

HIGH EFFICIENT LIGHT EMITTING DEVICES WITH ADDITIONAL SCATTERING LAYER AND REFLECTING MEDIUM FOR WHITE LIGHT GENERATION

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(Received 13 November 2007)

Abstract

Multiexcitation of phosphors, additional scattering layer around the chip and special reflecting medium were proposed to improve the luminous efficiency and color properties of LED devices. LED devices with an n-UV Ga(In)N chip as well as blue GaN chip and multiexcited phosphors were developed and created. These LEDs for white light generation show better quantum yield of green and red phosphors, higher total brightness, and improved color rendering index.

1. Introduction

White light-emitting diodes (LEDs), with the advantages of long lifetime, saving energy consumption, and environmental-friendly characteristics, are thought to be the most important solid-state light sources for substitution of widely used incandescent lamps and fluorescent lamps [1]. Great interest has been focused on these devices and tremendous progress has been achieved since the first commercial white-emitting LED was fabricated with about 450 nm blue-emitting GaN-based LED in 1997 [2]. At present, the most general and convenient method to obtain white light is to combine a yellow-emitting phosphor, for example, trivalent cerium activated yttrium aluminum garnet (YAG:Ce³⁺) wavelength converter or terbium aluminum garnet (TAG:Ce³⁺) with a GaN blue LED chip. However, there are some problems for such “blue+yellow” white LEDs, such as lower color rendering index (CRI) and lower luminous efficiency [3, 4]. Alternative techniques for white light obtaining comprise application of an UV-LED with RGB (red, green and blue) phosphors, or coupling a blue LED with RG phosphors [5]. Thus far, SrGa₂S₄: Eu²⁺ is still exploited for use as green phosphors in RGB-white LEDs, with no particular alternative available.

In this paper we report how to develop and improve the UV and blue LED devices for white light generation. We propose to use the multiexcitation of phosphors, additional scattering layer around the chip and special reflecting medium, consisting of powder with high reflectance and UV reflecting film. The synthesis of new efficient multiphase green phosphor based on strontium thiogallate and its application in LEDs are also discussed.

2. Experimental details

2.1. Synthesis

Blue, green and, red phosphors for UV LED application were synthesized by solid state reaction and described in our previous work [6].

Polycrystalline single phase $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor and multiphase $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ samples with improved properties were specially prepared for blue LED. For SrGa_2S_4 starting sulfide powders SrS and Ga_2S_3 were mixed in stoichiometric composition and annealed at 900 -1000°C with a carbon reduction atmosphere for 4 h. For multiphase samples we used the same raw materials with addition amounts of MgS and $\text{Mg}(\text{NO}_3)_2$ at the same synthesis conditions. The doping ions in both cases were introduced in the form of EuS . The method presented here provides powder samples with good crystalline properties as shown by X-ray diffraction measurements. The thiogallate single and multiphase samples exhibit a deep green color. Phosphor samples were characterized by crystalline structure and luminescence properties. Multiphase powder samples with 6 mol % Eu^{2+} concentrations were used as green phosphor in combination with red phosphor and blue LED chip for white light generation.

2.2. Sample characterization

2.2.1 X-ray diffraction measurement – The crystal structures of the prepared samples were determined by X-ray diffraction measurement using goniometer (PANalytical, X'Pert pro MPD with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. The scan speed was 3 seconds per step (0.02° step – 2θ) and covered the range between 10° and 90° .

2.2.2. EDS (Energy Dispersive Spectroscopy) and EPMA (Electron probe micro analysis) – Qualitative and Quantitative non-destructive elemental analysis was performed with EPMA machine, model SX-100 (the electron acceleration was 20 kV, beam current 10 nA, and the diameter of electronic beam was 50 μm , DT:0.3 S). It is the most precise and accurate micro-analysis technique available and all the elements from Beryllium to Uranium can be analyzed.

