CaAlSiN$_3$:Eu/glass composite film in reflective configuration
A thermally robust and efficient red-emitting color converter with high saturation threshold for high-power high color rendering laser lighting

Xu, Jian; Yang, Yang; Jiang, Zhi; Hu, Baofu; Wang, Xinliang; Ji, Haipeng; Wang, Jian; Guo, Ziquan; Du, Baoli; Dam-Hansen, Carsten

Total number of authors: 11

Published in:
Ceramics International

Link to article, DOI:
10.1016/j.ceramint.2021.02.094

Publication date:
2021

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
CaAlSiN$_3$:Eu/glass composite film in reflective configuration: a thermally robust and efficient red-emitting color converter with high saturation threshold for high-power high color rendering laser lighting

Jian Xu$^a$, Yang Yang$^a$, Zhi Jiang$^a$, Baofu Hu$^a$, Xinliang Wang$^{a,*}$, Haipeng Ji$^b$, Jian Wang$^a$, Ziquan Guo$^{c,*}$, Baoli Du$^a$, Carsten Dam-Hansen$^d$, Ole B. Jensen$^d$

$^a$Lab of New Energy Materials and Devices, School of Physics and Electronic Information, Henan Polytechnic University, Jiaozuo 454000, China

$^b$School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

$^c$Fujian Engineering Research Center for Solid-State Lighting, Department of Electronic Science, Xiamen University, Xiamen 361005, China

$^d$Diode Lasers and LED Systems Group, Department of Photonics Engineering, Technical University of Denmark, Roskilde 4000, Denmark

ABSTRACT

To achieve high color rendering and proper color temperature, a red color converter is essential for phosphor-converted white lighting devices. CaAlSiN$_3$:Eu$^{2+}$ (CASN) is a highly suitable red phosphor for white light-emitting diodes. However, it can be hardly used in high-power laser lighting due to poor thermal/chemical performance of the phosphor/silicone resin mixture. A series of all-inorganic CASN-based phosphors (e.g., composite ceramic and phosphor-in-glass) were developed to avoid the use of resin. However, new challenges emerged: none of them showed sufficient luminous efficacy (i.e., >50 lm/W) and adequate saturation-threshold (i.e., >30 W or 10 W/mm$^2$). Here,
we report a facile fabrication of CASN/glass composite films using a simple and
efficient blade-coating method. Upon 450 nm excitation, the resultant composite film
presents a high internal quantum efficiency of ~83%, comparable to that of pristine
CASN powder (~90%). When irradiated with a blue laser, the composite film shows a
record high luminous efficacy of 82 lm/W. Furthermore, its saturation threshold was
investigated in high power and high power density mode, respectively. When measured
in high power mode, it shows a high saturation threshold over 29.7 W (1.75 W/mm²),
thus achieving a high luminous flux of 1576 lm; when measured in high power density
mode, it shows a saturation threshold of ~10.2 W/mm² (1.13 W). With abovementioned
excellent properties, the CASN/glass composite film has great potential for use in high-
power and high color rendering laser lighting.

**Keywords:** Laser lighting; CaAlSiN₃:Eu; Reflective configuration; Saturation threshold;
Composite film

1. **Introduction**

   Compared with light-emitting diodes (LEDs), laser diodes (LDs) can maintain
higher wall-plug efficiency at a high current density (i.e., 30 kA/cm²) and have a much
smaller emitting area [1-4]. These favorable properties enable LD-based white-light
sources to achieve very high luminance and illuminance; therefore, they have a
promising future in applications like searchlights, auto headlamps, projectors, and street
lamps. Similar to white LEDs, commercial white LDs are usually made from a blue LD
chip and phosphor(s) [4-8]. Thus, phosphors are one of the key components and
significantly affect the colorimetric and photometric properties of white LDs.

