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INVESTIGATION Of YAG:Ce LUMINESCENCE PROPERTIES AND MANIPULATION OF PHOSPHOR CONVERTED WHITE LED's COLOR CHARACTERISTICS

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Ce^{3+} activated yttrium aluminum garnet ($Y_3Al_5O_{12}$:Ce, YAG:Ce) powder as luminescent phosphor was synthesized by the solid-state reaction method. The phase identification, microstructure and photoluminescent properties of the products were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) analysis.

Then high power phosphor converted white LEDs with different CCTs were fabricated with the use of blue InGaN dies and YAG:Ce phosphor and their light characteristics were measured and compared. The LEDs generated white light with the CCTs of 6444 K, 4624 K and 8825 K. Their optical parameters were measured in an integrating sphere at various driving currents, and the LEDs showed a luminous efficiency of 96 (81, 69) lm/W at 0.5 (2, 3.5) A.

Keywords: Light emitting diode; Luminescence; Phosphor
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1. INTRODUCTION

Light emitting diodes are bound to replace traditional light sources such as incandescent and fluorescent lamps in the nearest future, and the phosphor converted light white emitting diodes (pcLED) technology is the most promising one. There are a few ways to get white light with pcLEDs. One of them is to combine a UV LED with red, green and blue phosphors. But probably the most effective method of all is to use a blue LED covered with yellow emission phosphor, which will be discussed in this paper.

There are a lot of phosphors that can be used to convert LEDs blue emission into visible white light, but yttrium aluminum garnet- $Y_3Al_5O_{12}$ doped with small amounts of cerium Ce^{3+} seems to be the most practical among all of them because of its low price and ease of preparation. Yttrium aluminum garnet ($Y_3Al_5O_{12}$) doped with Ce^{3+} is not a new material, it has been widely used throughout the decades in such devices as cathode-ray tubes and field emission displays, and now has found a new application in lighting industry [1].

The quantum efficiency of YAG:Ce is usually very high reaching the value of 90% or even higher. Y_2O_3-Al_2O_3 system is known to have three different crystal phases: $YAlO_3$ (YAP) with a perovskite structure, $Y_4Al_2O_9$ (YAM) with a monoclinic structure and $Y_3Al_5O_{12}$ (YAG) with a cubic garnet structure [2], with the last one being more difficult to obtain compared to the other two. Pure phase YAG is synthesized by solid-state diffusion reaction methods, requiring sintering at high temperatures above 1550°C.

The phosphor coating is by far the most important step in LED packaging process as it is set side by side with such factors as amount of phosphor covering the LED dies, thickness of phosphor layer and phosphor coating technique. All these factors have an influence on the final light characteristics of an LED and its quality. The most important parameters of a pcLED are correlated color temperature (CCT), color rendering index (CRI) and luminous efficiency (lm/W).

2. EXPERIMENTAL SECTION

2.1 Phosphor synthesis

There are different synthesis methods of crystalline powders of YAG:Ce. Four methods are described by Pan et al. [3]. We used solid-state reaction method to prepare crystalline powder samples of YAG:Ce with 2% Ce^{3+} concentration. The reactants such as Y_2O_3, Al_2O_3 and CeO_2 were mixed in a stoichiometric amounts at 1500^0C for 2 hour (5% H_2, 95% N2 reducing atmosphere). To obtain uniform size the grinded samples were passed through different sieves. X-ray diffraction patterns were recorded using a Bruker 5000 diffractometer in standard θ-2θ geometry with CuKα radiation. All investigated samples turned out to be single-phase ones.

Photoluminescence (PL) excitation and emission spectra were recorded between 77 and 350 K on the FS 920 fluorescent spectrometer (Edinburgh Instruments) equipped with a Hamamatsu R928P red-sensitive photomultiplier (wavelength range from 200 to 850nm). An Oxford Optistat CF cryostat was used to cover a measurement temperature range from 4 to 500K and to record the TL properties.

