Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Highly effective synthesis and photoluminescence of $Sr_2Si_5N_8:Eu^{2+}$ red-emitting phosphor for LEDs

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This supporting information includes:

1. Experimental details

All commercially obtained reagents were used without further purification. Strontium halide (anhydrous, particle size: ≤200μm; Daejung Chemicals,) and Si powder (purity 99.9 %, particle size of ≤10-20 μm; Kanto Chemicals, Japan) were used as the feedstock powders. Polytetrafluoroethylene $(C_2F_4)_n$ and urea $(CO(NH_2)_2$ powders (particle size: ≤10 μm, Aldrich) were used as additives. The mixing of initial powders was carried out for 30-60 min using a ball-mill with zirconia balls (3-15 mm) and the as-prepared powder mixture was loosely filled into a cylindrical cup 4.0-6.0 cm in diameter and 10–12 cm in height. The cup was then placed in the center of a high-pressure reactor under a nickel-chromium wire. The air in the vessel was removed by application of a vacuum**,** and the combustion vessel was filled with nitrogen gas to a pressure of 2.0 MPa. The local ignition of the sample was initiated using a resistivity-heated nickel-chromium wire. After ignition a combustion wave was formed and propagated throughout the reaction mixture. During the combustion process, a data acquisition system (GL200A, Graphtec Co., Japan) was used to continuously record the time histories of tungsten-rhenium thermocouples (W/Re-5 versus W/Re-20; diameter, 100 μm) previously inserted into the reaction pellet for temperature measurements. After the combustion process was completed, the sample was cooled down to room temperature and was driven out. The combustion product was transferred to a beaker of 1000 ml, treated by hydrochloride acid/water=1/10 solution, washed several times by distilled water and dried at 80 ^{o}C.

The crystal structure and morphology of $Sr_2Si_5N_8:Eu^{+2}$ powders were characterized by an X-ray diffractometer with Cu Kα radiation (Siemens D5000, Germany), and a scanning electron microscope (SEM; JSM 5410, JEOL, Japan). Photoluminescence (PL) spectrum was recorded on

a Fluorescence spectrophotometer (F-7000, Hitachi, Japan) using a Xe lamp with an excitation wavelength of 450 nm at room temperature.

2. Combustion Synthesis

The combustion synthesis of $Sr_2Si_5N_8:Eu^{2+}$ phosphor (shortly CS-SSN) is based on exothermic nitridation of starting reaction mixture under the nitrogen pressure of 2.0 MPa. Generally, a number of sequential and parallel exothermic reactions occur in the combustion wave of SrX_2-Si-Eu_2O_3-$CO(NH_2)_2$-$(C_2F_4)_n$ system for resulting phase-pure $Sr_2Si_5N_8:Eu^{2+}$ phosphor. However, self-propagation of the combustion wave was basically supported by highly exothermic nitridation of silicon, and during the combustion process the maximum temperature was increased up to 1900 ^oC. In the given experimental conditions red-emitting phosphor powder with mean particle size 6.54 nm was obtained. The effect of the temperature on the size and morphology of the particles was also investigated. Fig. S1 shows the cross-section of the reaction pellets prepared at different combustion temperatures.

