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ORGANIC – INORGANIC HYBRID LUMINESCENT COMPOSITE FOR SOLID-STATE LIGHTING

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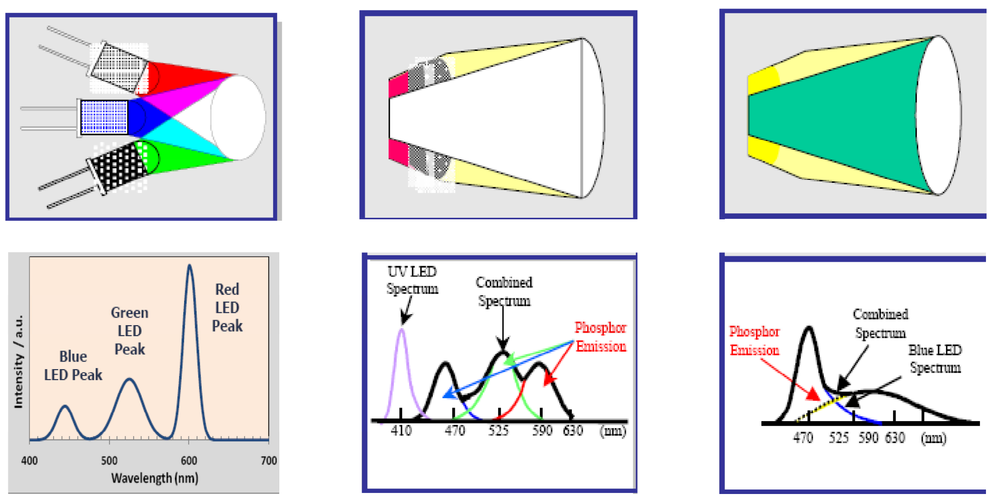
Abstract. *White light emitting diodes (WLEDs) were made by coating organic and inorganic hybrid composites on blue LED chips.* $Y_3Al_5O_{12}$*:Ce (YAG:Ce) nano powder prepared by low-temperature Sol-Gel method exhibited a broadband green emission spectrum with the peak at 521 nm. The white light was obtained by mixing blue light from emission of the blue LED chip - Indium Gallium Nitride (InGaN), green-red light from the fluorescence of nano- YAG:Ce and yellow light from Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) polymer. The hybrid nanocomposite-based WLEDs exhibited broad band emission spectra from blue light to red wavelengths and provided the white light with a CIE-1931 coordinate of* $x = 0.2986$*,* $y = 0.2620$ *and a colour rendering index* $R_a = 84.36$*. The obtained results suggest a potential application of nanocomposite based WLEDs in efficient solid-state lighting.*

I. INTRODUCTION

It is known that the solid-state lighting (SSL) is based on lighting from light emitting diode (LED) rather than conventional incandescent and fluorescent lights. Since SSL produces visible light while giving off less heat and reducing energy loss, it has potential applications in both the life and the lighting industrial technology. This technology holds promise for lower energy consumption and reduced maintenance [1, 2].

There are three methods to generate white light by semiconductor LED such as Red + Green + Blue LED, UV LED + RGB phosphor and Blue LED + Yellow phosphor (Fig. 1). Each method has own advantages and disadvantages [2-7]. By the fist method one can make white light by combining three LEDs with red, green and blue colors. It is a better choice to produce white light with long term, high efficiency, dynamic tuning of color temperature, excellent color rendering and very large color Gamut. However, this method has also limitations, for example, the color feedback requires accounting for LED degradation with temperature and time, the color mixing and the yellow green gap. In the second method the white light can be done by using UV-LEDs for the excitation of the RGB phosphor. The advantages of this method are following, the white point can be determined by a single phosphor, the color rendering is reasonable, and the phosphor possesses an excellent temperature stability. But the disadvantages of this method can be also mentioned such as a low-efficient blue LED pumped phosphor, different angle color uniformity, and the need of UV exposure packaging and the lack of the all-temperature stability of phosphor. In the last method the white light is obtained by combining the blue LED with yellow phosphor. This method is simple and useful for the generation of the white light and has the following advantages: single yellow phosphor versions available, decent color rendering, and temperature stability of phosphor. However, this method also faces to many challenges such as temperature stability of phosphor is not available in all colors, color uniformity strongly depends on the view angle. Besides the above mentioned advantages and challenges, this method has many disadvantages such as low conversion efficiency of the phosphor, stokes shift, self absorption, etc.



(a) (b) (c)

Fig. 1. Three methods used for producing the white light LEDs: (a) Red + Green + Blue LEDs, (b) UV LED + RGB phosphor and (c) Blue LED + Yellow phosphor.