The morphology of the samples was observed using the secondary electron detector of the S-3400N series type II scanning electron microscope (SEM) from HITACHI Company.

2.2 PcLED fabrication

PcLED arrays were fabricated on the basis of analyzed YAG:Ce phosphor and blue InGaN dies. They were manufactured by the chip on board technology. The advantage of such technology is that the dies are mounted directly onto the board, allowing heat to sink much better than in SMD type packages.

To assemble the LED package the Metal Core Printed Circuit Board (MCPCB) was used. First the dies were attached to the substrate using Delvotek's A1die placing equipment. 100 dies, 1 watt each, formed a matrix of 10×10, connected in series and in parallel. The dies used were 1×1 mm blue dies manufactured by MOCVD process. The dies were attached to the substrates by means of epoxy glue, to harden the glue the substrates were placed in a heater and kept there at 150°C for about an hour (fig. 1a,b). After that the samples were sent to the plasma-ion cleaning system where their surface was polished in ionized Ar for 3 minutes to make it free of dust and small particles.At the next stage the dies were electrically connected to each other, and the arrays were connected to the contact pads closing the circuit. The dies were bonded with the golden wire 25μm in diameter using a Delvotec G5 ultrasonic bonding machine (fig. 1c).

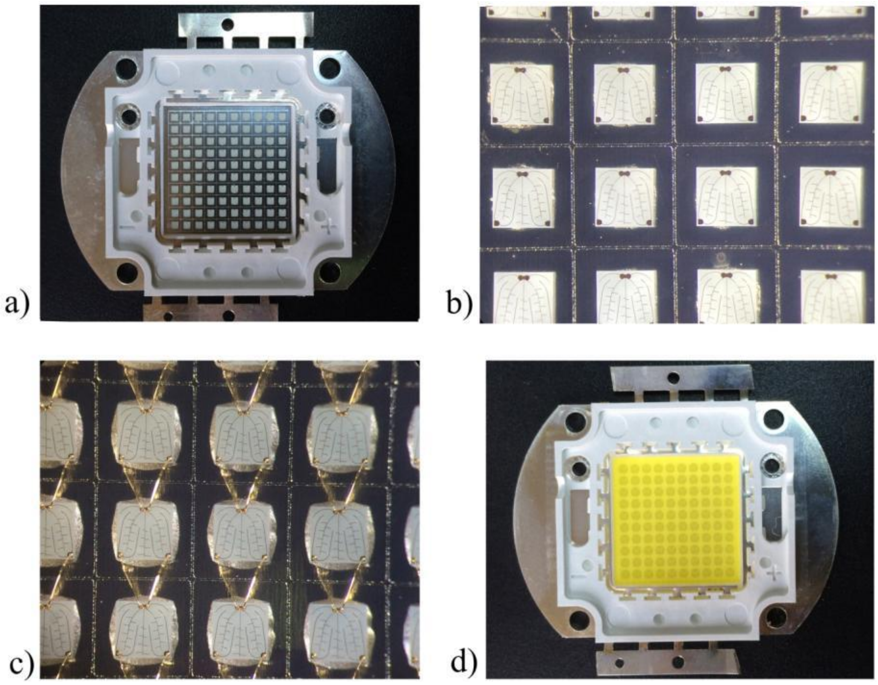
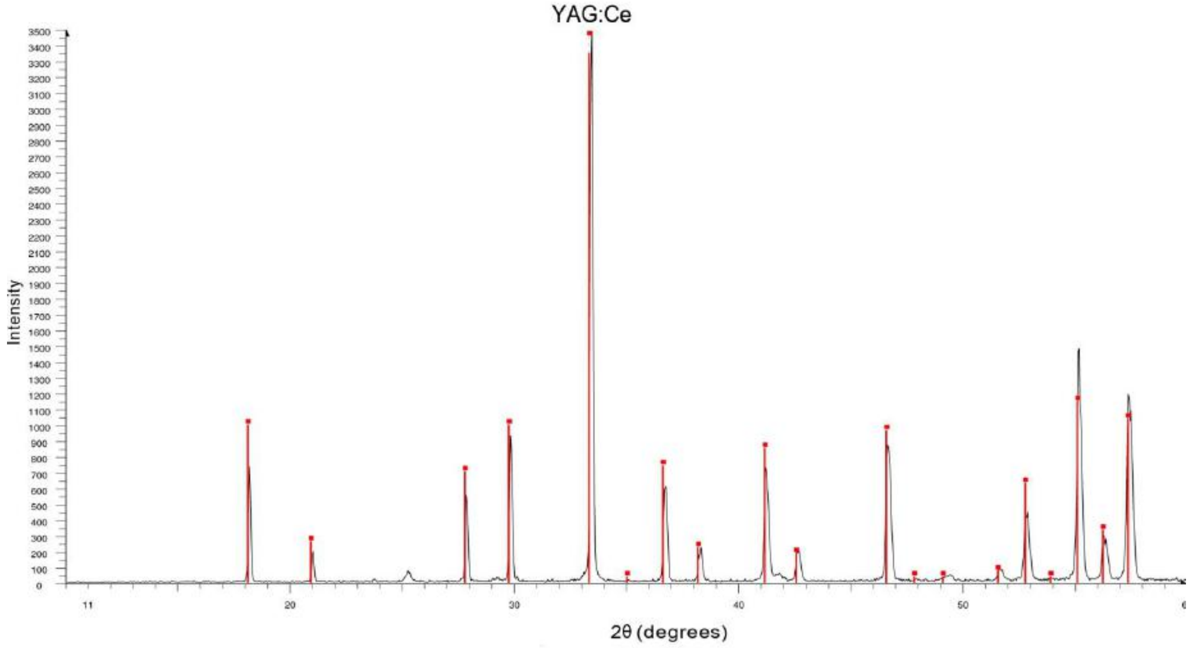


