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# Synthesis and Luminescence Properties of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> Phosphor for White Light-Emitting-Diode

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## Abstract

Red-emitting nitride phosphors recently attracted considerable attention because of their high thermal stability and high color rendering index properties. For excellent phosphor of white light-emitting-diode, ternary nitride phosphor of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> with different Eu<sup>2+</sup> ion concentration were synthesized by solid state reaction method. In this work, red-emitting nitride Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor was successfully synthesized by using multi-step high frequency induction heat treatment. The effects of molar ratio of component and experimental conditions on luminescence property of prepared phosphors have been investigated. The structure and luminescence properties of prepared Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors were investigated by XRD and photoluminescence spectroscopy. The excitation spectra of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors indicated broad excitation wavelength range of 300 - 550 nm, namely from UV to visible area with distinct enhanced emission peaks. With an increase of Eu<sup>2+</sup> ion concentration, the peak position of emission in spectra was red-shifted from 613 to 671 nm. After via multi-step heat treatment, prepared phosphor showed excellent luminescence properties, such as high emission intensity and low thermal quenching, better than commercial phosphor of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup>. Using Eu<sub>2</sub>O<sub>3</sub> as a raw material for Eu<sup>2+</sup> dopant with nitrogen gas flowing instead of using commercial EuN chemical for Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> synthesis is one of characteristic of this work.

*Keywords:* Luminescence, White LED, Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup>, Phosphor, Photoluminescence, Multi-step High Frequency Induction Heating, EuN

## 1. Introduction

White light-emitting-diode (LED) of a high degree of brightness with low cost and easy fabrication have attracted much attention since finding out cool white light emission could be generated by combining the blue emission of InGaN diode chip with yellow luminescence of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> (YAG:Ce<sup>3+</sup>) phosphor<sup>1-4</sup>). However, this white light has a low color rendering index (CRI) because the emitted yellow light lacks sufficient red emission. In order to obtain a warm and good color rendering white light output, LED emission should be adjusted by two methods. One is to compensate the red deficiency of YAG: Ce<sup>3+</sup>-based LED with a separate red light<sup>5</sup>) and the other is to combine UV chip with red, green, and blue-

emitting (RGB) phosphors<sup>6</sup>). In recent years, SiN<sub>4</sub>-base covalent nitride materials, including nitridosilicates, nitridoaluminosilicates and other nitrides etc., have been extensively studied as a good host lattices for White LED because nitride materials have strong absorption of the light emitted by the LED chips, i.e., UV (350 - 410 nm) or blue (440 - 480 nm) light. In general, the stronger absorption, the higher emitting efficiency. Another strong point is higher quantum or conversion efficiency. The other good point is chemical stability which refers to the stability in chemical composition and crystal structure of phosphor. Low chemical stability of a phosphor will not only make the production process more complex and costly, but also reduce the luminous efficiency and seriously shorten the lifetime of LED products. Consequently, the phosphor should be stable under the ambient atmosphere, and will not chemically

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react with CO, CO<sub>2</sub>, H<sub>2</sub>O, and air. M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> and MAlSi<sub>3</sub>N<sub>3</sub>:Eu<sup>2+</sup> (M = Ca, Sr, Sm, Ba) have been tried for Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> to be a stable and high emission intensity phosphor. But raw materials used for silicon nitride synthesis, for example, silicon diimide Si(NH)<sub>2</sub> or EuN are not only expensive or unobtainable commercially but also very sensitive to oxygen and moisture. Also, conventional carbothermal reduction and nitridation (CRN) method can significantly deteriorate optical properties of phosphors, since obtained phosphors can be easily contaminated by residual carbon impurity. Therefore, an efficient advanced new method is needed to synthesize the red Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor with pure-phase and enhanced luminescence properties. Xie et al.<sup>7)</sup> reported a synthetic route for Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor using SrCO<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Si<sub>3</sub>N<sub>4</sub> as raw materials. However, the resultant product was a complex mixture of Sr/SmSi<sub>5</sub>N<sub>8</sub>, α-Sr<sub>2</sub>SiO<sub>4</sub> and β-Sr<sub>2</sub>SiO<sub>4</sub>.

In this work, two points have characteristic. One is multi-step heat treatment process which was used to enhance luminescence after synthesizing Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor. The other is self-successful synthesis of EuN by using raw material of Eu<sub>2</sub>O<sub>3</sub> with nitrogen gas flowing. Especially EuN chemical which is essential for Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> synthesis, is impossible to buy commercially yet. All other raw materials used were commercially available low cost oxides and the synthesis can be accomplished in an ambient atmosphere. The effect of Eu<sup>2+</sup> ion concentration on the luminescence properties of the prepared phosphors were evaluated. Additionally, the structure and the luminescence properties of the synthesized Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor were investigated to compare with commercially available YAG: Ce<sup>3+</sup> phosphor.

