°C for 30 min and cooled in air at room temperature.

The photoluminescence (PL) spectra of the thus-synthesized samples were recorded with a Horiba Scientific spectrophotometer at an exciting light wavelength of 465 nm. The quantum efficiency of luminescence was measured with a Gamma Scientific optical sphere with the use of SpectralSuite 3.0 software. The thermal properties of the phosphor material were examined with an Optris PI450 stationary IR camera. For this purpose, LED units were fabricated, constituted by an X10 LED chip manufactured by Optogan [9] and a synthesized phosphor sample. A silicone elastomer served as a binding layer between the LED chip and the phosphor material. The electroluminescence (EL) spectra of the LED units were recorded with a Gamma Scientific optical sphere.

Figure 1a shows the PL spectra of samples of the phosphor material. The spectra show a peak at 560 nm, which corresponds to the excited state of Ce^{3+} ions in the $4f^05d^1$ configuration. It can be seen that the PL intensity grows with increasing YAG : Ce^{3+} concentration in the glass ceramic. At YAG : Ce^{3+} concentrations of 60 to 80%, the intensity varies only slightly, but there is a significant difference between the luminescence intensities at YAG : Ce^{3+} microparticle concentrations of 50 and 90%. Therefore, the conclusion can be drawn that a significant change in the concentration of the phosphor in the mixture will lead to a change in the luminescence intensity. It can also be suggested that the luminescence intensity reached at a phosphor content of 90% has the limiting value and raising the phosphor concentration in the mixture further will not lead to any significant rise in the luminescence intensity. The dependence of the quantum efficiency of samples of the phosphor material on the phosphor concentration in a sample was studied. The data obtained are presented in Table 1. It can be seen that the quantum efficiencies of all the samples fall within the range of 82–92%. It can also be stated that there is no direct dependence of the quantum efficiency on the concentration of phosphor microparticles.

Further studies were carried out with an LED unit constituted by an X10 LED assembly emitting blue light, a thin layer of the optical silicone elastomer used to fix the phosphor material in the assembly, and a sample of this material itself. The overall (EL from chips + PL from the phosphor) luminescence spectra of the LED units are shown in Fig. 1b. Measurements were made in the nominal operation mode of the LED assemblies: current 1 A, voltage 15 V.

It can be seen in Fig. 1b that the highest luminescence intensity is observed for LED units with phosphor samples nos. 3 and 5; however, their emission was blue, rather than white, with a particular low intensity of yellow light characteristic of the unit with phosphor sample no. 3. In units with phosphor samples nos. 1, 2, and 4, the lines of blue and yellow emission had approximately the same intensity; i.e., warm white emission was characteristic of these units. However, the samples had a low efficiency of about half that of commercial samples with a silicone elastomer, equal to 110 Lm/W. In our opinion, the low efficiency was possibly due to the formation of cracks and air bubbles in the silicone elastomer in the course of drying.

In the final stage of our study, we measured the temperature to which the surface of working LED units was heated. The measurements were made under the following conditions: working current, 1 A; voltage, 15 V; room temperature, 23°C; and operation time of the setup prior to the beginning of measure-

Table 2. Temperature to which the surface of LED units with samples of the phosphor material is heated

No.	Mass fraction of YAG : Ce^{3+},%	Maximum heating temperature of the sample surface, °C
1	50	185.1
2	60	181.4
3	70	264.1
4	80	165.2
5	90	185.7

ments, 30 min. Table 2 presents summary information on the maximum (over the sample area) temperature of heating of the surface of the units in relation to the concentration of YAG : Ce^{3+} microparticles in the glass ceramic.

It can be seen that unit no. 3 was heated to the highest, compared with the rest of the samples, temperature of 264.1°C. The temperatures to which other units were heated were about the same, 170 to 190°C. It can be noted that the concentration of YAG : Ce^{3+} microparticles in the glass ceramic had no direct effect on the temperature of heating and, therefore, the data for unit no. 3 require additional verification. The unit with phosphor sample no. 4 was heated to the lowest temperature of 165.2°C; however, all the temperatures to which the unit surfaces were heated exceeded the maximum heating temperature of the commercial sample in which YAG : Ce^{3+} microparticles were introduced into a silicone elastomer (103.2°C). Because the glass ceramic has a markedly higher heat conductivity than silicone, it can be assumed that the reason for such a pronounced surface heating was that the structure of the units we used contained several interfaces that hindered the effective heat transfer and, as already noted, structural heterogeneities in the cured silicone elastomer. Thus, the main problem to be solved by developers of phosphor materials based on glasses and glass ceramics consists in creating a technique for coupling of primary optical materials and semiconductor chips. Such a technique should, first, provide the best heat transfer from a chip to the optical material and, second, take advantage of the high refractive index of the glass in outcoupling of light from the structure. It is noteworthy that the so-called "remote phosphor" technique frequently employed in similar cases (see, e.g., [10]) is not optimal in the case under consideration because the air gap between the chip and the phosphor has a poor heat conductivity and low refractive index.

To conclude, it was shown that the optical properties of the phosphor material developed in the study compare well with those of the silicone-based material. The possibility of obtaining warm white light by using the phosphor material was confirmed. Additional studies are necessary for obtaining the required thermal properties.

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