Fig. 1. a) Substrate with attached dies, b) dies on the substrate (enlarged), c) dies bonded with gold wire (25μm), d) LED coated with phosphor.



▨ YAG:Ce -raw. Start: 10.000^0- End: 60.000^0-step: 0.040^0-step time 1.2 s –Tem: 25^{o}C (room temp.)- Time started: 17s- 2θ: 10.000^o- θ: 5.000^o C

▣ Aluminum Yttrium –Oxide – Al$_5$Y$_3$O$_{12}$ –Y: 105.49%-dx by: 1.-WL:1.5406 –Cubic –a 12.00890- b 12.00890- c 12.00890 –alpha 90.000-beta 90.000-gamma 90.000-Body centered-Ia3d(230)

Fig.1. XRD for YAG:Ce.

And at the last step the LED arrays were covered with YAG:Ce phosphor to convert the blue LED light into white light (fig. 1d). Epoxy resin was used as an encapsulating material, and was mixed with YAG:Ce powder in three different ratios. The concentrations of phosphor in 1 gr of epoxy were made: 7%, 10%, 16%, while the thickness of the encapsulating layer remained constant. This mixture was dispensed on top of the dies using a dispenser to achieve a uniform layer of phosphor throughout the substrate. Then the LEDs were baked in the binder at the temperature of 90°C for about 10 minutes to provide some hardening of the encapsulating material, but at the same time not long enough to keep it viscous. Then whole LEDs were covered with a second transparent layer of epoxy to protect the phosphor and the wires from damage. After that the LEDs were placed into the binder heater to give it the final bake at 120°C, at this temperature both layers fully hardened.

For the measurement of their optical and electrical parameters the LEDs were placed into the Everfine’s PMS-80 optical integrating sphere and tested at various currents: 0.5 A, 2A, 3.5 A. The forward voltage drop of a single die is 3 volts, and the whole array is powered by 30 volts, so at 3.5A the LED was pushed to 100 watts of electrical power.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD) analysis of YAG:Ce

XRD is a non-destructive analytical method used for identification and quantitative determination of the various crystalline forms (known as phases) present in samples. The phase identification is important because the properties of the phosphorescent powder are strongly dependent on the structure. The diffractogram shows the phases present (peak position), phase concentrations (peak heights), and crystalline size/strain (peak width). Figure 1 shows the XRD analysis of YAG:Ce, we observed the product to be a single-phase one.

