Journal of Materials Chemistry C

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Materials for optical, magnetic and electronic devices rsc.li/materials-c

Lu₂SrAl₄SiO₁₂:Ce³⁺

ISSN 2050-7526



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Journal of Materials Chemistry C



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Cite this: J. Mater. Chem. C, 2018, 6, 12159

Received 16th August 2018, Accepted 6th September 2018

DOI: 10.1039/c8tc04101f

rsc.li/materials-c

A highly efficient and thermally stable green phosphor (Lu₂SrAl₄SiO₁₂:Ce³⁺) for full-spectrum white LEDs⁺

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Traditional phosphor-converted white LEDs suffer from the so-called blue-green cavity in their emission spectra. Hence, satisfactory phosphors with sufficient emission around 490 nm are still lacking. Herein, we report a newly designed garnet-type phosphor, Lu₂SrAl₄SiO₁₂:Ce³⁺ (LSAS:Ce³⁺), through chemical unit cosubstitution, whose emission can well fill the blue-green cavity. Importantly, LSAS:Ce³⁺ exhibits nearly zero thermal quenching even at 473 K (200 °C) as well as a high internal quantum efficiency of 93.3%. Finally, the as-fabricated warm white LED device shows a high color rendering index of 97.6 with *R*9 = 94, indicating its great potential for white LEDs.

1 Introduction

The invention of highly efficient InGaN-based blue LEDs has initiated a significant revolution in the lighting industry, leading to the era of solid state lighting with the advantages of energy saving, environmental friendliness, wide color tunability and large design flexibility.^{1–7} Currently, the commercialized white LEDs (WLEDs) are by combining a blue LED chip with the yellow phosphor (Y,Gd)₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺), because of their high luminous efficiency and easiness to fabricate. However, the LED devices are restricted to several specific application fields due to their high correlated color temperatures (CCT > 5000 K) and low color rendering indexes ($R_a < 80$). Generally, in order to lower the CCT value and raise the R_a value, appropriate red phosphors should be added. Besides, blue-green (or green) phosphors peaking at 490–530 nm are indispensible to achieve

extra-high color rendering ($R_a > 95$) by filling the blue-green cavity around 490 nm in their emission spectra. Nonetheless, blue-green phosphors with highly efficient and thermally stable emission are still lacking and thus are desperately needed to widen the application fields of pc-WLEDs.^{8,9}

Recently, several strategies have been used to seek new phosphors, including chemical unit substitution or cosubstitution (or ionic engineering),^{10,11} combinatorial chemistry screenings,¹² and a single-particle-diagnosis approach.¹³ Among them, ionic engineering has been intensively investigated because this design strategy is usually efficient and targeted, and more importantly, the established structure-property relationships between the local crystal structure and photoluminescence (PL) properties can provide theoretical guidelines for discovering new phosphors and thus accelerate the development of luminescent materials.¹⁴ Garnet-type phosphors, known for the yellow phosphor YAG: Ce^{3+} , possess cubic symmetry with the general formula $\{A\}_3[B]_2(C)_3O_{12}$, where {A}, [B] and (C) correspond to the 12-coordinated, 6-coordinated and 4-coordinated sites, respectively. This group of phosphors is excellent in tuning the PL properties owing to the large flexibility of the composition of the garnet host by altering the substitution of host cations in the {A}, [B] and (C) sites. Accordingly, many new garnet compositions with modified PL properties have been designed by chemical unit substitution or cosubstitution, such as Si⁴⁺-N³⁻,¹⁵ Mg²⁺-Si⁴⁺¹⁶ and Ca²⁺-Si⁴⁺¹⁷ codoped Ce³⁺ activated YAG or Lu₃Al₅O₁₂ (LuAG), and other garnet-type phosphors with marked differences in chemical compositions like Ca₂(Lu,Y,Gd)Zr₂Al₃O₁₂ (blue-green),¹⁸ Ca₃Sc₂Si₃O₁₂ (green)¹⁹ and Lu₂CaMg₂(Si,Ge)₃O₁₂ (orange),²⁰ thus realizing tunable emission color covering nearly the whole visible spectrum only in the garnet-type oxides. However, much attention has been paid to redshifting the emission band of the yellow phosphor YAG:Ce³⁺ to enrich the red component of white light, and only a few studies have focused on enhancing the bluegreen one.²¹ Besides, most of them suffer from strong thermal quenching as well as low quantum efficiency (QE). It should be noted that all commercialized blue-green (or green) phosphors have their shortcomings, such as strong thermal quenching for

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 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ <code>c8tc04101f</code>

