Phys. Status Solidi A **212,** No. 12, 2964–2967 (2015) / **DOI** 10.1002/pssa.201532655

physica status solidi a
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applications and materials science

Na_2SiO_3 liquid glass-based phosphor material for white LEDs

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Received 7 August 2015, revised 8 September 2015, accepted 11 September 2015
Published online 2 October 2015

Keywords light-emitting diodes (LEDs), liquid glasses, luminescence, phosphors

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A liquid glass-based phosphor material for white light-emitting diodes (LEDs) is proposed. The material is based on sodium silicate (Na_2SiO_3) matrix with embedded microparticles of cerium-doped yttrium aluminum garnet (YAG:Ce^{3+}). The technique for the material synthesis is described. The results of investigation of the optical and thermal characteristics of the material and a white LED module with a primary optic element made of the material are presented. Advantages of the developed phosphor material for primary optics applications in high-power LED modules as compared to commercial silicone are demonstrated.

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1 Introduction Further progress of light-emitting diode (LED) technology requires integration of the elements of LED devices and the reduction of their size while increasing light emitting power per unit surface area of the device. This leads to increasingly large thermal load on an entire LED module and on a phosphor layer, which performs the function of the conversion of light wavelength and of primary optics, in particular. One solution to the problem of the removal of excessive heat from the LED structure is the replacement of the silicone elastomer used as a protective coating and a matrix for phosphor particles with more heat-conductive and more thermally stable glass [1–5].

Several approaches to the synthesis of thermally stable glass-based phosphor materials were considered. The first one used the technology of synthesis, when microparticles of yttrium aluminum garnet doped with cerium (YAG:Ce^{3+}), the most common light converter in modern LEDs, were formed directly inside the glass matrix as a result of the material synthesis process [6–11]. The second approach used glass compositions, which during the synthesis provided nucleation of light-converting quantum dots in the glass matrix [12–15]. The third approach utilized the sintering, under considerable pressure and at high temperatures, of a presynthesized mixture of a milled glass and YAG:Ce^{3+} particles [16–21]. All three of these techniques have a significant drawback, which is high sample processing temperature. This requires special equipment, and, among other things, does not allow one to apply phosphor-containing glass directly to LED chips, as takes place in the standard silicone elastomer LED technology [22]. As a result, these glass-based phosphors have poor thermal contact to LED chips, which deteriorates heat removal from the whole LED structure.

In the present work, we report on a new method of the synthesis of the glass-based phosphor material, which uses a matrix of sodium silicate, a liquid glass. We study the optical and thermal properties of the synthesized phosphor material and evaluate its quantum efficiency. The material is then used in the primary optics element of a high-power LED module, the optical and thermal characteristics of which are also reported on.

2 Sample preparation and characterization At the first stage, we prepared the water-based sodium silicate (Sigma–Aldrich Na_2O 10.6%, SiO_2 26.5%) solution with various mass concentrations of Al_2O_3 and YAG:Ce^{3+} microparticles (Table 1). The typical "diameter" of Al_2O_3 and YAG:Ce^{3+} microparticle was 20 and 25 μm, respectively. Next, a fixed amount of YAG:Ce^{3+} microparticles was added to the solution. The resulting mixture was stirred using a magnetic stirrer to reach a uniform distribution of the microparticles. In the preparation of some samples, we

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Table 1 Composition of synthesized samples.

sample #	liquid glass Na_2SiO_3 (mass%)	Al_2O_3 microparticles (mass%)	YAG:Ce^{3+} microparticles (mass%)
1	80	–	20
2	65	–	35
3	60	–	40
4	55	–	45
5	50	40	10
6	45	35	20
7	35	35	30
8	30	30	40

added Al_2O_3 microparticles (Table 1). These microparticles increased the solution viscosity, preventing sedimentation and thereby facilitating a more uniform distribution of YAG:Ce^{3+}microparticles in the liquid glass. From the resulting semiviscous solution, thick drops of the phosphor material were deposited with a pipette onto a predegreased medical glass. The samples were next dried in air for 1–1.5 h to exclude the formation of air bubbles and blisters in the process of further annealing. After drying, samples were placed in a muffle furnace, which was heated from room temperature to 150 °C during 2 h. The samples were maintained at this temperature for another 30 min. After annealing, the furnace was turned off and the samples were cooled within the furnace in the free mode. As a result, the maximum thickness of the Na_2SiO_3 liquid glass-based phosphor material layer was 300 μm.