3.2 SEM analysis of YAG:Ce

The morphology analysis of the samples was conducted on the new Hitachi S-3400N Variable Pressure SEM. It is equipped with a Secondary Electron Detector High Sensitivity Semiconductor BSE Detector, and is capable of giving a resolution of 10 nm at 3 kV and 3 nm at 30 kV. Fig. 2 shows the photo taken by the SEM at the WD=10.7 mm, the voltage on the gun -15 kV. It is evident from the figure that particles are of spherical shape and have various micron sizes and lengths.

3.3 PL properties of YAG:Ce

Figure 3 shows the energy levels of a Ce^{3+} ion, as well as the processes that take place when it's located in a host lattice. A free Ce^{3+} ion in its fundamental state has a 4f electron configuration which is split into two multiplets: $^2F_{5/2}$ and $^2F_{7/2}$, and in exited state it has a 5d electron configuration. When the Ce^{3+} ion gets to its excited state, the 5d electrons forma ^2D term, which is split into $^2D_{3/2}$ and $^2D_{5/2}$ multiplets by spin-orbit coupling [4]. $^2D_{5/2}$ is an unstable level, and its electrons tend to relax to $^2D_{3/2}$ level when they meet a photon. When a Ce^{3+} ion is placed in a host crystal such as YAG as an activator ion, its 5d electrons are influenced by the host crystal's atoms and two effects act on the 5d configuration: the centroid shift and crystal field splitting. The 4f configuration on the other hand is not much affected by these effects. Both of these effects lower the energy gap between 5d and 4f levels (red shift). In YAG:Ce, the Ce^{3+} ions occupy the dodecahedral sites in the host lattices, and in this case the energy gap between the fundamental and excited states becomes 22,000 cm^{-1}, which is equivalent to blue light.

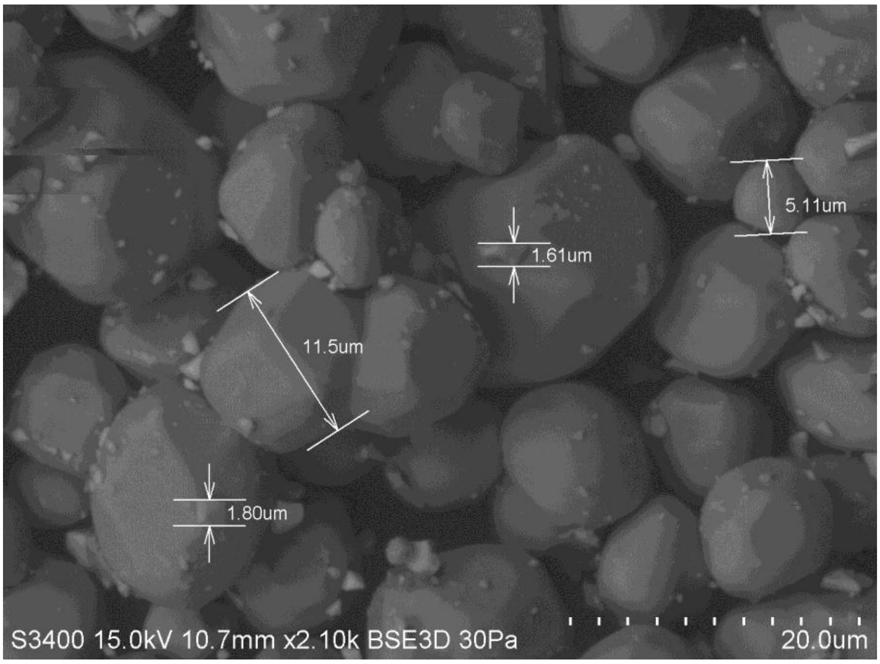


Fig. 2. SEM analysis of YAG:Ce.

