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Yellow YAG: Ce³⁺ phosphor in polyimide matrix for white light generation by laser diode

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Abstract— Polyimide polymers are characterized by high heat resistance and thermal stability. In this work, two polyimide films of different thickness are used as the encapsulating matrix for a yellow YAG: Ce³⁺ phosphor. The films are irradiated by a laser diode (LD) of 450 nm, down-converting the blue laser light into white light. The polymers underwent two aging processes, the first, under blue light from LEDs, and the second was laser irradiation. The effect of the aging process along with their colorimetric properties were investigated. The results showed that polyimide is a promising material for white light applications generated by laser diodes.

Keywords— Phosphor, laser diode, white light, polyimide

I. INTRODUCTION

Research on solid-state light sources (SSL) has seen a dramatic increase mainly due to their versatility. They are highly efficient, compact and have a better lifetime when compared to traditional incandescent light sources leading to a plethora of applications in fields such as interior and exterior lighting, biomedical imaging, displays, automotive industry and agriculture [1–4]. LEDs are the primary light source for white light generation, which is being achieved by either combining the light of blue, green and red LEDs [5] or by employing a blue LED and a down-converting phosphor [6].

Down-converting phosphors coupled with blue LEDs are dominating the white light sources market but they are not without drawbacks. Even though it is possible to achieve conversion efficiencies up to 80%, their performance suffers from efficiency droop, meaning that the external quantum efficiency, which is strongly dependent on the input current density, starts decreasing on higher current densities which is called current droop. The operating temperature of the device can also be the cause of efficiency droop and may even shift the emission peak wavelength, thus further decreasing the efficiency and changing the color characteristics of the light source due to what it is called thermal droop [7].

To overcome this, the replacement of the blue LED with a laser diode (LD) has been proposed. LDs are light sources with high luminance whose efficiency is linearly dependent on the operating current density [8]. Combined with other laser characteristics such as monochromaticity, directionality and coherence, a LD offers a lot of versatility to down-converting phosphor light devices. In a typical laser-driven

white light generation device the LD is coupled with a remote yellow-emitting phosphor and the mix of the blue and yellow light is perceived as white.

Regarding the materials in which the phosphor can be encapsulated, several approaches have been studied such as phosphor-in-glass (PiG), silicone and epoxy resins [9–10]. Choosing the right material is critical because during the light conversion process, part of the energy is lost to thermal effects. This is especially true in the case of LDs whose high optical flux density can be responsible for thermal damage in the case of phosphor matrices whose thermal stability is quite low [11].

In this work, we study a LD-phosphor configuration where a yellow YAG:Ce³⁺ phosphor is embedded in a polymer film of the polyimide family. Polyimides are known for their high heat resistance and low thermal expansion coefficients [12], rendering them a promising alternative to traditional phosphor matrix materials. In the present work, the aging of the polyimide film under blue light was studied along with the effect that it had on its colorimetric parameters. As it will be shown below, the CRI value of the phosphor was low. To address this, a blue phosphor was placed before the yellow phosphor to further increase the CRI value.

II. AGING MEASUREMENTS BY BLUE LEDs

In this part, the effect of blue light on the polyimide films was studied. Two thin films with a thickness of 65 μm and 130

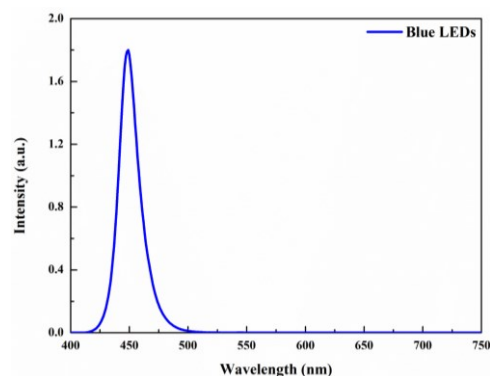


Fig. 1. Blue LEDs spectra

μm respectively and a phosphor concentration of 50%, were placed inside a box and where irradiated for 500 h with blue LED light. The LEDs were mounted on the inner upper surface of the box at a distance of 20 cm from the samples. The optical power generated by the LEDs was 7.3 mW. Measurements of the emission spectra of each sample were performed every 50 h. Figure 1 depicts the spectrum of the blue LEDs.