In this work, we report the preparation of the organic - inorganic hybrid luminescent composites (further shortly called composites) used to generate the white light for SSL applications. The composites were made from the nanostructure Ce-doped yttrium aluminum garnet (YAG:Ce) and conjugate polymer of (Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4- phenylene vinylene] (MEH-PPV). The aim of the work is getting broad band luminescence in the visible wavelengths to enhance the color rendering index (CRI) of white LED (WLED).

II. EXPERIMENTAL

The green YAG:Ce (G-YAG) nanopowder was prepared by low-temperature sol-gel method. The YAG:Ce powders with composition corresponding to the formula $Y_3Al_5O_{12}$:Ce were synthesized from precursor materials such as Y_2O_3, HNO_3, $Ce(NO_3)_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $C_6H_8O_7{\cdot}H_2O$ and ammonia ($NH_3{\cdot}H_2O$). The yttrium oxide (Y_2O_3) was dissolved in a hot nitric acid in flask three neck and obtained solution. The solution was agitated for 2 hours at temperature of 60 – 65 ^oC. Then the solution was added by the aluminum nitrate and cerium nitrate to get the bright yellow solution. In the next step, citric acid ($C_6H_8O_7 \cdot H_2O$) was added in the bright yellow solution. Citric acid was dissolved in this solution by half the mole of the total metal ions. The pH value of the solution was modulated to 4, and a gel was obtained for 1 h by immersing the solution in a water bath at 80 ^oC. Then the gels were dried to obtain canary xerogel. The xerogel was put into a muffle stove and a combustion reaction occurred at 245 ^oC for 20 minute, the spumous powder was obtained. The calcination was conducted at 700 ^oC with a heating rate of 2 ^oC /min and kept for 120 min, and then the temperature was raised up to different holding temperatures (800-1200 ^oC) at a rate of 10 ^oC /min for a fixed holding time of 120 min in air.

The pure MEH-PPV powder was prepared by dissolving in toluene solvent with a ratio of 1 mg of MEH-PPV powder in 2 ml toluene. The G-YAG nanopowder in the MEH-PPV solution was mixed in a liquid transparent epoxy. The obtained composite was then coated onto the glass substrate and the blue LEDs chip for the investigation of photoluminescence and electroluminescence characterization, respectively. The absorption and photoluminescent properties of composites were recorded on UV/VIS/NIR spectrophotometer "V570-Jasco" and a high resolution spectrometer "Microspec-235b", respectively. The electroluminescence characterizations were measured by using an integrating sphere equipped with a calibrated spectrophotometer – "LCS 100" (LED measurement System).

The blue InGaN-LED chip used in this research is the high power 1W LED chip with the emission peak at 455 nm (with the die size around 1100 μm x 1100 μm, as can be seen elsewhere [8]). The green phosphor and MEH-PPV polymer hybrid composite were dropped onto the surface area between the top of the LED chip to convert a part of blue light into green and red lights.

III. RESULTS AND DISCUSSION

The absorption and photoluminescent spectra of MEH-PPV films are showed in Fig. 2. From this figure one can notice that the MEH-PPV film has an absorption peak a 490 nm and two emission peaks at around 590 nm and 620 nm as reported in [8 - 10]. This proves that for the excitation of MEH-PPV polymer, InGaN blue LED chips with 460 nm peak of the emission are quite efficient.

In Fig. 3, both the XRD patterns and FE-SEM image of the G-YAG nanopowder prepared by low-temperature sol-gel method are presented. All the peaks revealed in the XRD diagram (Fig. 3a) consist with the main characteristic peaks of the bulk YAG crystal (PDF card No. 12005-21-9).

From the FE-SEM image (Fig. 3b) one can see that the particle size of the YAG:Ce nanopowder is about 10 nm with the quite homogeneous size distribution.

Figure 4 shows photoluminescent spectra of a G-YAG nanopowders sample and a MEH-PPV thin film, separately. The outcome of the superposition of the emission spectrum of G-YAG (the peak at 521 nm) and MEH-PPV (the peak at 590 and 620 nm) is an overall part of the spectra spreading from 450 to 750 nm. This expansion of the spectra shows a potential application of G-YAG and MEH-PPV hybrid composites for WLEDs.

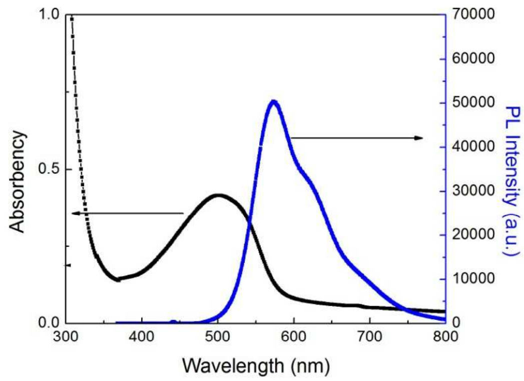


Fig. 2. Absorption and Photoluminescence spectra of MEH-PPV film.