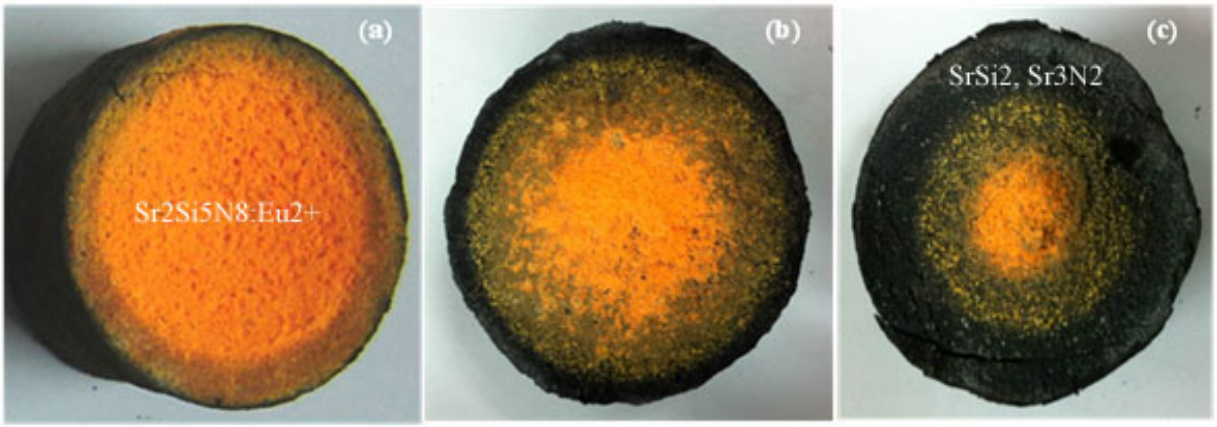

Fig. S1. Influence of the combustion temperature on the morphology of the phosphor samples: (a) 1850 ^oC; (b) 1400 ^oC; and (c) 1100 ^oC. (Black color is intermediate combustion products which are consisted of Si, $SrSi_2$, Sr_3N_2 and $Sr_2Si_5N_8$ phases).

One can see darkening of samples with decreasing the combustion temperature. XRD analysis detected residual silicon and a noticeable portion of intermediate phases ($SrSi_2$ and Sr_3N_2) in the dark region of the sample.

SEM images of CS-SSN particles synthesized under the different temperature conditions are shown in Fig. S2. As shown in Figure S2 the diameters of particles has been decreasing with temperature and finally the size of particles aspires to the nanodimension (0.1-0.3 μm) at 1100 ^{o}C (Fig. S2,d).