## 2. Experimental

### 2.1 Raw materials and equipment for synthesis

Raw material compositions for Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> synthesis are indicated in the Table 1. The high



Fig. 1. High frequency Induction Furnace used for synthesizing experiment.

frequency induction furnace designed for high speed heat treatment was showed in Fig. 1. The high frequency induction furnace have temperature range from R.T. to 2000°C and temperature rate with 100°C/min (increase) and 300°C/min (decrease) respectively. Vacuum was controlled as 10<sup>-3</sup> Torr with 1000 ml/min N<sub>2</sub> gas flow rate.

### 2.2 Synthesis and Analysis

#### 2.2.1 Synthesis of (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphors

(Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphors were synthesized by using a multi-step heating process from raw materials of strontium carbonate (SrCO<sub>3</sub>, 99.9%), samarium(III) oxide (Sm<sub>2</sub>O<sub>3</sub>, 99.9%), silicon nitride (Si<sub>3</sub>N<sub>4</sub>, 99.5%), europium oxide (Eu<sub>2</sub>O<sub>3</sub>, 99.99%), and activated charcoal nano powder (C, 99.99%). The concentration of Eu<sup>2+</sup> varied in a range of 0-20 at % with respect to Sr/Sm<sup>2+</sup>. They were stoichiometrically weighed and mixed thoroughly in an agate mortar. Mixtures were charged into a graphite crucible and placed into an induction furnace. The furnace chamber was evacuated and filled with pure N<sub>2</sub>, and a flow rate of 1000 ml/min was maintained during the heating process. For the first heating step, temperature was rapidly raised to 1100°C and maintained for 1 h to decompose SrCO<sub>3</sub> completely. After then, temperature was increased to 1400°C and maintained for 3 h to form (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor, which is called

Table 1. Prepared raw materials for Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> synthesis

	Molecular Formula	Purity (%)	Company
Strontium carbonate	SrCO <sub>3</sub>	99.90	Aldrich
Samarium(III) oxide	Sm <sub>2</sub> O <sub>3</sub>	99.90	Aldrich
Silicon nitride	Si <sub>3</sub> N <sub>4</sub>	99.90	Aldrich
Europium oxide	Eu <sub>2</sub> O <sub>3</sub>	99.99	Aldrich
Activated carbon	C	99.00	Aldrich

1<sup>st</sup> heat treated specimen. Finally, the 1<sup>st</sup> heat treated specimens were transferred into a molybdenum crucible, and sintered again at 1600°C under N<sub>2</sub> gas flow for 3 h. After firing, the obtained 2<sup>nd</sup> heat treated phosphors were cooled in a furnace under a continuous flow of N<sub>2</sub> gas.

### 2.2.2 Analysis of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup>

The crystalline structure of the synthesized Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> powder was measured using X-ray powder diffraction (SIEMENS X-ray diffractometer) with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The data were collected in the  $2\theta$  range from 10 to 70° with a scanning rate of 3°/min. Diffuse reflection spectra were obtained using a BaSO<sub>4</sub> powder calibrated UV-Vis spectrophotometer (UV-2200, SHIMADZU). Photoluminescence (PL) measurement was carried out at room temperature using 455 nm as the excitation wavelength with a Perkin Elmer LS-45 luminescence spectrometer. The temperature dependence of photoluminescence was measured with a multichannel spectrophotometer (model MCPD7000; Otsuka Electronics) equipped with temperature-controlled sample holders and a Xe lamp. Oxygen, nitrogen, and carbon residual impurity content of obtained phosphors were measured by using an oxygen/nitrogen analyzer (EMGA-930; HORIBA) and carbon/sulfur analyzer (SLE-CS-8520 SPECTRO).

## 3. Results and discussion

### 3.1. Structure and impurity concentration

The crystal structure of obtained Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors showed an orthorhombic lattice with the space group of *Pmn2*<sub>1</sub>. Fig. 2 gives the X-ray diffraction (XRD) pattern of the 2<sup>nd</sup> heat treated specimen compared by standard specimen. Most of the diffraction peaks of synthesized Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors showed identical peaks to the standard specimen and no apparent impurity phases were found. Moreover, it was also indicated that the doped Eu<sup>2+</sup> ions did not caused any significant change in the host structure, because of close ionic radii of Sr<sup>2+</sup>, Sm<sup>2+</sup> and Eu<sup>2+</sup>. Activated carbon nano powder which was used as reductant to decompose oxide raw materials. After the 1<sup>st</sup> heat treatment finishing, specimens were sintered again at 1600°C to eliminate residual impurities as low as possible (Table 2).