Conventional white LED encapsulation scheme involves the use of organic bonding materials (e.g., epoxy resin and silicone); they are mixed with phosphor powder and coated on the LED wafer. This scheme is, however, not applicable in laser lighting because organic packaging materials cannot withstand laser irradiation [6, 7, 9-11]. To accommodate the distinguishing features of LDs, a series of all-inorganic encapsulation schemes were explored, including phosphor-in-glass (PiG), phosphor ceramic, single crystal, and phosphor film [9, 12-23]. Many of these phosphors are capable of withstanding high power laser irradiation. So far, most of these all-inorganic phosphors are based on Ce$^{3+}$-doped $Y_3Al_5O_{12}$ (YAG:Ce). As a canonical yellow-emitting phosphor, YAG:Ce has many favorable properties such as fast luminescence decay time (~70 ns), efficient absorption of blue light (~455 nm), high external quantum efficiency (EQE >70%), and a broad emission band in the visible region [19, 24-27]. However, it is very difficult to achieve adequate color rendering index (CRI) and proper correlated color temperature (CCT) for lighting devices based on only YAG:Ce phosphor due to the deficiency of red emission component.

CaAlSiN$_3$:Eu$^{2+}$ (CASN) is a highly suitable red-emitting phosphor that can effectively compensate the deficiency of red light of YAG:Ce [11, 12, 28-33]. Several types of all-inorganic CASN-based phosphors have been developed to improve the colorimetric properties of white LDs. Zhu et al. developed a CASN-based PiG; however, it got saturated at only 0.5 W/mm$^2$ [29]. Zhang et al. recently reported a CASN-based PiG where the saturation threshold reached 1.90 W/mm$^2$. However, the maximum
luminous flux was only 49 lm [12]. Remarkable progress was made by Li et al.; they fabricated a CASN-based phosphor ceramic with a high luminous efficacy of 42 lm/W. Furthermore, a saturation threshold of 2 W/mm\(^2\) and a maximum luminous flux of ~205 lm were achieved [30, 33]. Further progress was made by Xu et al. who recently reported a CASN/glass composite film operating in transmission configuration. The composite film achieved an improved saturation threshold of 3.2 W/ mm\(^2\) (12.7 W), and the maximum luminous flux reached 189 lm [28]. Considering that the saturation threshold of YAG:Ce-based phosphors could be increased to higher than 10 W/mm\(^2\) (or 30 W) [8, 11, 13, 15, 19, 24, 25], the saturation threshold of CASN-based phosphor is expected to match with that of YAG:Ce. Unfortunately, despite the continuous progress made in this field, current CASN-based phosphors still did not achieve the desired saturation threshold.

Several reasons can be attributed to the insufficient saturation threshold of CASN-based phosphors. First, the luminescence decay of Eu\(^{2+}\) is relatively slow (~1 μs) [4, 6, 32]. Second, the Stokes loss is relatively large when converting blue light to red. Third, the co-firing process frequently involves the use of glass, corroding the CASN and introducing a luminescence quencher (i.e., Eu\(^{3+}\)) [4, 6, 7, 34]. Lastly, thick samples usually suffer from poor thermal conduction; it is very difficult to machine bulk PiG and ceramic to thinner than 150 μm (due to the brittleness). Considering that the Stokes loss and luminescence decay for a certain phosphor are intrinsic, the improvement measures should focus on the annealing strategy and thermal conduction management.

A survey of CASN-based phosphors conducted with these features in mind led us
to focus on the CASN/glass composite film in reflective configuration. Compared to CASN-based ceramic and PiG, a composite film can be much thinner (<50 μm) and therefore effectively facilitate heat dissipation. Compared to a composite film in transmission configuration, the distance from the laser irradiation spot to heat sink for the reflective configuration is obviously shorter, which can also benefit for dissipating heat. Furthermore, using a SnO-P₂O₅-ZnO glass, the annealing temperature can be reduced to 470 °C; thus, a CASN/glass composite film can maintain a high internal quantum efficiency (IQE) of ~83% (92% of that of pristine powder). With above favorable features, the resulting composite film shows a record high luminous efficacy of 82 lm/W. The laser-driven colorimetric and photometric properties were investigated in high power mode and high power density mode, respectively. A typical sample shows a saturation threshold of more than 29.7 W (1.75 W/mm²) for high power mode and 10.2 W/mm² (1.13 W) for high power density mode. These findings give us reasons to believe that this study will not only provide a robust and efficient CASN-based red phosphor for high-power laser lighting, but also provide valuable guidelines for improving the luminous efficacy and saturation threshold of other nitride phosphors.