The optical properties of the samples were studied with Horiba FluoroMaz-4 spectrofluorometer, the surface morphology was analyzed with a Nikon Eclipse E200 optical microscope, and the quantum efficiency was measured with a Hamamatsu C 9920-02 absolute quantum yield measurement system. The optical properties of the LED modules with the synthesized phosphors were investigated with an IC2 Integrating Cube (StellarNet, Inc.) with the use of the software SpectraWiz. An infrared optical camera Optris PI 450 was used for temperature measurements.

3 Results and discussion Optical microscopy was used to inspect the change of the surface morphology as a result of annealing of the samples. After the first step of the synthesis (i.e., stirring and drying), samples 1–3 were swollen and demonstrated a large number of air bubbles. These samples were not investigated further. Samples 4–8 demonstrated satisfactory visual structure and were studied in more detail. Figure 1a and b show surface the morphology of sample 4, before and after annealing, respectively. Figure 1c and d show the surface morphology of sample 5.

The images in Fig. 1a and b prove that the morphology of sample 4 before and after the annealing was homogeneous. Phosphor microparticles were distributed uniformly in the sample. At the same time, the images in Fig. 1c and d indicate that sample 5 possessed inhomogeneous structure. This was due, apparently, to the presence of Al_2O_3 microparticles in the composite mixture. These microparticles were unevenly distributed in the sample; it could be assumed that at the points of their accumulation increased light scattering might take place, which would result in nonuniform light output.

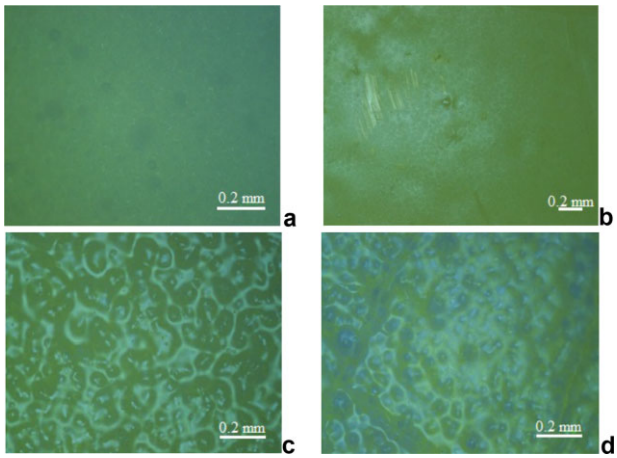

Figure 1 Surface morphology of samples 4 (a,b) and 5 (c,d) before (a,c) and after (b,d) annealing.

The quantum yield (QY) was measured for samples 5–8 using the standard procedure for LED QY measurements. The QY of YAG:Ce^{3+} particles embedded in silicone matrix, as used in commercial X10 LED module, according to this procedure, was 92%. The QY of our experimental samples appeared to be of the same order or higher. It comprised 91.5% for samples 5 and 7, and 93.5% for sample 8. Sample 6 showed a QY of only 85%, however, these data require additional validation. Generally, the QY of the studied samples could be regarded as high.

The developed phosphor material was used in a primary optics element of a high-power LED module X10 [21] produced by the OptoGaN group. It consisted of 9 LED chips placed on a common substrate. The phosphor material on the glass plate was placed directly on the LED chips, so there was an air gap between the substrate of the LED module and the plate, as shown in Fig. 2.