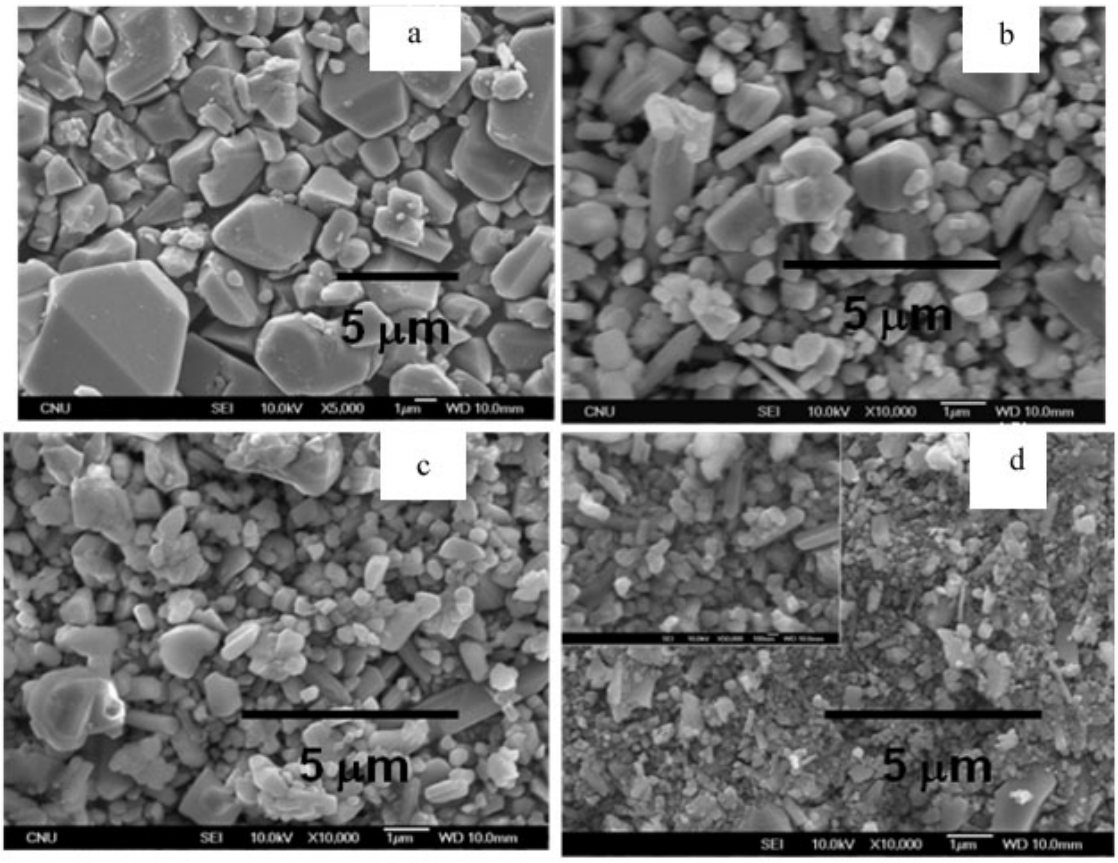

Fig. S2. Particle size of CS-SSN red-emitting phosphor versus the combustion temperature: a- 1850 ^{o}C; b- 1650 ^{o}C; c- 1400 ^{o}C; and d- 1100 ^{o}C.

3. Excitation spectra:

The red emission in $Sr_2Si_5N_8:Eu^{2+}$ was attributed to the large crystal-field splitting and strong nephelauxetic effect [1, 3]. The red phosphor emits an intense orange-red or red color, depending on the Eu^{2+} ion concentration. Fig. S3 shows typical luminescence excitation spectra of $Sr_2Si_5N_8:Eu^{2+}$. The excitation spectrum shows a broad band with peaks located at 260, 303 and 420 nm, which closely matches the emission wavelengths of NUV or blue LEDs.

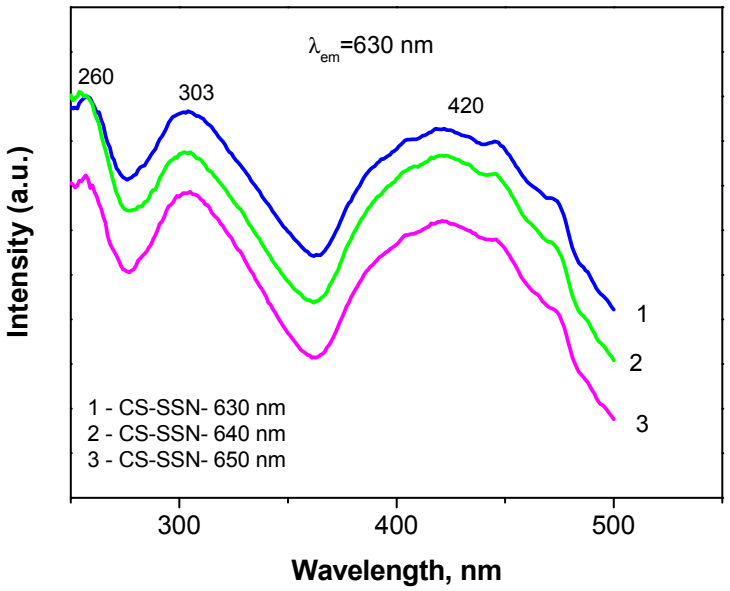

Fig. S3. Excitation spectra of $Sr_2Si_5N_8:Eu^{2+}$ phosphor with different Eu^{2+} concentration.

Generally, strontium-silicon-nitride phosphors prepared by combustion synthesis technique have demonstrated its superior suitability for use in white LED. We found that LED chip prepared from the combustion synthesized red-emitting phosphor shows excellent properties of high luminous efficacy, high chromatic stability, a wide range of white light with adjustable CCT, and brilliant color-rendering properties.

