OBTAINING WHITE LIGHT BY THE COMBINATION OF Gd₃Al₅O₁₂:Ce³⁺ AND Y₃Al₅O₁₂:Ce³⁺ PHOSPHORS IN LIGHT EMITTING DIODES

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This paper reports on the use of $Gd_3Al_5O_{12}$:Ce³⁺ phosphor mixed with $Y_3Al_5O_{12}$:Ce³⁺ phosphor for the manufacturing of white light emitting diodes as a way of increasing their optical performance as opposed to purely $Y_3Al_5O_{12}$:Ce³⁺ based LEDs. Such optical parameters as luminous flux, correlated color temperature, color rendering index and purity of white light of WLEDs with the addition of $Gd_3Al_5O_{12}$:Ce³⁺ phosphor are being studied.

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1. INTRODUCTION

Currently, most commercially available white LEDs are generated by combining a blue LED with a yellow phosphor Y₃Al₅O₁₂:Ce³⁺ [1,2] (phosphor converted white LEDs), but these LEDs produce "cool" white light with a high color temperature >6000K and color rendering index (R_a) within the 70-80 range. The YAG:Ce phosphor achieves only cold white light due to the fact that the red component is not intense enough for warmer emission tones. And increasing the thickness of the layer makes the radiation excessively yellow. By adding a phosphor with a higher intensity in the red region, it is possible to improve such optical parameters as the correlated color temperature, color rendering index, and luminous flux of the LED emission [3]. Usually the red emitting centers in phosphors are introduced by the Eu^{2+,} Eu³⁺, Sm³⁺, Pr³⁺ ions and some traditional metal ions, such as Cr3+, Mn⁴⁺, which are suitable for improving the color rendering index and color temperatures. In other cases, by replacing yttrium Y ions in the Y₃Al₅O₁₂:Ce³⁺ structure with smaller or larger ions, the emission spectrum can be adjusted. In particular, the replacement of Y³⁺ in its dodecahedrally coordinated region by a large Gd^{3+} ion leads to a red shift [4]. In this paper we are using the Gd₃Al₅O₁₂:Ce³⁺ phosphor for the manufacture of white light emitting diodes.

2. EXPERIMENTAL SECTION

For this experiment, we used blue GaN LED chips manufactured by Fullsun, 1x1 mm in size with a dominant wavelength of 450 nm and a power of 1W. The phosphors used were $Y_3Al_5O_{12}:Ce^{3+}$ and $Gd_3Al_5O_{12}:Ce^{3+}$ (fig.1) with different peak wavelengths (~ 550 nm and 580 nm respectively) and full widths at half amplitude, the emission spectra of which are shown in fig. 2. LEDs were made as follows: 1) the chips were deposited on a substrate with conductive glue; 2) then heated to 150°C in a furnace; 3) transparent silicone and phosphors were mixed in the ratio of 1 gram of powder to 10 grams of silicone; 4) the $Y_3AI_5O_{12}:Ce^{3+}$ phosphor was mixed with $Gd_3AI_5O_{12}:Ce^{3+}$ in two concentrations - 10% and 20% (the total amount of powder and encapsulant remains unchanged), and one of the samples remained free of $Gd_3AI_5O_{12}:Ce^{3+}$ for comparison; 5) phosphor composites were dispensed and completely cured. Dispensed materials in each package were carefully weighed at each distribution to ensure that: a) the same amount of encapsulating material was used in each package; b) the encapsulation height was the same in each LED within a small error.

3. RESULTS AND DISCUSSION

The emission spectra of samples with all three concentrations of Gd₃Al₅O₁₂:Ce³⁺ are shown in Figure 3. The converted spectrum of these three LEDs is wide, covering the wavelength range from 400 to 650 nm, including a significant presence of red in the spectrum in case of $Gd_3Al_5O_{12}$: Ce^{3+} presence. All three spectra consist of a peak at 450 nm with a full width at half amplitude of 75 nm and each of the three phosphor compositions has its own spectrum band, which have different peak intensities and full widths at half amplitude. For pure Y₃Al₅O₁₂: Ce³⁺ phosphor, the peak value is at 530 nm, and the full width at half amplitude -91 nm; with the addition of 10% $Gd_3Al_5O_{12}$:Ce³⁺ the peak value is 562 nm, and the full width at half amplitude is 100 nm; and with the addition of 20% $Gd_3Al_5O_{12}:Ce^{3+}$, these values are 570 nm and 83 nm.

Table 1 shows the results of the LEDs' optical measurements. Although the red phosphor should have less conversion efficiency than yellow, due to greater Stokes shift, the amount of yellow emission in this case is reduced, but the red emission compensates for the decline by its contribution in the total light flux. As a result, the luminous flux shows ever so slightly higher value with an increase in the concentration of red $Gd_3Al_5O_{12}$:Ce³⁺ to 20%. In contrast, the color temperature decreases with increasing concentration of $Gd_3Al_5O_{12}$:Ce³⁺, since the red component is added to the radiation spectrum, as can be seen from fig. 3. The color rendering index is maximal at the concentration

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of $Gd_3Al_5O_{12}:Ce^{3+}$ equal to 10%, and this ratio is optimal for obtaining white light, since it is obvious that with a further increase in the percentage of $Gd_3Al_5O_{12}:Ce^{3+}$, the coordinates of the resulting emission will have shifted far into the red region.

