PH1-2
Invited

Design of phosphors and color converters for laser-driven solid-state lighting

Rong-Jun Xie

rjxie@xmu.edu.cn
College of Materials, Xiamen University, No. 422 Sinming-nan Road, Xiamen Fujian 361005, China
Keywords: phosphors, laser lighting, luminance saturation.

ABSTRACT

Laser-driven solid-state lighting are attracting attentions for super-brightness, compact and directional lighting. Under high power density excitation, phosphors are usually experienced luminance saturation, which making them hard to produce lighting devices with high lumen and luminous efficiency. In this report, we will present interesting nitride phosphors for laser-driven solid-state lighting.

1 INTRODUCTION

InGaN-based solid state lighting (SSL) technologies, such as white light-emitting diodes (wLEDs), play key roles in energy saving, carbon emission reduction and environmental production, because they promise high electricity-to-light conversion efficiency, high brightness and long lifetime [1-2]. Phosphor-converted wLEDs are the mainstream of SSL as they have simple device structure, manipulated spectrum, super-high color rendition and tunable color temperature. With advances in SSL technologies, laser diodes (LDs) will be used to produce super-bright and directional white light, which can find special applications in high-beam headlamp, laser project, and laser cinema [3-5]. However, since the power density of LDs is much higher than that of LEDs, the phosphors used as color converters may have problems of luminance saturation and thermal quenching [6-8]. Therefore, phosphors for laser-driven SSL, *i.e.*, laser phosphors, needs to be reconsidered from their crystal structure, chemical composition, dopant as well as materials form (powder, phosphor-in-glass, film or ceramic).

The yttrium aluminum garnet $Y_3Al_5O_{12}:Ce^{3+}$ is the mostly investigated yellow phosphor for laser-driven SSL as it has a very shot decay time (~ 60 ns) and high quantum efficiency [6, 9-12]. However, the color rendering index of the laser-driven white light using $YAG:Ce^{3+}$ is lower than 70. To increase the color quality, it is necessary to develop red phosphors with small luminance saturation and high thermal stability. In this contribution, the development or search for red-emitting laser phosphors is concentrated on the Ce^{3+}-doped nitride materials. The high-pressure phase $CaSiN_3:Eu^{2+}$ (HP-$CaSiN_2$) was screened out as a red phosphor and its suitability in laser lighting was investigated. The Al-doped $La_3Si_6N_{11}:Ce^{3+}$ (LSN:Ce^{3+}, Al^{3+}) was developed as a red-enhanced phosphor to improve the color rendering index of laser-driven white light.

2 EXPERIMENT

The HP-$CaSiN_2:Ce^{3+}$ phosphor was synthesized by firing the powder mixture of Ca_3N_2, Si_3N_4 and CeN at 1700°C for 3 h under a nitrogen pressure of 0.7 MPa in a gas pressure sintering furnace (Shimadzu, Kyoto, Japan). The $La_{2.9}Al_xSi_{6-x}N_{11-x/3}:0.1Ce^{3+}$ phosphors were prepared by firing the starting powders of LaSi, CeSi, Si_3N_4 and AlN at 1750-1850°C for 7 h under 0.9 MPa nitrogen in the gas pressure sintering furnace. The phosphor-in-glass (PiG) films were prepared by following the procedures reported elsewhere [7].

The photoluminescence spectra were measured with a steady-state fluorescence spectrometer (FLS980, Edinburgh Instruments, UK), while the decay curves were recorded by using the kinetic mode of FLS980 with a 445 nm LD as the excitation source. The temperature-dependent luminescence was tested by a home-made system, which consists of a 450 nm LED light source, a temperature controlled stage (THMS600E, Linkam, UK), and a charge-coupled device (CCD) spectrometer (USB2000+, Ocean Optics, USA), in a temperature range from 25 to 300°C with a step of 25°C and a heating rate of 100°C/min. The optical performances of HP-$CaSiN_2:Ce^{3+}$-Al phosphor wheel and the LSN:xAl^{3+},Ce^{3+}-PiG films under laser excitation were evaluated in a reflection and transmissive configuration on a sphere-spectroradiometer system, respectively [13].The quantum yield was measured with an absolute PL quantum yield spectrometer (Quantaurus-QY, Hamamatsu Photonics, Tokyo, Japan).