To obtain the emission spectra for each sample, a blue LD (ThorLabs, 450 nm, L450P1600MM, 1600 mW) was employed as the excitation source. A TCLDM9 Peltier module was also used as a temperature controller for the LD. The emitted white light from the irradiated films was obtained using a spectroradiometer (SpecBos 1201), which recorded the excitation spectra and calculated the colorimetric properties of the samples such as the Correlated Color Temperature (CCT) and the Color Rendering Index (CRI).

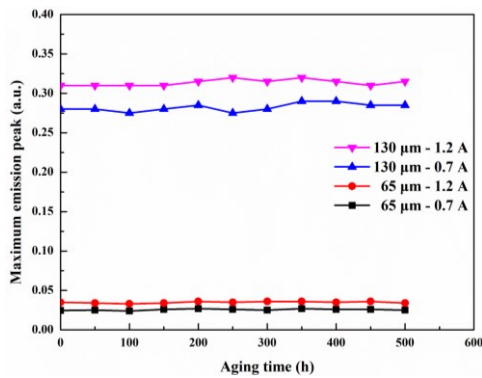


Fig. 2. Evolution of maximum of emission peaks for polyimide films

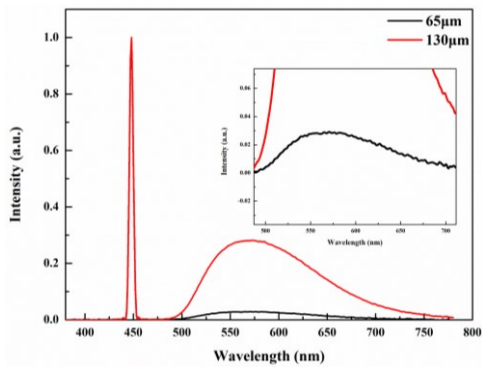


Fig. 3. Emission spectra of polyimide films

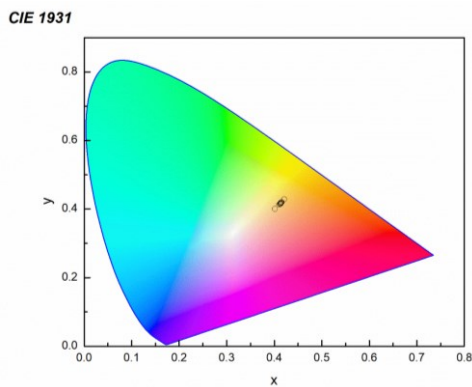


Fig. 4. Variation of chromaticity coordinates during aging process

Figure 2 shows the variation of the maximum of emission peak for different aging times. Each time point was measured for two driving currents i.e. 0.7 A and 1.2 A. We observed that even after 500 h of blue light irradiation, the maximum emission peaks are stable. This led us to the conclusion that the small fluctuations observed during the measurements, especially in the case of the 130 μm film, were caused by the LD. Even though the temperature of the LD was fixed at 30°C by the temperature controller, we verified that the real value had a variation of $\pm 1^\circ\text{C}$. That variation affects directly the intensity of the emission of the LD, which in turn affects the emission spectrum. Figure 3 depicts the emission spectra for both films before the aging process. Regarding the colorimetric parameters, the value of CRI was 63 and was the same for every aging time point. At the same time, the CCT value presented small variations during the aging process. These variations can be seen in figure 4, where the CCT has an average value of 3500 K. All the above refer to the case of the polyimide film with a thickness of 130 μm . Due to the low emission peak of the 65 μm film, its colorimetric characteristics could not be determined.