Packaging of white LEDs with a phosphor composition deposited on a blue emitting LED chip can be interpreted from the point of view of their color coordinates in the CIE 1931 color chart. The main goal is to estimate the required amount of phosphor needed for the coordinates to be located at the certain parts of the color diagram. To solve this problem, the method described below is used. It is based on calculating the distance d separating the color coordinate of the white LED and the position of the blue LED on the CIE color diagram:

$$d = \sqrt{(x_{white} - x_{blue})^2 + (y_{white} - y_{blue})^2}$$
(1)

where *x* and *y* are the coordinates corresponding to the points of the blue chip and the yellow phosphor, which can be used to calculate the position of the resulting color coordinate.

Fig. 4 shows the CIE 1931 coordinates of the blue chip and both of the phosphors, which are connected by black dashed lines, and it is obvious that these line segments do not intersect the parts of the Planck curve with a color temperature close to 6500K. The blue LED determines one position on the color chart, the coordinates of the phosphors set the other two point. The color of the LED created by the combination of the phosphor and the chip, has to be located on a line connecting their coordinates on the CIE diagram [5,6]. The resulting coordinate of the composition of the two phosphors is situated between the two coordinates of the phosphors, and the line connecting it with the coordinate corresponding to the blue chip will intersect the resulting coordinates inherent to this LED. The coordinate of the resulting white emission of the blue emitting chip and phosphors will be located somewhere in this segment, depending on the amount of applied phosphor. With an increase in the concentration of either of the two phosphors, the resulting line will shift to the side corresponding to the coordinate of this phosphor, which, in this case, is the side of wavelength decrease (blue shift), in accordance with the equation (1).

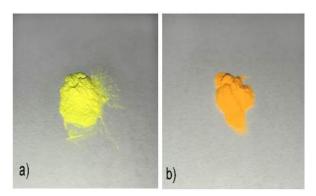


Fig. 1. a) $Y_3Al_5O_{12}$: Ce³⁺ b) Gd₃Al₅O₁₂:Ce³⁺ phosphors.

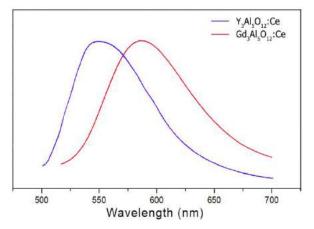


Fig. 2. a) Y₃Al₅O₁₂:Ce³⁺ b) Gd₃Al₅O₁₂:Ce³⁺ emission spectra.

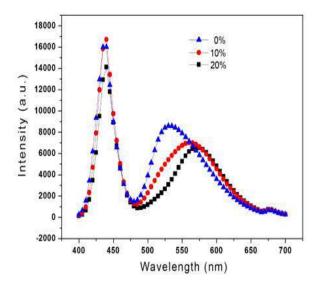


Fig. 3. Emission spectra of LEDs with different concentrations of $Gd_3Al_5O_{12}$:Ce³⁺.

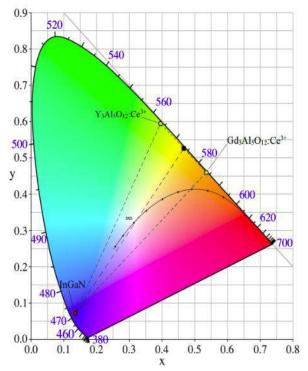


Fig. 4. CIE 1931 diagram depicting LEDs' chromaticity.

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Table 1

| Light | narameters | at various | concentrations | of | $Gd_3Al_5O_{12}:Ce^{3+}$ |
|-------|------------|------------|----------------|----|--------------------------|
| Light | parameters | ut various | concentrations | 01 | 0037113012.00 |

| Concentration Gd ₃ Al ₅ O ₁₂ :Ce ³⁺ | ССТ, К | R _a | Flux, Lm | CIE X | CIE Y |
|--|--------|----------------|----------|-------|-------|
| 0% | 7134 | 70 | 73,1 | 0.334 | 0.256 |
| 10% | 6433 | 75 | 75,3 | 0.315 | 0.307 |
| 20% | 5204 | 71 | 79,2 | 0.328 | 0.332 |

4. CONCLUSION

The conducted study shows, as seen from the chromaticity coordinates, that addition of a $Gd_3Al_5O_{12}$:Ce³⁺ phosphor with enhanced red emission improves the color characteristics of the phosphor converted LED, bringing the coordinates closer to pure

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white light. The concentration of 10% $Gd_3Al_5O_{12}:Ce^{3+}$ phosphor shows the best results at obtaining white light in phosphor converted WLED improving its CCT, R_a and luminous efficiency. The use of several phosphors with different chemical compositions is a good alternative to multiple chip LEDs of different wavelengths, allowing to obtain white light.

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