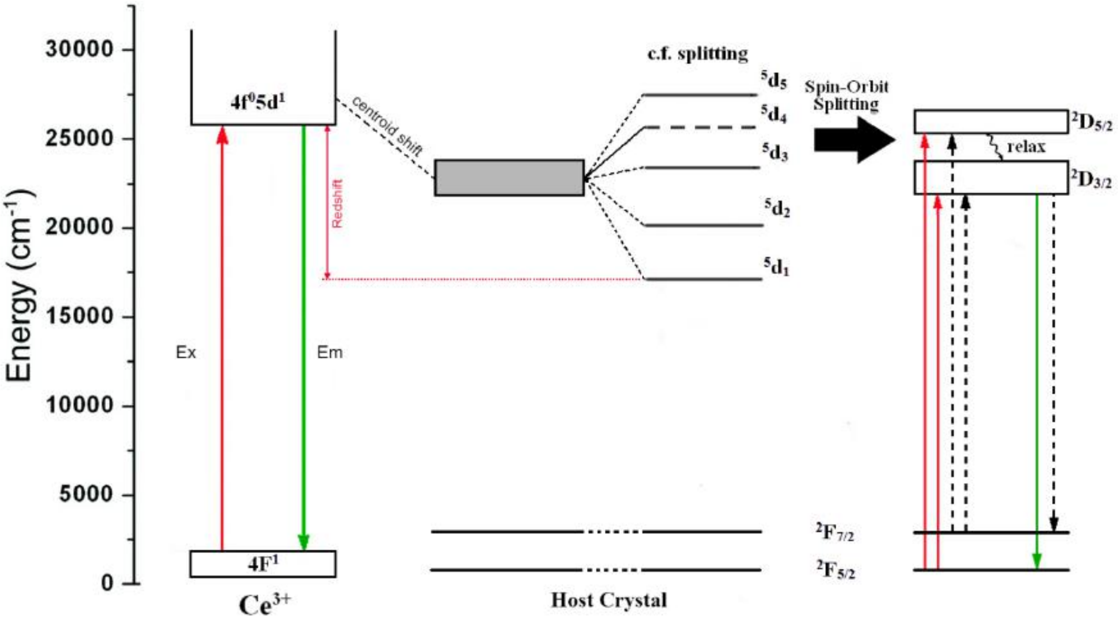


Fig. 3. A schematic energy level diagram for Ce^{3+} showing its excitation (Ex) and emission (Em) processes and the effects of a host crystal A.