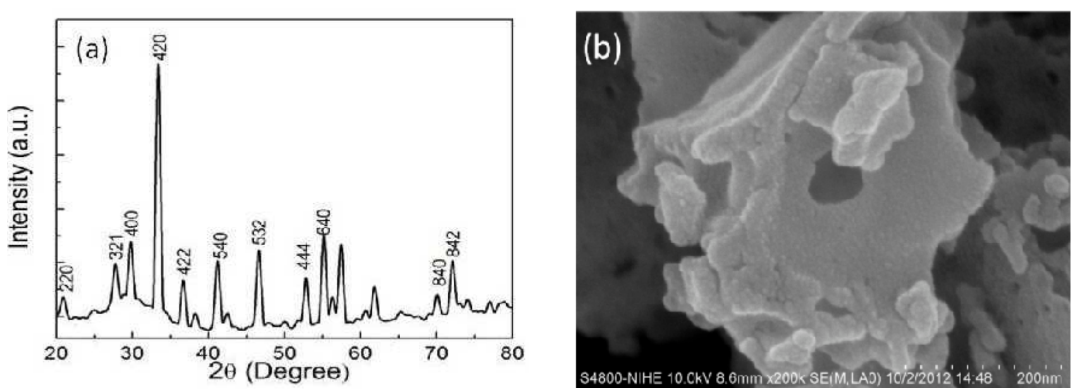


Fig. 3. XRD partterns (a) and FE-SEM image (b) of a YAG:Ce nanopowder sample.

The result shown in Fig. 4 also demonstrate that the mixture of G-YAG and MEH-PPV can extend the luminescent spectrum from short wavelengths to long wavelengths. This behavior is due to the contribution of the G-YAG, which extends on short wavelengths (about 450 nm) and of MEH-PPV polymer which extends on the long wavelengths (about 750 nm). This is one of the advantages of the G-YAG and MEH-PPV hybrid composite. Indeed, the realization of using the hybrid composite to make a WLED gave a total emission spectrum as demonstrated in Fig. 5.

The electroluminescence spectra of a blue LED, photoluminescence spectra of G-YAG:Ce and MEH-PPV polymer are presented in the follow Fig. 5. From this figure one can expect that the light emitted from three components as blue the LED chip, G-YAG and MEH-PPV polymer could exhibit the white light with a broadband luminescent spectrum and a high CRI. Especially, with the use of G-YAG and MEH-PPV hybrid composite, the spectral region is enhanced around the wavelength of 521 nm. This is due

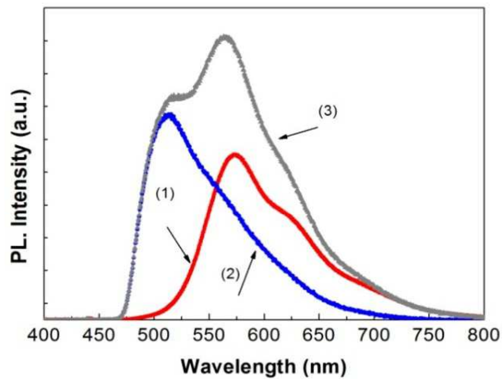


Fig. 4. Photoluminescence spectra of MEH-PPV film (curve 1), G-YAG (curve 2) and G-YAG + MEH-PPV hybrid composite (curve 3).

to the contribution of the emission of the G-YAG. The increase of the intensity of the 521 nm peak enables the color rendering index increased.

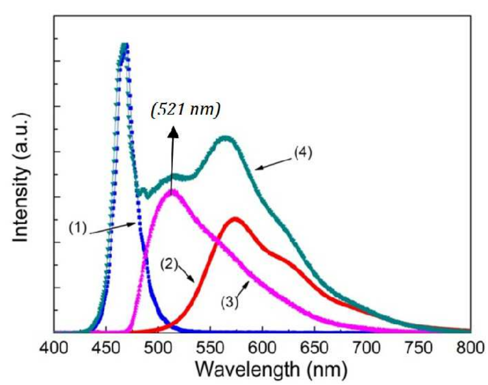


Fig. 5. Emission spectra of components of WLEDs made from nanocomposite: Blue LED (curve 1), MEH-PPV (curve 2), G-YAG:Ce nanopowder (curve 3) and the total spectrum of the Blue LED, G-YAG:Ce and MEH-PPV (curve 4).