The low CRI value of the sample is attributed to the absence of blue light between the region of 450 nm and 500 nm wavelengths. To solve this, the blue LD we used was replaced by a violet LD of 405 nm (USHIO, HL40085G, 1000 mW), and a blue BAM ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ Sigma Aldrich) phosphor was placed just before the yellow phosphor. The blue phosphor was responsible for the conversion of the laser light to blue light and then that blue light excited the yellow phosphor. The white light, which was the result of the mix of the blue and yellow light, was recorded by the spectroradiometer. Four blue phosphors, each with a different concentration ranging from 10% to 40%, were tested with each of the two film samples to find the optimal combination. Figures 5 and 6 show the spectra of the blue phosphors combined with the 65 μm and the 130 μm respectively. Table I contains the colorimetric parameters of the tested combinations. The results showed that in the case of the 130 μm film, the increase of the CCT and the CRI was minimal. CCT reached an average value of 3472 K whereas its CRI moved to 70. On the other side, the combination of the 65 μm film with the blue phosphors led to an important increase of the CCT to an average 5967 K and a CRI value of 85. It should be noted that the combination of the 10% BAM with the 65 μm film showed the highest value for both parameters, with a CCT of 8040 K and a CRI of 89.

III. LUMINOUS EFFICACY AND LUMINOUS FLUX

In addition to the aging measurements, the luminous efficacy of the polyimide films was also measured. Luminous efficacy is an important parameter for lighting applications and can be determined by measuring the luminous flux Φ_v and then dividing that value by the radiant flux Φ_e . To perform these measurements, an integrating sphere with a BaSO_4 high reflectance coating was employed. The spectroradiometer and the LD were mounted on opposite portals of the integrating sphere. Luminous efficacy K is defined by the following formula:

$$K = \frac{\Phi_v(\lambda)}{\Phi_e(\lambda)} = K_{max} \frac{\int_0^\infty V(\lambda) \cdot \Phi_e(\lambda) d\lambda}{\int_0^\infty \Phi_e(\lambda) d\lambda} \quad (1)$$