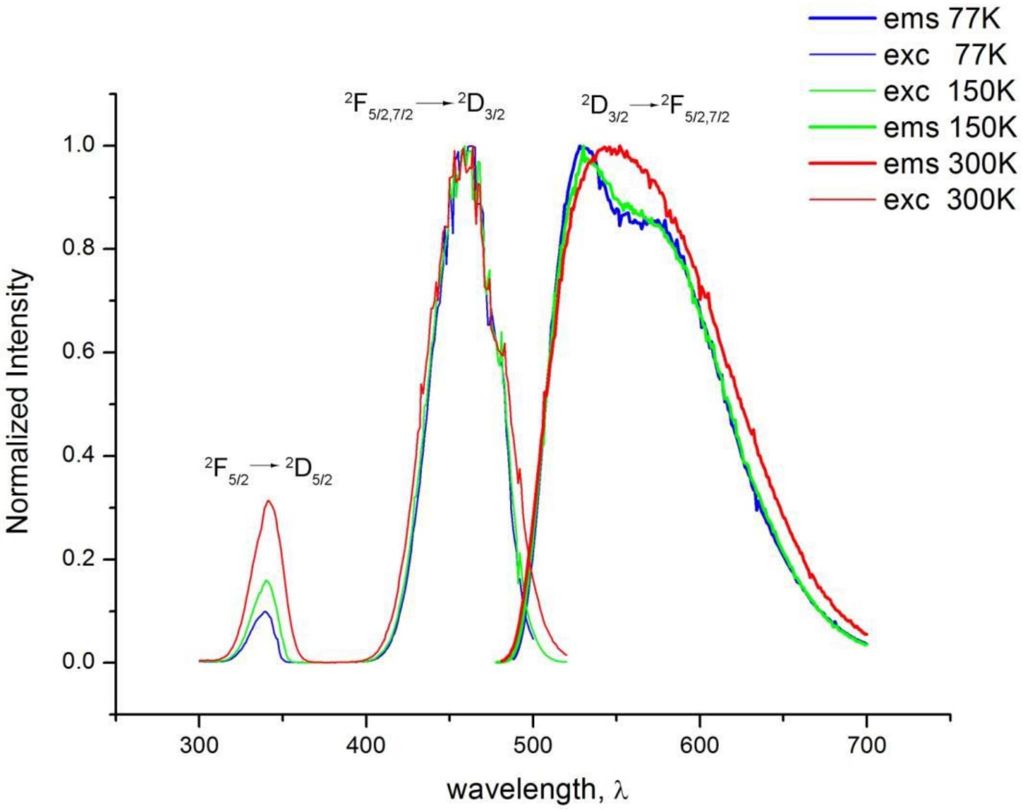


Fig. 4. The excitation and emission spectra of YAG:Ce at different temperatures.

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Fig. 4 presents the photoluminescence spectra of YAG:Ce at different temperatures: 77, 150, 300K, where two excitation bands with the peaks at 341 and 460 nm (at room temperature) can be discerned, which should be attributed to $^2F_{5/2}\rightarrow{}^2D_{3/2}$ ($^2D_{5/2}$) and $^2F_{3/2}\rightarrow{}^2D_{3/2}$ ($^2D_{5/2}$) transitions. The emission spectra at room temperature (T=300K) is a broadband spectra with a peak at 553 nm excited by 460 nm which occurs by the $^2D_{3/2}\rightarrow{}^2F_{7/2}$ ($^2F_{5/2}$) transitions. Apparently at 77K and 150K the excitation spectrum is found to be asymmetrical, stemming from the $5D\rightarrow{}^2F_{5/2}$ and $5D\rightarrow{}^2F_{7/2}$ transitions. It also becomes clear from the graph that the emission spectra changes with the increase of temperature from 77 K to 300 K, shifting from 528 nm to 533 nm. In theory this shift occurs on account of the increasing number of non-radioactive transitions, which also leads to phosphor's efficiency drop too.

3.4 Measurement of pcLED's optical parameters

Fig. 5 shows how the EL spectra of the blue InGaN LED matches the photoluminescence excitation spectrum of YAG:Ce phosphor, and also its emission spectrum. The LED dies that were used for the fabrication of the LED arrays emitted light with a peak wavelength of about 447 nm. It can be observed on the graph that the phosphor's excitation and blue LED's emission bands overlap with each other.

Fig. 6 shows the EL spectra of the blue LED coated with the YAG:Ce phosphor driven at the various forward currents: 0.5 A, 2 A and 3.5 A. The graph shows an arrow peak which is created by the blue LED. The rest of the spectrum is YAG:Ce phosphor's broadband emission spectra ranging from green 500 nm up to red 650 nm wavelengths. The luminous efficiency of the pcLED was 96 lm/W at 0.5 A, 81 lm/W at 2 A and 69 lm/W at 3.5 A, so it's obviously decreasing with increasing current. This effect is partially due to InGaN LED's luminous efficiency droop with current growth, as well as phosphor's luminous efficiency droop. One of the reasons to this is that the heat generated by the LED dies is transferred to the phosphor, raising its temperature, and as a result we see a drop in phosphor's quantum efficiency η_e.