The emission spectrum of the WLED recorded under a supply voltage of 3.5 V is plotted in Fig. 6, this clearly shows a better electroluminescence spectrum torwards the white light region.

To determine the CRI of the WLED made from a 300 μm - thick hybrid nanocomposite film, the device was put on the integrating sphere equipped with a calibrated spectrophotometer LCS-100 and supplied with a 3.5 V voltage and 200 mA current. The obtained results from the measurements for the colour coordinates at $x = 0.2986$ and $y = 0.2620$ is shown in Fig. 7. One can notice that the white light region is located inside

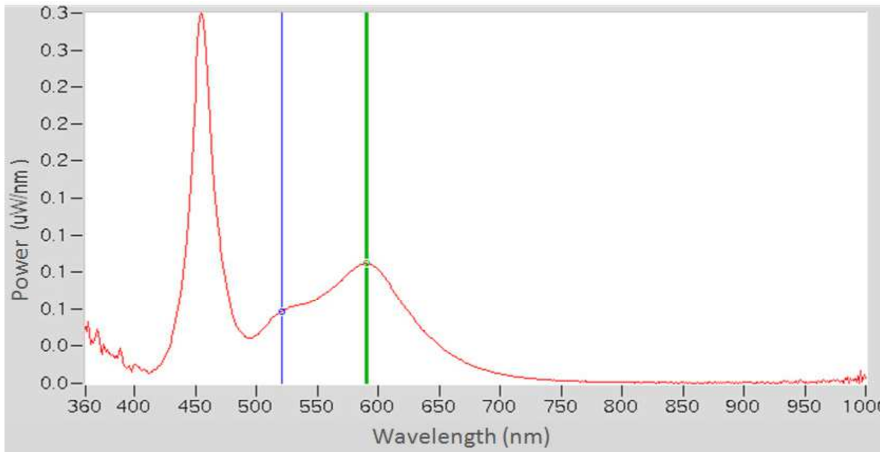


Fig. 6. Emission spectrum of WLED made by coating G-YAG and MEH-PPV hybrid composite onto InGaN blue chip.

the ellipse with the centre at E ($x = 0.33$ and $y = 0.33$). It is seen that for the WLED, the CRI was found to be as high as $R_a = 84.36$.

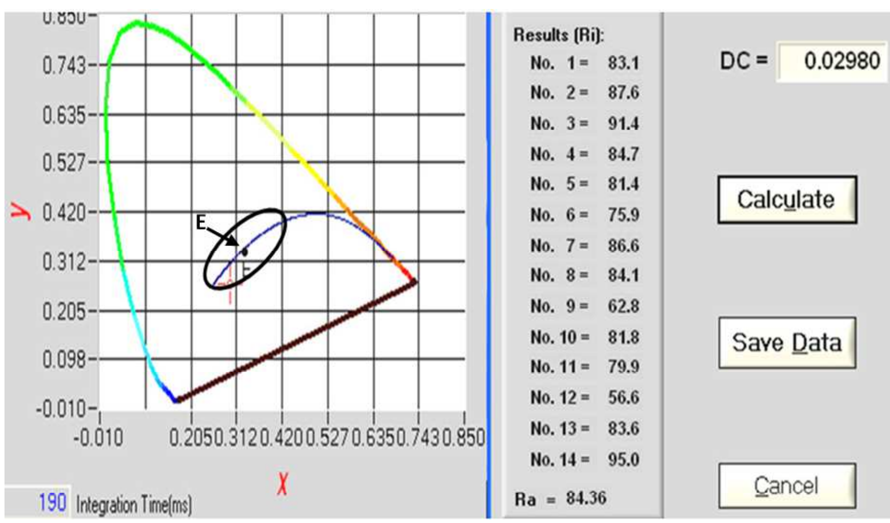


Fig. 7. CIE-1931 coordinate of WLEDs fabricate by InGaN blue chip and G-YAG:Ce and MEH-PPV hybrid composite.

IV. CONCLUSION

The results on the fabrication and characterization of white LED with broadband white light emission spectrum were reported. Photo- and electroluminescent spectra of the hybrid nanocomposite of the green YAG:Ce and MEH-PPV conjugate polymer showed that a novel white LED composed of YAG:Ce and MEH-PPV polymer and InGaN chip giving a high CRI can be made. This WLED exhibits a broad band emission spectrum from blue to red light that is more adapted to the human eye sensitivity. The hybrid nanocomposite based WLEDs provided the white light with a CIE-1931 coordinate of $x = 0.2986$, $y = 0.2620$ and a colour rendering index $R_a = 84.36$. The obtained results suggest a potential application of nanocomposite based WLEDs in efficient solid-state lighting, consequently in the valuable contribution to the energy sustainability.

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