3 RESULTS & DISCUSSION

3.1 HP-$CaSiN_2:Ce^{3+}$

To search for red-emitting Ce^{3+}-doped nitride phosphors, two selection criteria were proposed, *i.e.*, (i) suitable host band gap PBE E_g (2.4 ~3.5 eV); and (ii) short coordination bond length (R_{av}) and large distortion index (D) of the local coordination environment [14]. Among 45 nitridosilicate candidates, HP-$CaSiN_2$ was selected because it had a suitable E_g (4.44 eV), smaller R_{av} (2.570 Å) and the largest D (0.096) [14]. A phase pure sample was obtained by using gas-pressure sintering. HP-$CaSiN_2$ (*Pbca*) was reported as a high-pressure phase, the lattice parameters of which were refined to be a = 5.1339(1) Å, b = 10.3044(3) Å, c = 14.5316(6) Å and V = 768.75(0) Å^3. The experimental E_g (optical band gap) is about 4.36 eV.

As shown in Fig. 1a, HP-$CaSiN_2$:Ce^{3+} shows a broad emission band centered at 610 nm and a full-width at half-maximum (FWHM) of 160 nm. The emission maximum is much shorter than that of the standard $CaSiN_2$:Ce^{3+} (prepared under ambient pressure, λ_{em} = 530 nm). The excitation spectrum also displays a wide band covering the range of 250-550 nm, showing a maximum at 400 nm. It is quite different from the excitation spectra of the standard and cubic $CaSiN_2$:Ce^{3+} phosphors, the latter of both showing a maximum at 550 nm [15, 16]. This means HP-$CaSiN_2$:Ce^{3+} is more suitable for blue light irradiation. It has a quantum efficiency of 40.3% and absorption efficiency of 80.4% under the excitation of 450 nm. HP-$CaSiN_2$:Ce^{3+} has a large thermal quenching, the PL intensity of which remaining 61.4% at 100°C.

The optical properties of HP-$CaSiN_2$:Ce^{3+} were evaluated by using a phosphor wheel, which was prepared by coating the HP-$CaSiN_2$:Ce^{3+} phosphor powder on an aluminum plate. As seen in Fig. 1b, the phosphor wheel has a luminance saturation threshold of 5.47 W of the incident laser power, corresponding to 10.89 W/mm^2. It indicates that HP-$CaSiN_2$:Ce^{3+} has a smaller luminance saturation than $CaAlSiN_3$:Eu^{2+} (which is 0.5 W/mm^2 for a PiG sample) [6]. The maximal luminous flux of the phosphor wheel is about 1087 lm.

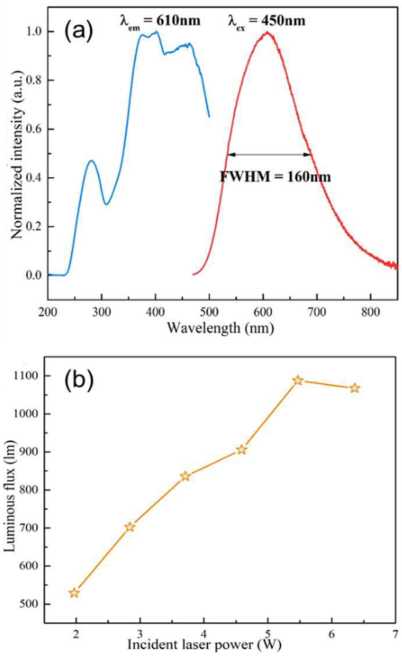

Fig. 1 (a) Photoluminescence spectra of HP-$CaSiN_2$:Ce^{3+} and (b) luminous flux as a function of incident laser power.

3.2 $La_{2.9}Al_xSi_{6-x}N_{11-x/3}$:$0.1Ce^{3+}$

$La_3Si_6N_{11}$:Ce^{3+} is a broadband yellow-emitting phosphor, and also has a high thermal stability. A previous study demonstrates that it is a promising color converter for laser lighting, which has a luminance saturation threshold of 12.91 W/mm^2 for a PiG film [13]. However, the color rendering index of the fabricated laser-driven white light is only 70, and color temperature is about 7600 K. To improve the color rendition and reduce the color temperature, the emission of $La_3Si_6N_{11}$:Ce^{3+} needs to be redshifted.

By co-doping Al in $La_3Si_6N_{11}$:Ce^{3+}, it is seen that an additional emission band centered at 600-665 nm appears (Fig. 2a). This red emission is not assigned to Ce^{3+} occupying the La site, but to Ce^{3+} entering into an interstitial site that is the [Si8N8] void in the c~1/2 layer [17]. Such an interstitial Ce^{3+} site is produced as a charge compensator for the aliovalent substitution of Si^{4+} by Al^{3+} ions. On the other hand, the $La_3Si_6N_{11}$:Ce^{3+}, Al^{3+} phosphor shows a significant reduction in PL intensity as the Al concentration is increased.