Fig. 7 shows the Commission Internationale de l'Eclairage (CIE 1931) color coordinates of three pcLED's with different amounts of YAG:Ce phosphor. The LEDs with the 1) 7%, 2) 10%, 3) 16% concentrations of phosphor in 1 gr of epoxy are depicted on the diagram as Δ, □ and ◊, respectively. So by varying the phosphor concentration it is possible to control the correlated color temperature of the emitted light, which goes down with the increase of phosphor amount. The color coordinates of the LED with the 10% phosphor concentration are located right on the Planckian Locus near to the D65 point, and it gives pure white light with the CCT T_2=6444K, while other two LEDs (Δ, ◊) give warm (T_1=4624K) and cool (T_3=8825K) white light. The CRIs of three samples were: R_1=61, R_2=67, R_3=72. The color coordinates were overall stable and changed only marginally when applied current was increased.

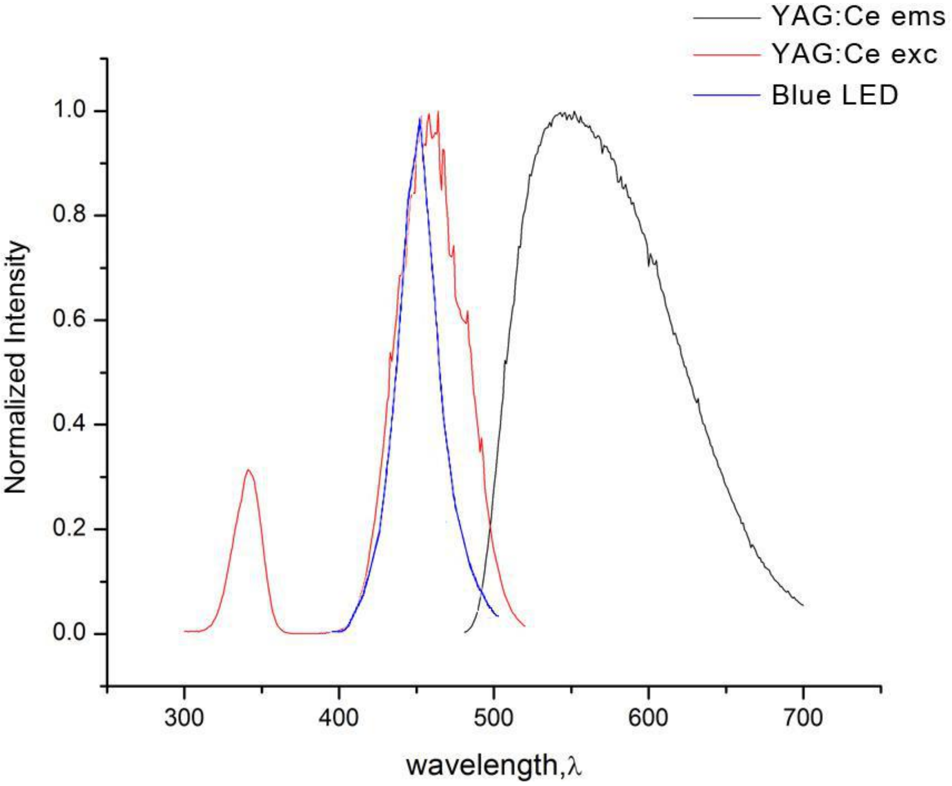

Fig. 5. PL and PLE spectra of YAG:Ce and EL spectra of blue LED.