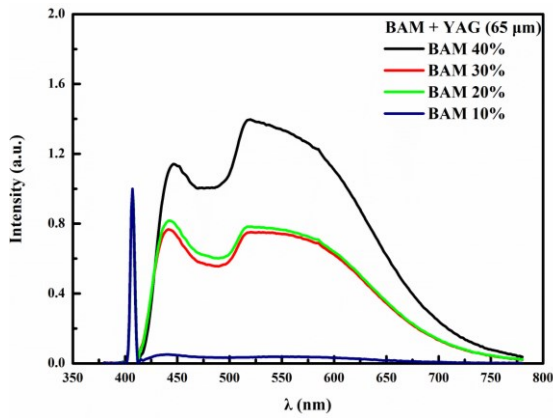


Fig. 5. Emission spectra of blue phosphors and 65 μm film

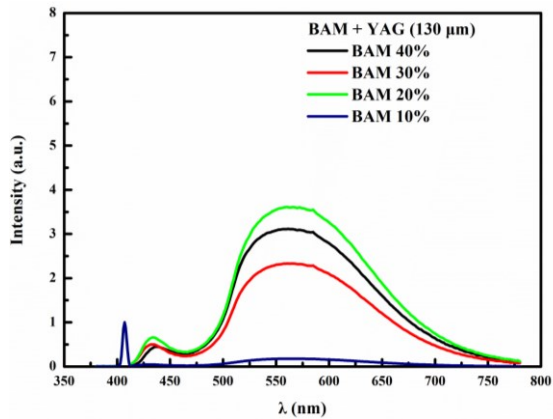


Fig. 6. Emission spectra of blue phosphors and 130 μm film

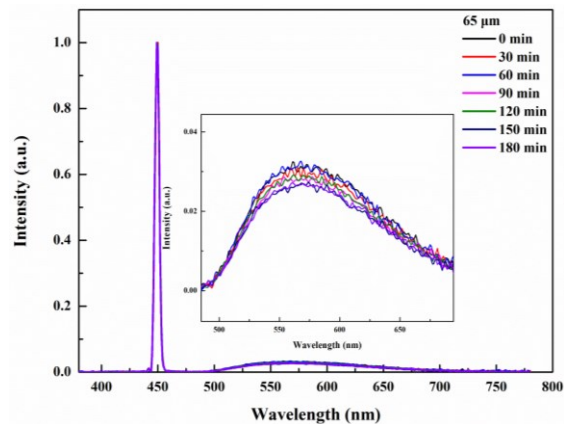


Fig. 7. Laser irradiation of 65 μm film

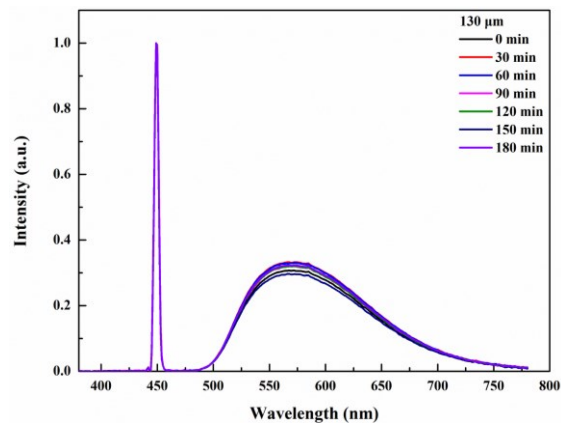


Fig. 8. Laser irradiation of 130 μm film

TABLE I. CCT AND CRI VALUES FOR BLUE AND YELLOW PHOSPHOR COMBINATIONS

Combination	CCT (K)	CRI
BAM 10% + 65 μm	8040	89
BAM 20% + 65 μm	6193	85
BAM 30% + 65 μm	6045	84
BAM 40% + 65 μm	5664	82
BAM 10% + 130 μm	3788	70
BAM 10% + 130 μm	3687	70
BAM 10% + 130 μm	3752	70
BAM 10% + 130 μm	3743	69

with the maximum value of the photometric radiation being equal to $K_{max} = 683 \text{ lm/W}$. For the polyimide film with a thickness of 65 μm , its luminous efficacy was found to be equal to $K = 262 \text{ lm/W}$ and $K = 268 \text{ lm/W}$ when operating the LD with 0.7 A and 1.2 A respectively. The luminous efficacy for a thicker sample i.e. 130 μm amounted to $K = 316 \text{ lm/W}$ for an operating current at 0.7 A while in the case of 1.2 A the value was $K = 307 \text{ lm/W}$.

Moreover, the luminous flux for each of the respective samples was calculated. The incident power of the LD was measured by a power meter (Newport 843 – R) equal to 0.11 W and 0.22 W (operating currents 0.7 A and 1.2 A respectively). For the polyimide film with a thickness of 65 μm , the corresponding luminous flux amounted to 29 lm and 54 lm while the sample of 130 μm thickness presented luminous flux values at 35 lm and 61 lm respectively. Table II summarizes the luminous efficacy and luminous flux values for each sample.

TABLE II. LUMINOUS EFFICACY AND LUMINOUS FLUX VALUES

Film thickness	Luminous efficacy (0.7 A)	Luminous efficacy (1.2 A)	Luminous flux (0.7 A)	Luminous flux (1.2 A)
65 μm	262 lm/W	268 lm/W	29 lm	54 lm
130 μm	315 lm/W	307 lm/W	35 lm	61 lm

IV. AGING BY LASER IRRADIATION

A second series of aging measurements was performed on the two samples. This time, the effect of the laser irradiation on the films was studied. To do so, each sample was irradiated by the LD for 180 minutes and every 30 minutes, measurements of its emission spectrum were performed to see if there are any changes to the material. Figures 7 and 8 show the collective emission spectra for each sample. The first thing we observed was that in both cases, the emission peak had a small fluctuation with a decreasing tendency. This decrease seemed to stabilize after the 150 min measurement for the 65 μm film whereas the maximum of the emission peak for the 130 μm film increased again and stabilized at the same value as the 90 min measurement. While this behavior indicates that

the emission peak fluctuates, this fluctuation is quite small and the fact that eventually it was stabilized, let us assume that the material is stable even after 180 minutes of continuous laser irradiation.