Figure 3 presents electroluminescence spectra of LED modules with phosphor material samples 4–8. As can be seen, the spectra consist of two lines, one corresponding to the emission of the semiconductor chip, and the other, to that

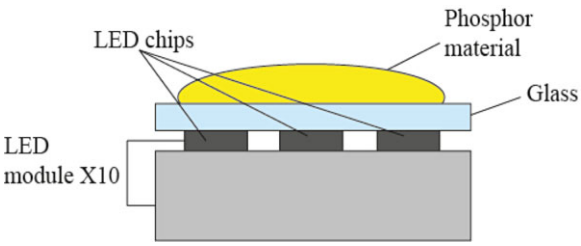

Figure 2 Schematics of a LED module with composite phosphor material on the top.

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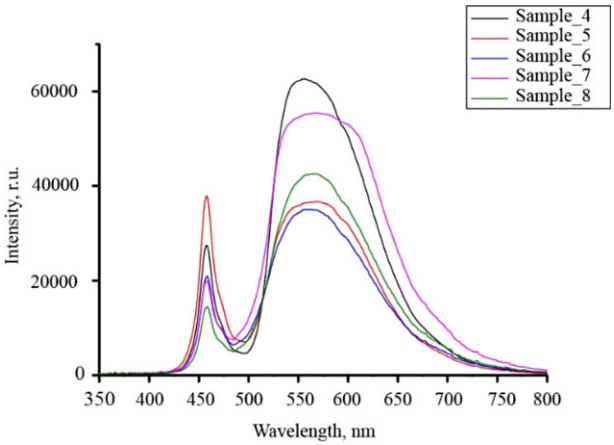

Figure 3 Electroluminescence spectra of LED modules X10 with the developed phosphor material. Sample numbers correspond to those in Table 1.

of the phosphor particles. The intensities of the second line differed depending on the concentration on the particles, yet the full widths at half-maximum (FWHM) of these lines remained similar, 100–120 nm.

Analysis of the spectra of LED modules with phosphor material samples 5–8 showed a decrease in the intensity of blue light and an increase in that of yellow light with the increase in the concentration of YAG:Ce^{3+} microparticles. It is worth noting that the increase in the intensity of the yellow light was not directly proportional to the increase in the concentration of YAG:Ce^{3+} in the phosphor material. The highest intensity of yellow light was observed for an LED module with phosphor material sample 4. The intensities of yellow light in LED modules with phosphor material samples 5 and 6 were similar. Strong yellow emission was also observed for the LED module with phosphor material sample 7. However, this LED module demonstrated a strong disproportion between blue and yellow light components; to balance them one needs either to reduce the thickness of the phosphor sample or to decrease the concentration of YAG:Ce^{3+} microparticles. The best balance between blue and yellow components is demonstrated by a LED module with phosphor material sample 5, and we believe that more precise adjustment of the components in this phosphor material may eventually lead to the fabrication of a LED module with warm white light.

To assess the thermal properties of the developed phosphors, we measured the temperature of the surface of phosphor material in the working LED modules. Measurements were performed with an ambient temperature of 23 °C with LED modules working at nominal current of 1 A and voltage of 11 V, after 30 min of operation. Table 2 gives the maximum surface temperature of the LED modules depending on the YAG:Ce^{3+} fraction. The thermal images of the heated surface of phosphor material samples 5 and 8 are shown in Fig. 4a and b, respectively.

From Table 2 and Fig. 4 one could conclude that increasing the concentration of YAG:Ce^{3+} microparticles in the phosphor material, in general, led to an increase in the temperature of the sample surface of LED modules. Figure 4 also suggests that the heat was distributed over the surface of the module quite evenly, indicating good thermal conductivity of the developed phosphor material.