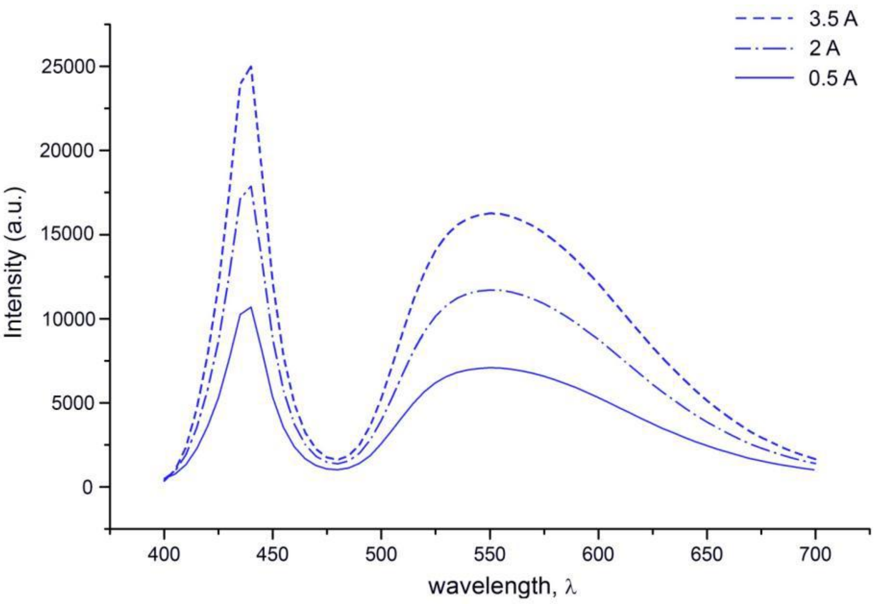

Fig. 6. EL spectra of the pcLED at various driving currents: 0.5A, 2A, 3.5A.

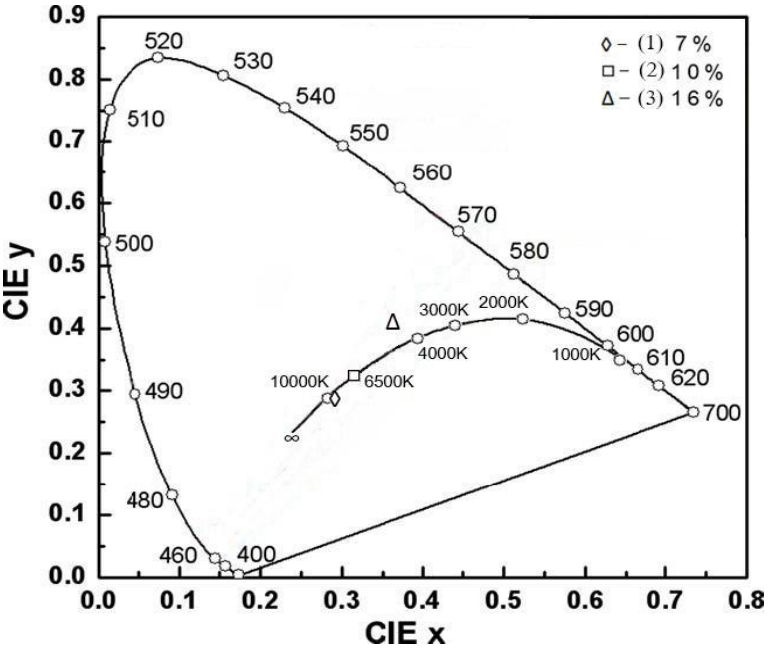

Fig. 7. The Chromaticity diagram color coordinates of pcLEDs with various phosphor concentrations: 1) 7%, 2) □- 10%, 3) ◊- 16%.

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4. CONCLUSION

The yellow Yttrium Aluminum Garnet phosphor activated with Ce^{3+} ions has been analyzed and used to fabricated powerful pcLEDs on its basis. By varying the phosphor quantity in the epoxy covering the blue LED it is possible to manipulate the CCT, and we managed to get pure white light pcLED with the CCT of 6444K, the CRI of 67 and the efficiency of ~80 lm/W. YAG:Ce phosphor produces an intense emission in the green and yellow wavelength band, however, it somewhat lacks the warm reddish spectra and the CRI is quite low because of it. Therefore, it is ideal for the manufacture of cool white light pcLEDs, which are suitable for use in street lighting and spotlighting.

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