V. CURRENT AND TEMPERATURE MEASUREMENTS

In this last section, the emission spectra of the 130 μm film were studied for different driving current and temperature values. A series of measurements was performed where the driving current of the LD was varied from 0.6 A to 1.5 A. As it is shown in figure 9, that variation did not have any serious effect on the white light emission from the sample. This indicates that even at low current densities, the conversion efficiency of the sample remains satisfactory which in turn is also a positive for the LD because the operation at low current translates to a longer lifetime. Concerning the colorimetric parameters of the sample, its CRI remains stable at the value of 63. On the other hand, the CCT value tends to shift to warmer light as the driving current of the LD increases. Table III collects both the CCT and the CRI values of the above measurements.

TABLE III. COLORIMETRIC PARAMETERS FOR DIFFERENT LD OPERATING CURRENTS

I (A)	CCT (K)	CRI
1.5	3454	63
1.4	3465	63
1.3	3478	63
1.2	3489	63
1.1	3502	63
1	3516	63
0.9	3521	63
0.8	3536	63
0.7	3548	63
0.6	3557	63

The effect of the temperature of the LD on the emission spectra was also studied. Using the temperature modulator, we recorded the emission of the film for four different temperatures, ranging from 30°C to 60°C. The temperature modulation led to a small increase of the white light emission peak. This can be attributed to the shift of the LD spectrum to longer wavelengths. This shift improves the blue light down-conversion process and thus assists in the generation of white light with slightly higher intensity. Figure 10 shows the emission spectra of the temperature modulation measurements.

VI. CONCLUSIONS

We studied the use of a yellow phosphor in a polyimide film as alternative to traditional phosphor materials such as silicone, epoxy resin and phosphor in glass. The samples underwent aging under blue light coming from LEDs and laser irradiation from a LD to investigate their stability after long exposure to blue and laser light. The aging measurements were followed by colorimetric characterization where the CCT and CRI values of the material were determined under different current densities and temperatures of the LD source. Furthermore, the luminous efficacy and the luminous flux of the material was measured. The results of the study were quite

promising and indicate that polyimide is an interesting candidate for SSL systems. It should be noted that it would be interesting to replace the yellow YAG:Ce³⁺ diffused in the matrix with other phosphors or even mix different phosphor concentrations to produce white light with better colorimetric quality.