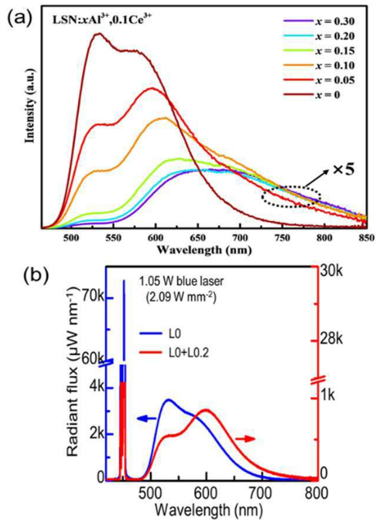

Fig. 2 (a) Emission spectra of $La_{2.9}Al_xSi_{6-x}N_{11-x/3}$:$0.1Ce^{3+}$ with different Al concentrations and (b) Electroluminescence spectra of laser-driven white light (L0 – $La_3Si_6N_{11}$, L0.2 - $La_{2.9}Al_{0.2}Si_{5.8}N_{10.93}$:$0.1Ce^{3+}$).

To enhanced the color rendering index (CRI) of the lighting device using the $La_3Si_6N_{11}$:$0.1Ce^{3+}$ PiG film (L0), an additional $La_3Si_6N_{11}$:$0.1Ce^{3+}$, $0.2Al^{3+}$ PiG film (L0.2) was covered [17]. As seen in Fig. 2b, the emission spectrum of the double film layer is obviously enhanced in the red spectral part, leading to a higher CRI of 78 (*vs* 69 for the single PiG film). A warm white light with a color temperature of 3321 K can be obtained. Under the blue laser irradiation of 2.09 W/mm^2, the luminous flux and luminous efficiency of the single-layer are respectively 188.6 lm and 179.6 lm/W, but they are decreased to 43.6 lm and 41.5 lm/W for the double-layer PiG film. The reduction in the optical properties is attributed to the low quantum efficiency (only 9%) of $La_{2.9}Al_xSi_{6-x}N_{11-x/3}$:$0.1Ce^{3+}$. Much efforts need to be made to understand the luminescence quenching mechanism and to improve the luminescence efficiency of $La_3Si_6N_{11}$:Ce^{3+}, Al^{3+}.

4 CONCLUSIONS

Red-emitting laser phosphors with small luminance saturation are urgently required for laser lighting and displays. In this paper, two Ce^{3+}-doped red-emitting nitride phosphors, HP-$CaSiN_2$ and $La_3Al_xSi_{6-x}N_{11-x/3}$, were developed and investigated. When applied as a phosphor wheel, HP-$CaSiN_2$:Ce^{3+} (λ_{em} = 610 nm) has a high luminance saturation of 10. 89 W/mm^2 and a luminous flux of 1087 lm. The use of $La_3Al_xSi_{6-x}N_{11-x/3}$:$Ce^{3+}$ (λ_{em} = 600-665 nm) enables to increase the color rendering index up to 78. However, both phosphors have a lower quantum efficiency than the Eu^{2+}-doped counterparts (*e.g.*, $CaAlSiN_3$:Eu^{2+} and $Sr_2Si_5N_8$:Eu^{2+}). It is necessary to clarify the luminescence quenching mechanism in both materials and provide guidelines for improving their luminescence efficiency. In addition, it would be a correct way to search for red laser phosphors in Ce^{3+}-doped compounds (typically in nitridosilicates).

ACKNOWLEDGEMENT

The financial support from the Natural Science Foundation of China (nos. 51832005 and 51572232) is greatly appreciated.

REFERENCES

[1] S. Pimputkar, J.S. Speck, S.P. DenBaars and S. Nakamura, Prospects for LED Lighting, Nat. Photonics, Vol. 3, pp. 180−182 (2009).

[2] M.H. Crawford, LEDs for solid state lighting: Performance challenges and recent advances, IEEE J. Sel. Top. Quantum Electron., Vol. 15, pp. 1208-1040 (2009).

[3] S. Li, L. Wang, N. Hirosaki and R.-J. N.; Xie, Color conversion materials for high-brightness laser-driven solid-state lighting, Laser Photonics Rev., Vol. 12, pp. 1800173 (2018).