2. Experimental

2.1 Fabrication of CASN/glass composite film

A viscous ink was made by mixing a glass powder (SnO-P₂O₅-ZnO, T_g ≈ 390 °C), CASN powder (Yantai Shield, SDR-630), and organic vehicle. The weight of CASN phosphor was fixed at 1 g. The “glass to phosphor” (hereafter denoted as “GtP”) weight
ratios were 60%, 80%, 100%, 120%, and 140%, respectively. The organic vehicle was prepared by mixing 0.5 g of ethylcellulose (Aladdin, 98%), 5 mL of ethyl acetate (Aladdin, 99.5%) and 2 mL of terpineol (Aladdin, 95%). The viscous ink was printed on a corundum (α-Al₂O₃, 99%) substrate (14 × 19 × 2 mm³) using a blade-coating technique. The printed layer was annealed at 120 °C for 3 h to remove all the organics and subsequently heated to 470 °C with a heating rate of 5 °C/min (the soaking time is zero).

2.2 Characterization

The microstructure was observed using a scanning electron microscope (SEM, Hitachi, TM-3000 PLUS). The photoluminescence was investigated using a spectroradiometer (HORIBA, Fluorolog-3). The luminescence and QE were measured using a spectroradiometer (Edinburgh Instruments, FLS-1000) equipped with a 30 cm integrating sphere. The QE measurement system has an empirical error of ±3%. The luminescence saturation behaviors were measured using a home-made sphere-spectroradiometer system. The setup for high power mode consists of a 38 W (4.75 W × 8, Nichia, NUBM-08) blue LD module, a fiber-coupled integrating sphere with a diameter of 15 cm, and an array spectrometer (Instrument Systems, CAS-140-CT-151). The spot size of the laser module is ~0.17 cm². The setup for high power density mode consists of a single 4.5 W blue LD (Nichia, NDB7A75), a fiber-coupled integrating sphere (Labsphere, RT-060-SF), and the same array spectrometer (Instrument Systems, CAS-140-CT-151). A lens system consisting of a cylindrical lens (f = 10 mm), a
cylindrical lens \((f = 150 \text{ mm})\) and an achromatic lens \((f = 200 \text{ mm})\) was used to shape and focus the light from the LD. The laser beam profile was captured using a scanning slit beam profiler (Photon, Beamscan 2180). The output optical power of the blue laser module was measured using a laser power meter (Ophir, NOVA-II).

3. Results

Fig. 1(a) Fabrication schematic of composite film using the blade-coating method; the digital images are a typical sample and its lighting effects (when pumped with a UV LED and a blue laser); (b-f) SEM images of surfaces of composite films with different glass mass ratios; (g-k) SEM images of cross sections of composite films with different glass mass ratios.

Fig. 1a shows the fabrication schematic of a composite film (see Section 2.1 for
details). The morphologies of composite films were investigated using SEM. The SEM images of pristine CASN powder and glass powder are shown in Fig. S1. The surface (top-view) SEM images of composite films in Fig. 1 b-f show that the CASN particles are well-wetted and embedded in the pore-existing glass matrix. It was found that the CASN particles are uniformly dispersed in the glass matrix. With increasing GtP ratio, the porosity gradually decreases. Fig. 1 g-h show the cross-sectional SEM images of composite films with different glass mass ratios. It was found that the films are tightly bonded to the corundum substrate, indicating a good adhesion. Notably, the glass mass ratio can slightly affect the thickness. Fig. S2 shows a clear boundary between the glass matrix and CASN particle, indicating that no obvious erosion occurs during the heat treatment. This means the composite films could inherit the high IQE from CASN powder.

![Fig. 2(a) PL mission spectra and (b) thermal quenching behaviors of GtP-60% and pristine powder; (c) IQE vs. Glass to Phosphor Mass Ratio](image)
IQE of composite films with different GtP; (d) EL spectra of GtP-60% pumped using 2.72 W blue laser power.