Table 2 Maximum temperature at the surface of phosphor material placed on operating LED modules.

sample #	YAG:Ce^{3+} microparticles (mass%)	maximum measured temperature (°C)
4	45	92
5	10	95
6	20	92
7	30	130
8	40	140

According to the data obtained, the presence of Al_2O_3 microparticles generally produced higher sample temperatures. However, the observed temperatures were still quite comparable with the maximum heating temperature 106 °C of commercially produced X10 LED modules, where YAG:Ce^{3+} particles are embedded in the silicone elastomer. For LED modules with phosphor samples 4–6, the temperatures provided by the developed phosphor material were 11–14 °C lower than that typical of commercial X10

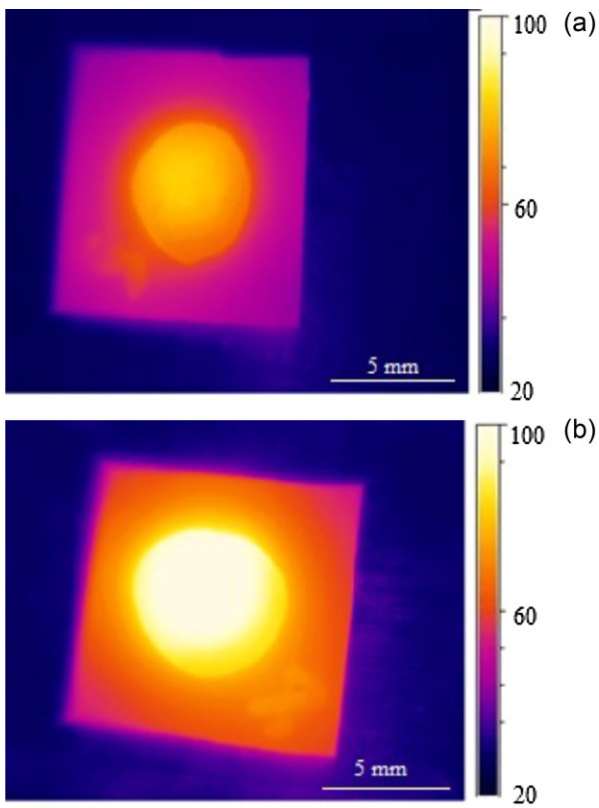

Figure 4 Temperature distribution at the surface of working LED modules with phosphor material, samples 5 (a) and 8 (b).

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modules. Therefore, we can conclude that the use of liquid glass as a matrix for YAG:Ce^{3+} microparticles is quite promising and that the obtained phosphor material is capable of solving the problems of the removal of excessive heat from LED structures. The increase in the temperature with the fraction of the YAG:Ce^{3+} particles increasing (with some reservations, as follows from Table 2), can be probably related to the fact that the greater the density of the particles, the more light they absorb, so more heat associated with the Stokes shift is released. The next step in the development of this technology should be devoted to the improvement of the design, which would allow for eliminating the glass plate from the construction of the LED module or replacing it by a more suitable material (with sapphire being a prospective one). Direct casting of the developed phosphor material on LED chips at this stage proved to be impossible because of chemical reactions between Na_2SiO_3 and the chips. It should be noted that the glass plate between the LED chip and the phosphor material, which we used here, could withstand temperatures much higher than 150 °C and its properties could not affect the purity of the experiment.

4 Summary In this work, we proposed an approach for the fabrication of phosphor material for white LEDs. Our phosphor is based on sodium silicate matrix and YAG:Ce^{3+} microparticles, and to the best of our knowledge, represents one of the first successful attempts to utilize liquid glass in LED phosphor technology (another example can be found in Ref. [23]). The obtained material, by virtue of its optical and thermal properties, appears to be more advanced than commercially produced silicone-based phosphor materials. The developed phosphor material is shown to be very promising for use in primary optics elements in high-power LEDs and LED modules.

Acknowledgements This research received support from ITMO University International Research Laboratory program. E.S. and I.K. acknowledge the support from the project "Nano-geometry and entanglement for design and prototyping of ceramic-based high-performance nano-composites" (SLOFY12160T).

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