2.2.3. Raman spectroscopy - Raman scattering spectra of SrGa_2S_4 and multiphase prepared phosphors were measured by a Renishaw 3000 spectrometer with a He-Ne laser (excitation wavelength of $\lambda = 633 \text{ nm}$ and $\lambda = 785 \text{ nm}$) and a photomultiplier counter at room temperature in back scattering configuration. The spectral resolution of spectrometer is about 4 cm^{-1} at 633 nm and 1 cm^{-1} at 785 nm.

2.2.4. Photoluminescence (PL) measurement – Optical spectroscopy and PL characteristics were estimated on the basis of emission and excitation spectra registered at room temperature (Xe 500 W lamp) with DARSA PRO 5100 PL System (Professional Scientific Instrument Co, Korea). Excitation spectra were corrected for the energy distribution of the Xe-lamp. The excitation was performed with a 460 nm radiation, which is usually used in blue LED.

2.2.5. Morphology and size measurement – Particle sizes and morphologies of the investigated phosphors were determined by scanning electron microscope (SEM) Hitachi-S-3000N. In order to control the particle size and to find the size distribution the Laser diffraction was carried out using HELOS particle size analysis system.

3. Results and discussion

3.1. UV LED

A schematic view of a scattering layer-coated LED with reflecting medium is presented in Fig. 1. In this figure there is shown light-emitting device 1 comprising UV-emitting LED 2 covered with special scattering layer 3, phosphor composition 4 comprising a phosphor blend containing green-emitting phosphors, blue-emitting phosphors, and red-emitting phosphors being excitable by UV-emitting LED, the reflecting medium consisting of powder 5 with high reflectance and/or UV reflecting film 6 and diffusive or specular reflector cup 7 reflecting light from the shell.

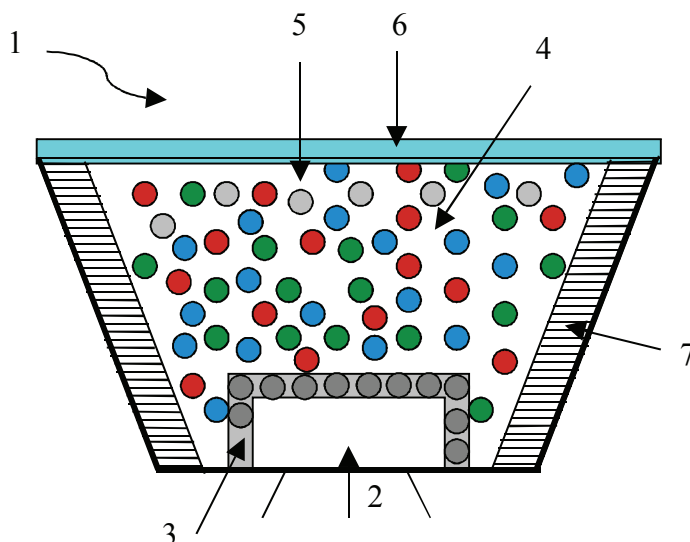


Fig. 1. Schematic cross-sectional view of a scattering layer-coated LED with reflecting medium.

GaN and InGaN UV-emitting LEDs 2 are generally known in the art. UV-emitting LED 2 has an emission peak at 360-420, optionally about 380-400 nm. Usually, a combination of three phosphors – blue, green, and red, excited by the UV emission from LED 2, is applied to generate a white light.

The different possibilities of phosphor packaging around the chip are shown in Fig. 2.

The best results from our experiments have been obtained in the case of uniform distribution of phosphors in reflector cup (b). In order to improve the color properties of the LED devices and the quantum yield of phosphor blend in this work we propose some new nontraditional ways: a) multiexcitation of phosphors; b) scattering layer around the chip; c) reflecting medium consisting of powder with high reflectance and/or UV reflecting film. This idea was described in detail in our previous patents [7-9] and realized in practice.