 $(Ba,Sr)_2SiO_4:Eu^{2+}$,²² high price for LuAG:Ce³⁺, and strong thermal quenching as well as high price for $BaSi_2O_2N_2:Eu^{2+}$.²³

Herein, we report a newly designed efficient garnet-type phosphor, Lu₂SrAl₄SiO₁₂:Ce³⁺ (LSAS:Ce³⁺), with the blue-shifted emission peaking at 514 nm through chemical unit cosubstitution of LuO₈/AlO₄ by SrO₈/SiO₄ in the LuAG host. Compared with the green phosphor LuAG:Ce³⁺, it has a reduced dosage of Lu₂O₃ with high price and can be prepared at only 1400 °C for three hours by traditional solid state reactions. Moreover, LSAS:Ce³⁺ shows extraordinary thermal stability. Finally, a warm WLED with a color rendering index of 97.6 was fabricated using a mixture of the LSAS:Ce³⁺ green phosphor and a red phosphor, commercial CaAlSiN₃:Eu²⁺, based on a blue LED chip.

2. Results and discussion

(a)

ntensity (a.u.)

5K

The crystal structure was confirmed by XRD Rietveld structure refinement where the structure of LuAG was taken as a starting

30

LSAS: 6% Ce³ Raw data Calculated line Difference

Bragg positions

70

1111 11 10 1000 0000 0 00 0000

50

20 (degree)

structure where Sr ions occupy the Y site of $[YO_8]$ and Si ions occupy the Al site of $[AlO_4]$ (b)

model for the refinement shown in Fig. 1(a). The result of the Rietveld refinement shows that the sample is isostructural with LuAG and can be well indexed to the space group $Ia\bar{3}d$ of the cubic system without any impurity phase, indicating the formation of a single-phase garnet-type crystal with designed composition. It is reasonable to assume that Sr and Si atoms will enter the Y site of $[YO_8]$ and the Al site of $[AIO_4]$, respectively, since other sites are too small for Sr^{2+} and too large for Si^{4+} . The low final R factors and refined lattice parameters (Table S1, ESI⁺) demonstrate that LSAS retains the typical cubic garnet structure with the cosubstitution of LuO₈ and AlO₄ by SrO₈ and SiO₄, respectively, as shown in Fig. 1(b). The as-prepared sample was also analyzed by energy dispersive X-ray spectroscopy (EDS). The EDS spectrum confirms the presence of strontium (Sr), lutetium (Lu), aluminium (Al), silicon (Si), and oxygen (O) elements and cerium (Ce) of LSAS:6%Ce³⁺, and the detected atomic ratios are approximate to what we expected (Fig. S1 and Table S2, ESI[†]).

After optimizing the Ce^{3+} doping concentration of LSAS, we found that the highest PL intensity of LSAS: Ce^{3+} appears at a

LuSr

AlSi

(a) (b)

0.9

Fig. 1 Rietveld refinement for LSAS:6%Ce³⁺ (a) and schematic diagram of the crystal structure of LSAS shown along the c axis, exhibiting a typical garnet



Fig. 2 PLE and PL spectra of LSAS:6%Ce³⁺ (a) and emission colors in the CIE 1931 chromaticity diagram for LSAS:6%Ce³⁺ (b). The inset shows the fluorescence microscopy PL image for LSAS:6%Ce³⁺ powder under 450 nm excitation.



Fig. 3 Temperature dependent PL spectra of LSAS:6%Ce³⁺ under 450 nm excitation (a), the relative integrated PL intensities for LSAS:6%Ce³⁺ and the red solid line is the fitted curve by the Arrhenius equation (b), and a contour plot of the PL spectra (*y*-axis) and temperature (*x*-axis) showing the color stability with increasing temperature (c).

 Ce^{3+} concentration of 6% (Fig. S2, ESI⁺). Fig. 2(a) shows the PL excitation (PLE) and PL spectra of LSAS:6%Ce³⁺. LSAS:6%Ce³⁺ exhibits a broad green emission with a peak at 514 nm, a shoulder at 547 nm and a full width at half maximum of approximately 105 nm. Compared with the Ce³⁺ emission peaking at 540 nm in LuAG,²⁴ LSAS:6%Ce³⁺ can be used for filling the aforementioned blue-green cavity to achieve extra-high color rendering because its PL intensity at 490 nm still remains at 65% of that at 514 nm (Fig. S3, ESI⁺). The asymmetric emission band can be well decomposed into two Gaussian bands (dashed lines in Fig. 2(a)) on the energy scale peaking at 503 nm (19881 cm⁻¹) and 547 nm (18282 cm⁻¹), respectively. Their energy difference is about 1599 cm⁻¹, corresponding to the energy separation between the ²F_{7/2} and ²F_{5/2} ground levels of Ce³⁺.²⁵ The estimated Stokes shift of the Ce³⁺ emission in LSAS is about 2440 cm⁻¹. The PLE spectrum of LSAS:6%Ce³⁺ consists of two bands located around 448 nm and 350 nm, which originate from the transitions of the 4f ground state to the lowest and second upper 5d sates of Ce³⁺, respectively. The internal QE was measured to be as high as 93.3% upon 448 nm excitation (Fig. S4, ESI⁺). Besides, the emission color point of LSAS:6%Ce³⁺ in the Commission Internationale de l'Eclairage (CIE) chromaticity diagram was determined to be (0.333, 0.570) (Fig. 2(b)), and the fluorescence microscopy PL image shows that they are irregular micro-sized particles with intense green emission.