The optical properties of films are shown in Fig. 2. The excitation spectrum of GtP-60% (monitored at 620 nm) is shown in Fig. S3 covering a very broad range of 250-620 nm, indicating its suitability for combining with blue LDs. The PL emission spectra of pristine CASN powder and GtP-60% are shown in Fig. 2a. Under excitation of 450 nm, GtP-60% shows a broad and asymmetric emission band with peak at 620 nm, which can be attributed to the 5d-4f electronic transition of Eu$^{2+}$. In general, the PL profile of GtP-60% is very similar to that of CASN powder. However, a clear blue-shift (626 nm → 620 nm) is observed, which can be attributed to the mitigated self-absorption effect. The luminescence thermal quenching behaviors of pristine powder and GtP-60% are shown in Fig. 2b. With the increase of temperature, the lattice vibration provides the activation energy for thermally activated cross over (5d to 4f) and thermal ionization (5d to conduction band) process. These factors often cause decline in IQE and decrease of absorbance [35-37]. Thus, both samples present a monotonic decline in PL intensity. GtP-60% inherits the thermal quenching behavior from CASN powder; the intensity drop at 200 °C is ~19%. The IQEs of samples (under 450 nm excitation) with different GtP ratios are shown in Fig. 2c. It was found that the GtP ratio significantly affects the IQE. GtP-60% and GtP-80% have a high IQE of 80% and 83%, respectively. Subsequently, the IQE continuously decreased with increasing GtP ratio. GtP-140% with the highest GtP ratio showed the lowest IQE of ~69%; even so it is still an acceptable value. The lower IQE of GtP-140% is probably caused by the
elevated corrosion rate resulting from the higher glass ratio. Laser-driven photometric and colorimetric properties of a typical sample (GtP-60%) were evaluated using a sphere-spectroradiometer system. Under excitation of 2.72 W (0.13 W/mm²) blue laser power (high power mode), GtP-60% provides an intense red emission centered at 622 nm (as shown in Fig. 2d), it yields a high luminous flux of 181 lm (at a CCT of 1303 K); therefore, a high luminous efficacy of 67 lm/W was successfully achieved. These favorable properties can be attributed to the high IQE (~80%) of the sample.

![Schematic of sphere-spectroradiometer measurement system for high power mode](image)

**Fig. 3** (a) Schematic of sphere-spectroradiometer measurement system for high power mode; (b) EL spectra of GtP-60% pumped with varying laser powers; (c and d) luminous flux and luminous efficacy of samples with various GtP mass ratio as a function of pumping laser power.