Fig. 3 schematically illustrates a double excitation of green phosphor (II) and a triple excitation of red phosphor (III). In Fig. 3 a radiation source UV LED emits radiation incident on three luminescent materials, such as first (blue) phosphor I, second (green) phosphor II, and third (red) phosphor III. The main principal difference of this model in comparison with traditional LED consists in important choice of green phosphor. The best candidate of green phosphor was synthesized on the basis of strontium thiogallate $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ with additional MgGa_2O_4 phase. This phosphor must be excited by UV LED and blue phosphor and excite the red phosphor. For higher quantum yield of red phosphor and for better color rendering index and brightness of device it is desirable to carefully select a combination of red, green,

and blue phosphors capable of absorbing UV and visible blue-green range of spectra. The detailed analysis of these phosphors and their possible combinations was given in our article [6].

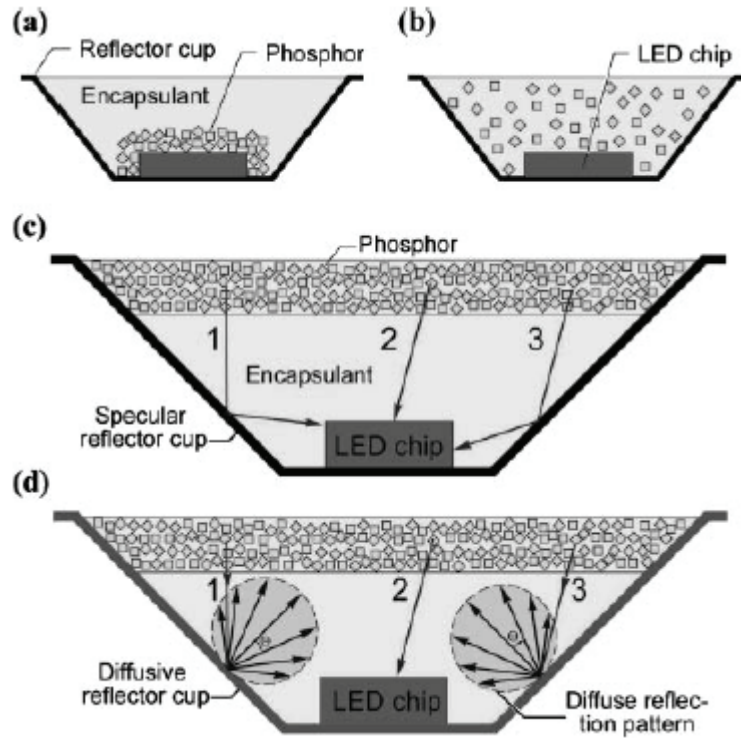


Fig. 2. Arrangements of phosphor in white LED: (a) conformal distribution directly on LED chip; (b) uniform distribution in reflector cup (phosphor-in-cup); (c) uniform distribution of thin layer above LED chip (remote phosphor); (d) remote phosphor distribution in diffuse reflector cup.