References

[1] R.-J. Xie, N. Hirosaki, *Sci. Tech. Adv. Mater*, 2007, **8**, 588.

[2] R.-J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T. Suehiro, K. Sakuma, *J. Phys. Chem. B,* 2004, **108** , 12027.

[3] Y.Q. Li, A.C.A. Delsing, G. de With, H.T. Hintzen, *Chem. Mater*. 2005, **15,** 4492.

Fig. S2. Excitation spectra of CS-SSN powders synthesized with different Eu^{2+} concentration: 1. 0.04mol; 2. 0.1 mol; and 3. 0.15 mol.

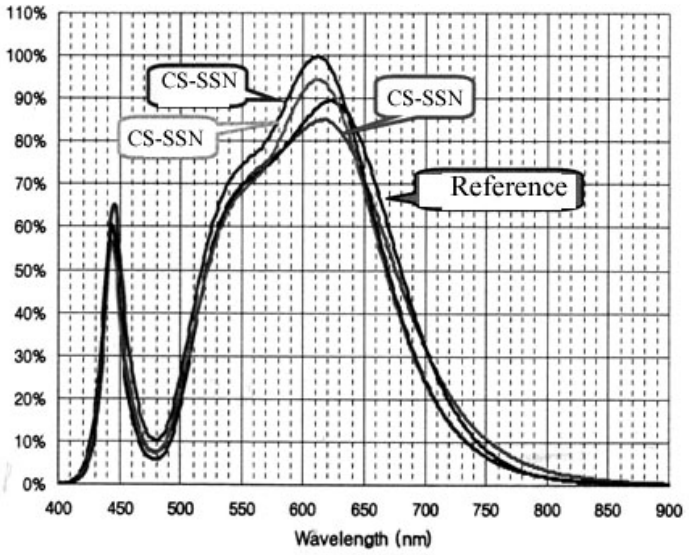

Fig. S3. Warm light package spectrum data for CS-SSN and Reference samples.

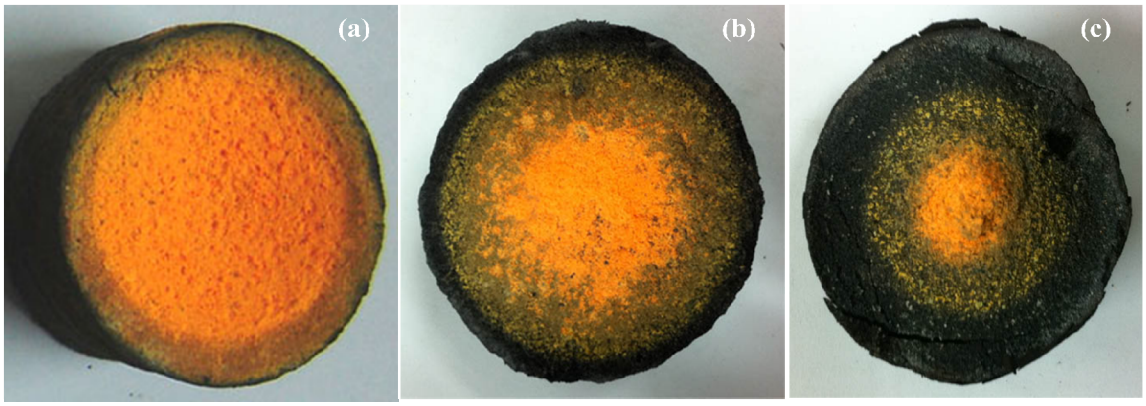

Fig. S4. Influence of the combustion temperature on the morphology of the phosphor samples: (a) 1850 ^{o}C; (b) 1400 ^{o}C; and (c) 1100 ^{o}C. (Black color is intermediate combustion products which is consisted of $SrSi_2$, Sr_3N_2 and $Sr_2Si_5N_8$ phases).

References