Luminescence saturation is a significant obstacle for the development of CASN-based phosphors for laser lighting. The luminescence saturation behaviors of composite
films were systematically evaluated in a very wide laser power range (up to 29.7 W). Schematic of sphere-spectroradiometer measurement system for high power mode is shown in Fig. 3a. Fig. 3b shows the EL spectra of a typical sample (GtP-60%) pumped with an elevated laser power. The EL emission intensity increases monotonously from 1.07 W to 29.7 W. However, the increase becomes very small from 24.65 W to 29.70 W, indicating that the saturation threshold is very close. The luminous flux and luminous efficacy of different samples as a function of incident laser power are shown in Fig. 3c-d. In a low laser power range (<5 W), the GtP ratio slightly affected the photometric properties; all the samples exhibited a high luminous efficacy of 57-67 lm/W. Surprisingly, GtP-140% showed the best robustness; it maintained a high luminous efficacy of 51 lm/W even when the incident laser power reached 29.7 W. This indicates that it has a remarkably high saturation threshold, and thus an ultrahigh luminous flux of 1576 lm could be successfully achieved. Notably, GtP-60% and GtP-80% showed a higher IQE (≥80%) than GtP-140% (~69%), but their saturation thresholds are lower. Theoretically, higher IQE means less conversion loss leading to less heat generation. In this case, the heat dissipation capability of sample probably plays the major role affecting the saturation threshold. The high porosity of GtP-60% and GtP-80% leads to lower thermal dissipation. In contrast, GtP-140% clearly shows a lower porosity than the other counterparts. This enables it to effectively remove the generated heat and thus achieve the highest saturation threshold. Based on these results, GtP-140% is more suitable for laser lighting applications at a high power level (i.e., >20 W).
The luminescence saturation behavior of the GtP-140% was also evaluated in a very wide laser power density range (up to 10.2 W/mm²). Schematic of sphere-spectroradiometer measurement system for high power mode is shown in Fig. 4a. The variation of the laser power and spot area as a function of driving current were presented in Fig. 4b. Notably, the laser spot area increases with the increasing driving current. This is attributed to the changing transverse mode at different current, as well as the related astigmatism of the blue LD. With the exact spot sizes of the LD at various current, the laser power densities on the sample at various laser power were obtained. Fig. 4c shows the EL spectra of a typical sample (GtP-140%) pumped with an elevated laser power and laser power density. The EL emission intensity increases monotonously from 1.87 W/mm² to 9.04 W/mm². From 9.04 W/mm² to 10.2 W/mm², the intensity remained unchanged, indicating the occurrence of luminescence saturation. The luminous flux and luminous efficacy of the GtP-140% as a function of incident laser power are shown in Fig. 4d. The luminous flux of sample initially increases linearly with the increasing incident laser power (laser power density). After 6.56 W/mm² (0.58 W), the increase slows down sharply. The luminous efficacy decreases steadily with the increasing incident laser power (laser power density). At 1.87 W/mm² (0.04 W), the luminous efficacy of the GtP-140% reaches 82 lm/W which is obviously higher than the value (~63 lm/W) measured under high power mode (1.07 W, 0.06 W/mm²). This is probably because of the following two reasons: (1) the single LD (for high power density mode) has better monochromaticity and shorter wavelength (~443 nm, see Fig. 4c), which is beneficial to improving the absorption of blue light for CASN (see Fig. 4d).
S3); (2) the lower laser power (0.04 W) for high power density mode leads to less thermal load.

Fig. 4 (a) Schematic of sphere-spectroradiometer measurement system for high power density mode; (b) the variation of the laser power and laser spot area of the single LD as a function of the driving current; (c) EL spectra of GtP-140% pumped with varying laser power; (d) luminous flux and luminous efficacy of GtP-140% as a function of pumping laser power.

Conclusions

A thermally robust and efficient red-emitting composite film was fabricated by cofiring the CASN and glass powders on a corundum substrate. Owing to the low corrosion of SnO-P2O5-ZnO glass and the moderate annealing process (470 °C, soaking time is zero), the resulting composite film maintains a high IQE of 83% (92% of that
of pristine powder). When pumped with blue laser (1.87 W/mm$^2$, 0.04 W), the composite film (GtP-140%) attained a record high luminous efficacy of 82 lm/W. Furthermore, its saturation threshold was investigated in high power and high power density mode, respectively. For high power mode, the GtP-140% shows a saturation threshold over 29.7 W (1.75 W/mm$^2$), thus yielding a high luminous flux of 1576 lm. For high power density mode, it shows a saturation threshold of ~10.2 W/mm$^2$ (1.13 W). These results suggest that when the laser power reaches to very high level, even very low power density can saturate a phosphor. With these favorable properties, we believe this study will not only provide a suitable red-emitting phosphor for laser lighting, but also provide valuable guidelines for improving the luminous efficacy and saturation threshold of other nitride phosphors.

Acknowledgements

This work was supported by National Natural Science Foundation of China (51802083 and 51772076), Danish Energy Technology Development and Demonstration program (EUDP 64017-0588), Natural Science Foundation of Fujian/Henan Province (2019J05022, 20A430018, 182300410193) and Training plan of young backbone teachers in Colleges and Universities of Henan Province (2019GGJS060)

References

[1] J.J. Wierer, J.Y. Tsao, D.S. Sizov, Comparison between blue lasers and light-


[20] Q.-Q. Zhu, Y. Meng, H. Zhang, S. Li, L. Wang, R.-J. Xie, YAGG:Ce Phosphor-