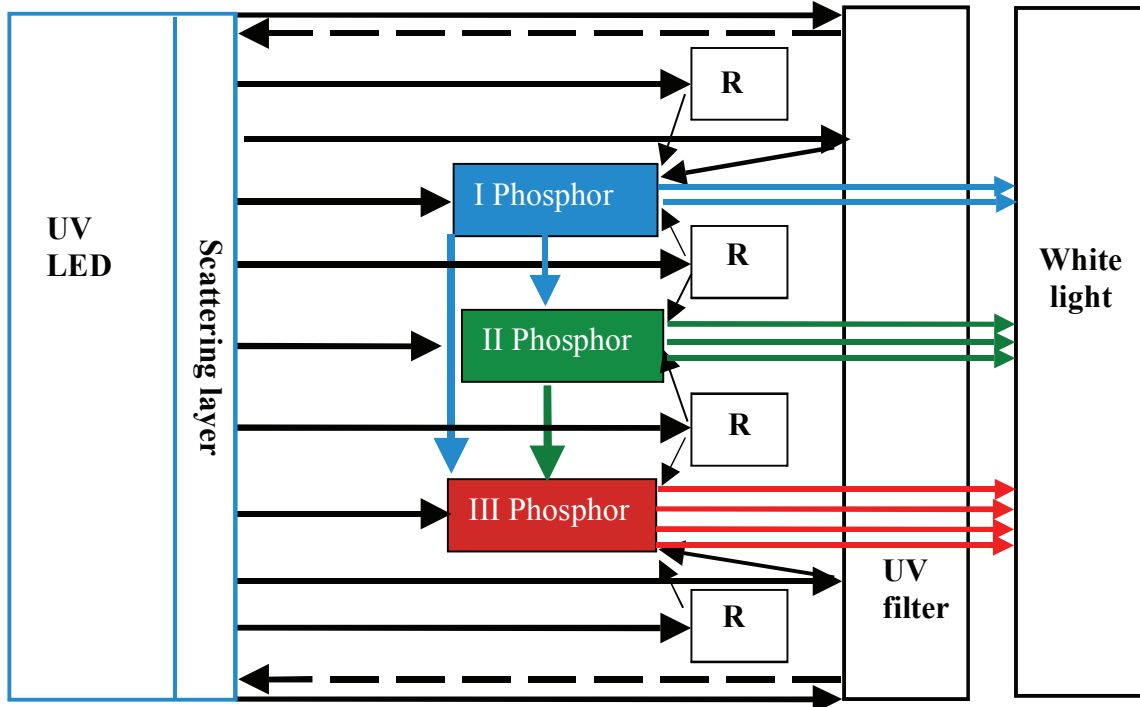


Fig. 3. Proposed scheme of the white light illumination system with a reflecting medium and multiexcitation of phosphors.

The reflecting powder medium (R) comprises at least one powder selected from the group of MgO , BaSO_4 , Al_2O_3 , ZrO_2 , TiO_2 , or any other with high reflecting index. When the incident UV light gets into these particles it is reflected and excites again one of the phosphors.

Another type of reflecting medium may be the UV reflecting film. Multilayer dielectric film (band pass filter) serves for total UV reflectance and maximum visible light transmission. The scheme of such a filter is shown in Fig. 4.

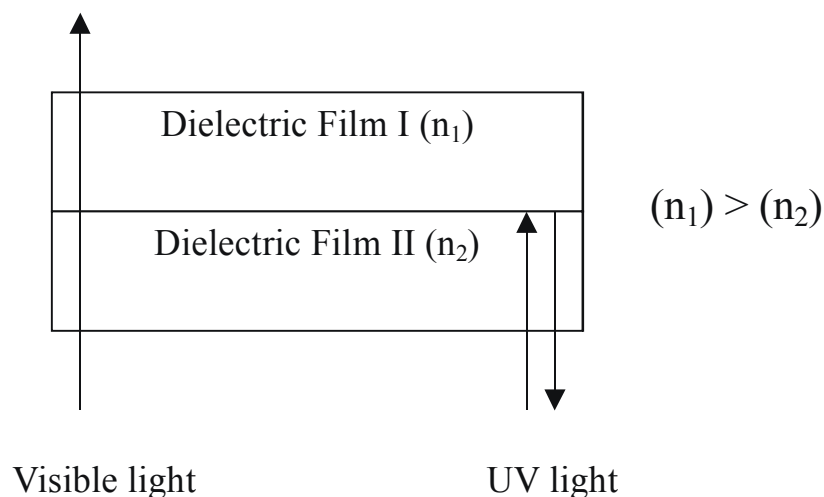


Fig. 4. Schematic view of the multilayer UV reflecting filter.

This filter covers the outside optical surface of the device and is placed over the phosphors. The multilayer film consists of alternate layers with high refractive index (about 1.82-2.5) and low (about 1.35-1.45) refractive index. Usually, TiO_2 ($n=2.38$), ZrO_2 ($n=1.99$) and MgF_2 ($n=1.38$), LiF_2 ($n=1.39$) are applied. The number of layers is about 15-40 and the thickness of one layer is 50-500 nm. Using such a filter, we essentially increase the intensity of LED, because reflected UV light excites repeatedly the phosphor blend.