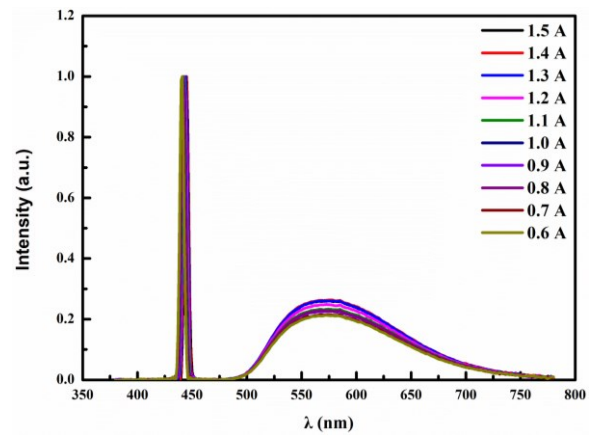


Fig. 9. Emission spectra for different driving current values

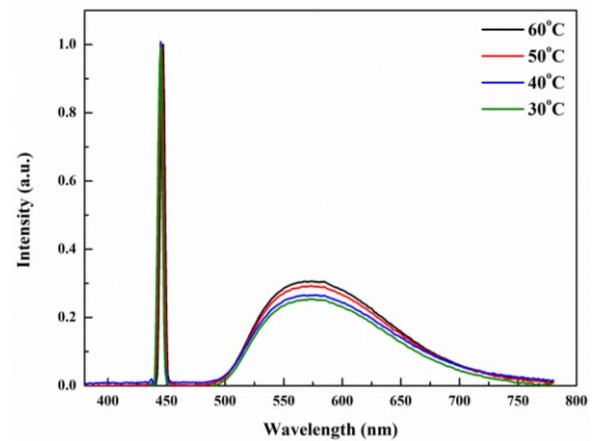


Fig. 10. Emission spectra for varying temperatures.

REFERENCES

- [1] S. Pimputkar, J. Speck, S. DenBaars and S. Nakamura, "Prospects for LED lighting," *Nature Photon* 3, 2009, pp. 180–182.
- [2] A. M. Srivastava, M. G. Brik, H. A. Comanzo, W. W. Beers, W. E. Cohen and T. Pooock, "Spectroscopy of Mn⁴⁺ in Double Perovskites, La₂LiSbO₆ and La₂MgTiO₆: Deep Red Photon Generators for Agriculture LEDs," *ECS J. Solid State Sci. Technol.* 7, 2018, pp. 3158–3163.
- [3] Y. Lai, N. Cordero, F. Barthel, F. Tebbe, J. Kuhn, R. Apfelbeck, D. Würtenberger, "Liquid cooling of bright LEDs for automotive applications," *Appl. Therm. Eng.* 29, pp. 1239-1244, April 2009.
- [4] H. E. Lee, J. H. Shin, J. H. Park, S. K. Hong, S. H. Park, S. H. Lee, J. H. Lee, I. Kang, K. J. Lee, "Micro Light-Emitting Diodes for Display and Flexible Biomedical Applications," *Adv. Funct. Mater.* 29, 2019.
- [5] S. Muthu, F. J. P. Schuurmans and M. D. Pashley, "Red, green, and blue LEDs for white light illumination," *IEEE J Sel Top Quantum Electron.* 8, pp 333–338, March-April 2002.
- [6] D. Bera, S. Maslov, J. Lee, J. Xue, F. So, and P. H. Holloway "Optimization of down-conversion phosphor films for high efficiency white organic light-emitting diodes," *J. Photonics Energy* 1, January 2011.
- [7] A. David, N. G. Young, C. Lund, and M. D. "Thermal droop in high-quality InGaN LEDs," *Appl. Phys. Lett.* 115, 2019.

- [8] K. A. Denault, M. Cantore, S. Nakamura, S. P. DenBaars, and R. Seshadri, "Efficient and stable laser-driven white lighting," *AIP Adv.* 3, 2013.
- [9] J. Y. Park, W. C. L., J. W. Chung, H. K. Yang, "Phosphor-in-glass (PiG) plates for blue laser diode driven white-light emission," *J. Alloys Compd.* 842, 2020.
- [10] C. Cozzan, G. Lheureux, N. O'Dea, E. E. Levin, J. Graser, T. D. Sparks, S. Nakamura, S. P. DenBaars, C. Weisbuch, and Ram Seshadri, "Stable, Heat-Conducting Phosphor Composites for High-Power Laser Lighting," *ACS Appl. Mater. Interfaces* 10, 6, 2018, pp. 5673–5681.
- [11] Y. Ma, X. Luo, "Enhancing opto-thermal performances of the reflective phosphor-converted laser diode by stacking a sapphire substrate for double-sided phosphor cooling," *Int. J. Heat Mass Transf.* 143, 2019.
- [12] Z. Dang, Y. Lin, H. Xu, C. Shi, S. Li, J. Bai, "Fabrication and Dielectric Characterization of Advanced BaTiO₃/Polyimide Nanocomposite Films with High Thermal Stability," *Adv. Funct. Mater.* 18, 2008, pp. 1509–1517.