For pc-WLED applications, the thermal stability of a phosphor is another key parameter, because the temperature is usually up to 150 °C or even higher during LED operation.³ The temperature dependent PL spectra (Fig. 3) show that the LSAS:6%Ce³⁺ phosphor exhibits extraordinary thermal stability in that the PL intensity still remains at 98.8% at 473 K (200 °C). Moreover, the large activation energy (ΔE) of 0.49 eV was obtained using the Arrhenius equation. The relatively small Stokes shift may be responsible for the high thermal stability, possibly resulting from the more rigid coordination environment of Ce^{3+} owing to the introduction of heavy ion Sr^{2+} and highly charged ion $Si^{4+,26-28}$

To illustrate the great potential of the newly designed green phosphor LSAS:6%Ce³⁺ for application in pc-WLEDs, we fabricated a pc-WLED by combining a 450 nm LED chip (30% power conversion efficiency) with a blend of the green phosphor LSAS:6%Ce³⁺ and the commercial red phosphor CaAlSiN₃:Eu²⁺. The emission spectrum and a photo of the WLED are depicted in Fig. 4. Apparently, the spectrum is smooth, covering almost the whole visible range without a notable blue-green cavity. The R_a , CCT and luminous efficiency (LE) values were determined to be 97.6, 3718 K and 62.53 lm W⁻¹, respectively, at a forwardbias current of 20 mA. In particular, *R*9 and *R*12, reflecting the rendering abilities of saturated red and blue colors, were determined to be as high as 94 and 81, respectively. It should be noted that a much higher luminous efficiency is expected



Fig. 4 The emission spectrum of a blue-chip (450 nm) based pc-WLED using LSAS:Ce³⁺ and CaAlSiN₃:Eu²⁺ phosphors driven by a current of 20 mA. The inset shows a photo of the WLED package.

since a blue LED chip with more than 50% power conversion efficiency is available. These results demonstrate that warm WLEDs with extra high color rendering can be obtained only by using a mixture of the green phosphor LSAS:6%Ce³⁺ and a red phosphor, which confirms that LSAS:Ce³⁺ exhibits excellent PL properties and can be used as a green phosphor for pc-WLEDs.

3. Conclusions

In conclusion, we successfully designed a new phosphor, $Lu_2SrAl_4SiO_{12}:Ce^{3+}$ (LSAS:Ce³⁺), based on $Lu_3Al_5O_{12}:Ce^{3+}$ through chemical unit cosubstitution by partially replacing LuO₈/AlO₄ by SrO₈/SiO₄, which was confirmed by Rietveld structure refinement and EDS measurements. LSAS:Ce³⁺ exhibits blue-shifted green emission peaking at 514 nm with an internal QE as high as 93.3% upon 448 nm excitation, which has sufficient emission around 490 nm to fill the blue-green cavity effectively. Moreover, LSAS:Ce³⁺ shows extraordinary thermal stability in that its PL intensity still remains at 98.8% at 473 K and 78.8% at 623 K of that at room temperature, benefiting from the rigid coordination environment of Ce³⁺ owing to the introduction of heavy ion Sr²⁺ and highly charged ion Si⁴⁺. Thanks to the filled blue-green cavity, the as-fabricated pc-WLED device shows an extra high color rendering index of 97.6 with R9 = 94 and R12 = 81 at a CCT of 3718 K. All results demonstrate that LSAS:Ce³⁺ shows great potential for application in pc-WLEDs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by the National Key R&D Program of China (Grant No. 2016YFB0400605, 2016YFB0701003, 2017YFB0403104), the National Natural Science Foundation of China (Grant No. 11874055, 51772286 and 11604330), and the Natural Science Foundation of Jilin Province (Grant 20160520171JH).

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