In order to increase a quantum yield of LED and, as consequence, the total brightness and light intensity of device, the UV-emitting LED is covered by a scattering layer. With reference to Figs. 5-7, there is shown a scattering layer coating LED of single coating material with identical particle sizes (Fig. 5), single coating material with different particle sizes (Fig. 6), and different coating materials with different particle sizes (Fig. 7).

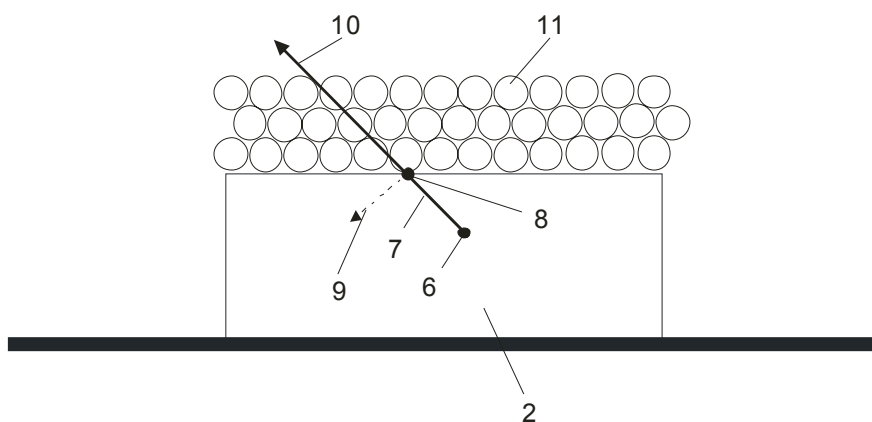


Fig. 5. Schematic cross-sectional view of a scattering layer, which coats the LED and consists of single coating material with identical particle size (11).

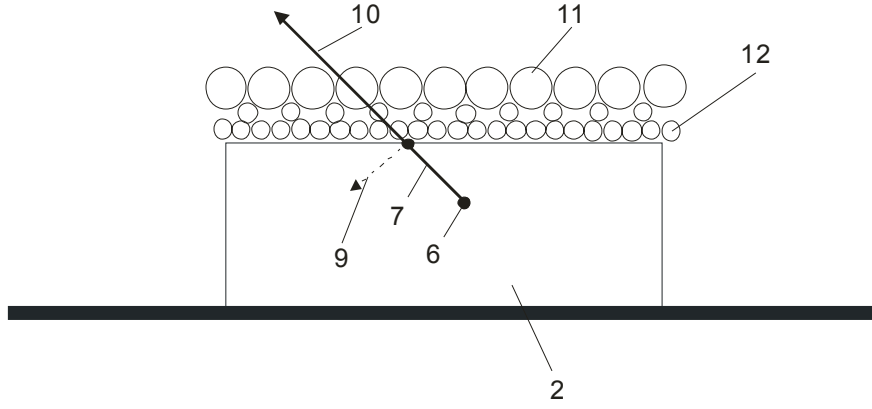


Fig. 6. Schematic cross-sectional view of a scattering layer, which coats the LED and consists of single coating material with different particle size (11 and 12).

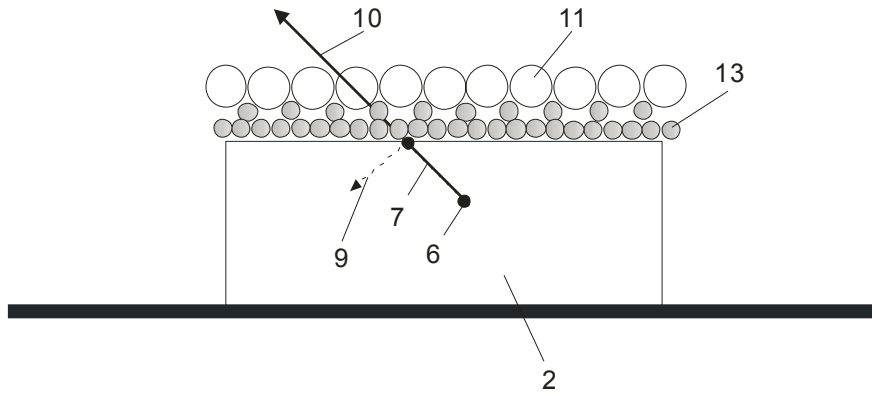


Fig. 7. Schematic cross-sectional view of a scattering layer, which coats the LED and consists of different coating materials with different particle size (11 and 13).