[4] J. Wierer, J. Y. Tsao, D.S. Sizov, Comparison between blue lasers and light-emitting diodes for future solid-state lighting, Laser Photonics Rev., Vol. 7, pp. 963−993 (2013).

[5] S. Li, Q. Zhu, L. Wang, D. Tang, Y. Cho, X. Liu, N. Hirosaki, T. Nishimura, T. Sekiguchi, Z. Huang and R.-J. Xie, $CaAlSiN_3$:Eu^{2+} translucent ceramic: a promising robust and efficient red color converter for solid state laser displays and lighting, J. Mater. Chem. C, Vol. 4, pp. 8197−8205 (2016).

[6] Q.Q. Zhu, X. Xu, L. Wang, Z.F. Tian, N. Hirosaki and R.-J. Xie, A robust red-emitting phosphor-in-glass (PiG) for use in white lighting sources pumped by blue laser diodes, J. Alloys Compd., Vol. 702, pp. 193-198 (2017).

[7] P. Zheng, S. Li, L. Wang, T.-L. Zhou, S. You, T. Takeda, N. Hirosaki, R.-J. Xie, Unique Color Converter Architecture Enabling Phosphor-in-Glass (PiG) Films Suitable for High-Power and High-Luminance Laser Driven White Lighting, ACS Appl. Mater. Interfaces, Vol. 10, pp. 14930-14940 (2018).

[8] J. Park, J. Kim and H. Kwon, Phosphor-aluminum composite for energy recycling with high-power white lighting, Adv. Opt. Mater., pp.1700347 (2017).

[9] S. Li, Q. Zhu, D. Tang, X. Liu, G. Ouyang, L. Cao, N. Hirosaki, T. Nishimura, Z. Huang and R.-J. Xie, Al_2O_3-YAG:Ce composite phosphor ceramic: a thermally robust and efficient color converter for solid state laser lighting, J. Mater. Chem. C, Vol. 4, pp. 8648−8654 (2016).

[10] M. Cantore, N. Pfaff, R.M. Farrell, J. Speck, S. Nakamura and S.P. DenBaars, High luminous flux from single crystal phosphor converted laser-based white lighting system, Opt. Express, Vol. 24, pp. A215−A221 (2016).

[11] S. Arjoca, E.G. Víllora, D. Inomata, K. Aoki, Y. Sugahara and K. Shimamura, Ce:$(Y_{1-x}Lu_x)_3Al_5O_{12}$ single-crystal phosphor plates for high-brightness white LEDs/LDs with high-color rendering (Ra > 90) and temperature stability, Mater. Res. Express, Vol. 1, pp. 025041 (2014).

[12] P. Zheng, S. Li, R. Wei, L. Wang, T. Zhou, Y.R. Xu, T. Takeda, N. Hirosaki and R.-J. Xie, Unique design strategy for laser-driven color converters enabling superhigh-luminance and high-directionality white light, Laser Photonics Rev., v. Vol. 13, pp. 1900147 (2019).

[13] S. You, S. Li, P. Zheng, T. Zhou, L. Wang, L. Liu, N. Horisaki, F. Xu and R.-J. Xie, A thermally robust $La_3Si_6N_{11}$:Ce-in-glass film for high-brightness blue-laser-driven solid state lighting, Laser Photonics Rev., Vol. 13, pp. 1800216 (2019).

[14] Y. Xia, S. Li, Y. Zhang, T. Takeda, N. Hirosaki and R.-J. Xie, Discovery of a Ce^{3+}-activated red nitride phosphor for high-brightness solid-state lighting, J. Mater. Chem. C, accepted.

[15] X.M. Wang, X. Zhang, S. Ye and X.-P. Jing, A promising yellow phosphor of Ce^{3+}/Li^+ doped $CaSiN_{2-2\delta/3}O_\delta$ for pc-LEDs, Dalton Trans, Vol. 42, pp. 5167−5173 (2013).

[16] R. Le Toquin and A.K. Cheetham, A. K. Red-emitting cerium-based phosphor materials for solid-state lighting applications, Chem. Phys. Lett., Vol. 423, pp. 352−356 (2006).

[17] Y. Shi, S. Li, Y. Jia and R.-J. Xie, Interstitial site engineering for creating unusual red emission in $La_3Si_6N_{11}$:Ce^{3+}, Chem. Mater., Vol. 32, pp. 3631−3640 (2020).