Usually, the refractive index of a chip substrate exceeds the one of an encapsulant. It leads to significant light losses because of the total internal reflections (TIR) (9) and Fresnel reflections (FR). Index mismatch between LED/Epoxy and LED/phosphors reduces extraction/out-coupling efficiency of LED light due to TIR and FR losses. Losses become more significant when phosphors are mixed with a lower index epoxy, further reducing the effective index below 1.8. In order to increase the extraction and efficiency of emitted light we propose to use a special scattering cover layer around the chip. The main goal of this layer is modification of the mechanism of TIR and symmetry of ray paths from the chip emitting areas. When the distance between particles in the scattering layer and the chip surface is comparable or less than the emitted light wavelength, the tunneling process of the light into the scattering particles takes place. The light can go out of this layer (10) or reflect again into the chip. In this case the symmetry of light rays in the chip is changed because of nonspecular reflection, and the emitted light efficiency increases. The refraction index in the scattering layer must be comparable or more than the refraction index of the chip. The particle sizes must be sufficient for the light scattering ($d_{\text{particles}} \geq \lambda_{\text{emission}}$) and optimized for the best tunneling process. The number of the particle monolayers in the scattering layer is also optimized and usually does not exceed 5 monolayers. A special additional subcoating layers (with particle size less than in the basic scattering layer and not more than the emitted light wavelength) can be applied for better penetration of light into the basic scattering layer (Figs. 6 and 7).

The optimized parameters for the particle sizes and refractive index of the coating layer are presented in Figures 8 and 9. The silicon encapsulant and subcoating particles with size 250 nm of phosphor with the refractive index 1.82 were used in theoretical ray-tracing simulation.

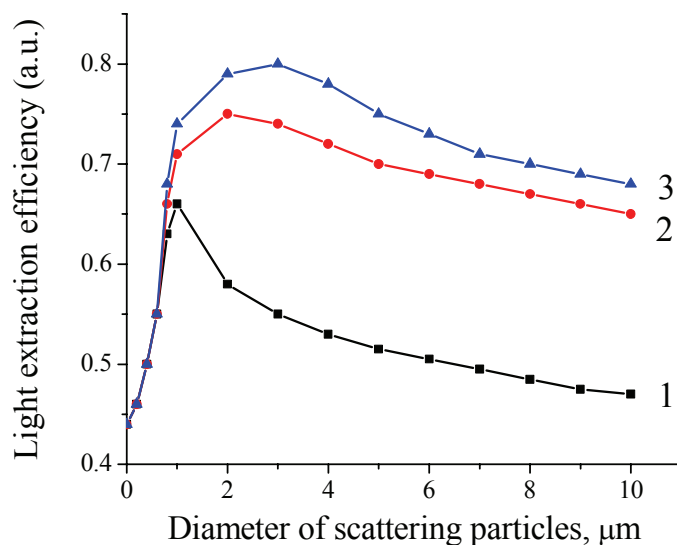


Fig. 8. Efficiency of chip light extraction in dependence on particle size in the scattering layer. 1 - sapphire particles without subcoating, 2 - sapphire particles with sapphire subcoating, 3 - sapphire particles with additional phosphor subcoating.

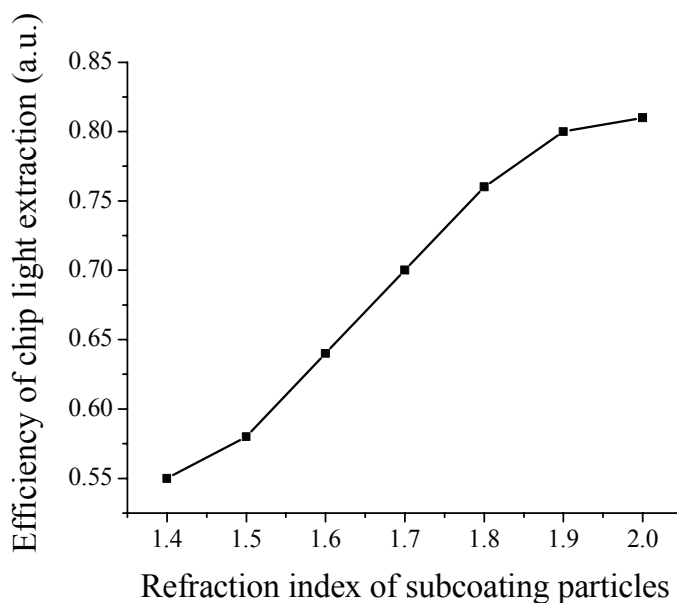


Fig. 9. Efficiency of chip light extraction versus a refractive index of subcoating particles.

As a result of multiexcitation of phosphors and scattering layer around the chip and applying the reflecting medium, the quantum yield of green phosphor increases by about 5%, the quantum yield of red phosphor increases about by 15%, the total brightness and light intensity of device increase by about 20%. The light emitted from the chip and phosphors has the same spatial and angular distribution in the device output and CRI is improved by about 15%.

3.2. Blue LED

White light in blue LED is usually obtained by combining a 465 nm blue light from the GaN-based LED and yellow light from the phosphor YAG:Ce or TAG:Ce. However, the “white” light from this combination route has an undesirable color balance, the deficiency of the red light in the visible spectra (around 600 nm) results in a low color rendering index. Another approach for obtaining white light is to combine a blue LED (around 460 nm) with green and red phosphors. White light consists of the blue light of the chip and red and green light emitted from the two-color phosphors while excited by the blue LEDs. So, here we can apply the same method (as in UV LED) of double excitation of a red emitting phosphor by the blue LED and by the green phosphor in order to obtain white light with higher color rendering index. The detailed analysis of phosphor combination was made in our previous article [6]. The scattering layer around the chip considered above and all conclusions for UV LED are also available for the blue LED.

In this part of our work we pay attention only to the reflecting powder influence on the LED device efficiency. A simplified scheme of the white light illumination system with a phosphor blend containing green-emitting phosphor and red-emitting phosphor and a reflecting medium is presented in Fig. 10. The reflecting powder medium comprises at least one powder selected from the group of MgO, BaSO₄, Al₂O₃, ZrO₂, TiO₂, or any other with high reflecting index.

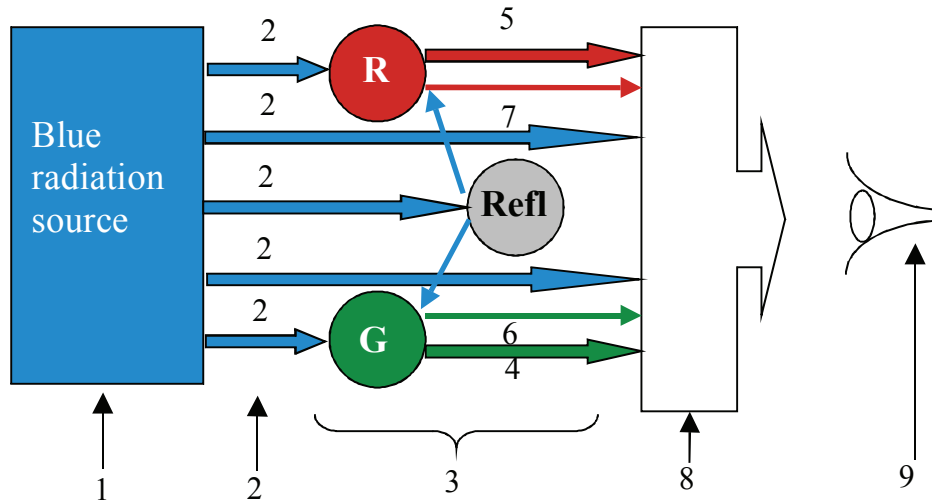


Fig. 10. Schematic illustration of the white light illumination system with a phosphor blend comprising a reflecting medium. R is red phosphor, G is green phosphor, Refl is reflecting powder (for example, MgO).

In Fig. 10, a radiation source 1, such as a blue LED, emits radiation 2 incident on the blend of phosphors comprising a green-emitting phosphor (G), a red-emitting phosphor (R), and a reflecting medium from powder samples with high reflectance (Refl) 3; human observer 9 perceives the combination of blue (2), green (4, 6), and red (5, 7) light as white light 8. The two phosphors R and G and the reflecting powder may be blended together (3) or separated (as shown in Fig. 10) and may comprise discrete overlying layers. Most preferably, the reflecting medium powder is over the green-emitting phosphor and the red-emitting phosphor. In this case, the additional excitation from the reflecting medium could be absorbed by the green-emitting phosphor and the red-emitting phosphor and additional light (6 and 7) in-

creases the total brightness of the device. Besides, the CRI also increases. The purity of reflecting powders, exclusion of true absorption and extensive reflecting medium are the main factors that increase the total brightness. When the refractive index of the reflecting medium is higher than the environment index the intensity also increases because of the total internal reflection (TIR).

The optimized parameters for the particle sizes for different reflecting powders are presented in Figure 11. The silicon encapsulant and the most popular reflecting materials in the powder form were used in the theoretical ray-tracing simulation.

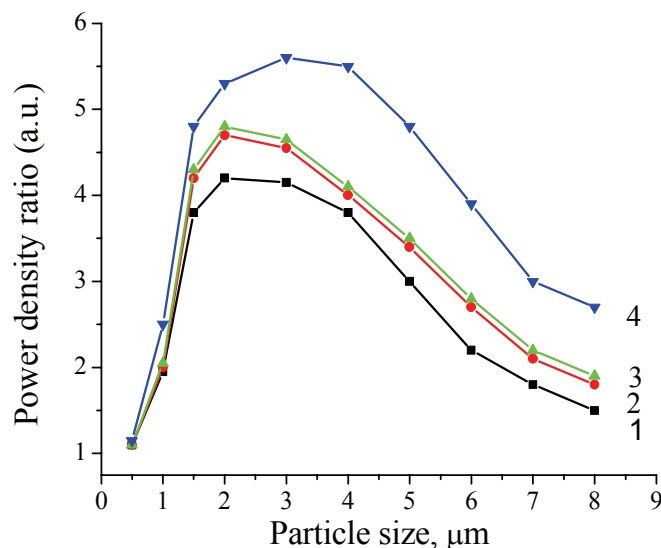


Fig. 11. Efficiency of LED intensity in dependence on particle size in the reflecting medium: 1 - BaSO₄, 2 - MgO, 3 - Sapphire, 4-ZrO₂.

For the most reflecting materials the optimal particle size is between 2 and 4 micrometers.

The ratio of reflecting powder amount and phosphor is very important in the blend composition. There is an optimal concentration of reflecting powder amount and phosphors and it depends on reflectance and absorption in reflecting medium as well as geometry of chip packaging. The optimized results were achieved when the reflecting medium blend accounts about 50% phosphors.

4. Conclusions

Multiexcitation of phosphors, scattering layer around the chip, and the reflecting medium consisting of powder with high reflectance and UV reflecting film were proposed to improve the color properties of LED devices. The optimal particle size in scattering layer and in reflecting powder was calculated for different materials. This model was realized in practice for UV and blue chips; the quantum yield of green phosphor increased by about 5%, the quantum yield of red phosphor increased by about 15%, the total brightness and light intensity of device increased by about 20%. The light emitted from the chip and phosphors had the same spatial and angular distribution in the device output and CRI was improved by about 15%.

Acknowledgements

This research was supported by the International Cooperation Research Program of the Ministry of Science and Technology, Republic of Korea.

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