### 3.2 Photoluminescence properties

Photoluminescence (excitation/emission) spectra of

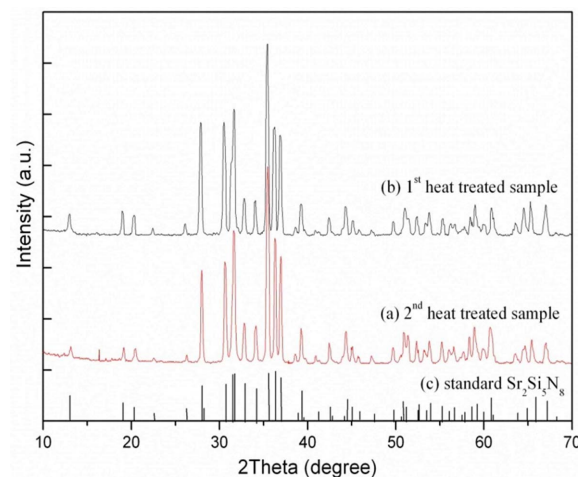


Fig. 2. XRD patterns of 2<sup>nd</sup> heat treated sample (a), 1<sup>st</sup> heat treated sample (b) and standard Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (c).

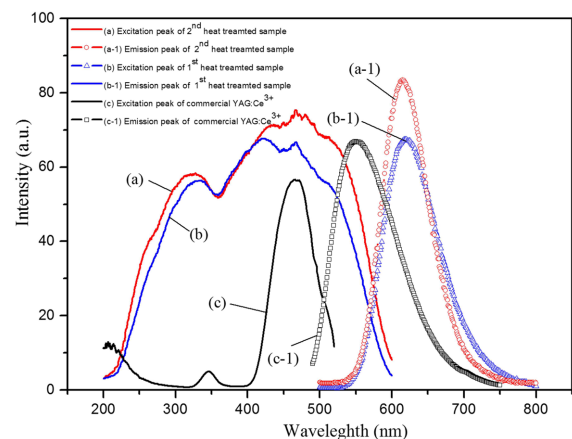


Fig. 3. Typical photoluminescence spectra of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at%) samples with 2<sup>nd</sup> heat treatment (a), 1<sup>st</sup> heat treatment (b) and commercial YAG:Ce<sup>3+</sup> phosphor (c).

Table 2. Oxygen, nitrogen, and carbon residual contents (wt%)

Sr/SmSi <sub>5</sub> N <sub>8</sub> :Eu <sup>2+</sup>	O	N	C
1 <sup>st</sup> heat treated sample	1.70	25.10	0.26
2 <sup>nd</sup> heat treated sample	0.82	25.90	0.04
Ideal	0	26.20	0

the Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at %) phosphor, together with that of standard YAG:Ce<sup>3+</sup> (P46-Y3) for comparison are plotted in Fig. 3. Excitation spectra consist of a broadband covering wave lengths from the UV to visible region. The broad band emission peak at 628 nm of the Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at %) phosphor at the excitation of 455 nm is assigned to the allowed 4f<sup>6</sup>5d<sup>1</sup> → 4f<sup>7</sup> transition of Eu<sup>2+</sup> ion<sup>8)</sup>. Due to the high covalent environment around Eu<sup>2+</sup> ion, emission of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor was observed at a fairly

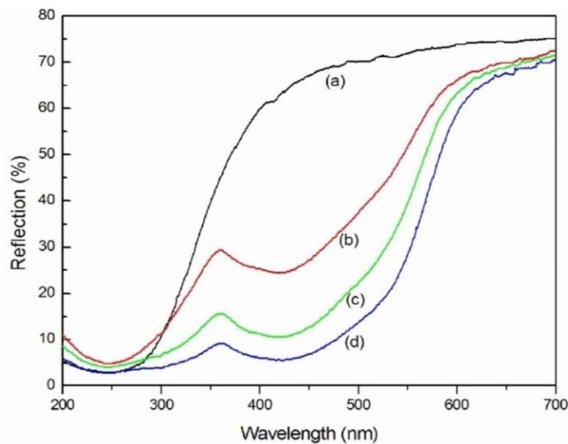


Fig. 4. Diffuse reflection spectra of Sr/SmSi<sub>5</sub>N<sub>8</sub> (a) and (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor with x = 0.02 (b), 0.1 (c), and 0.2 (d).

longer wavelength region compared to MF<sub>2</sub>:Eu<sup>2+</sup> or M<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> (M=Sr/Ba)<sup>8-9</sup>. Owing to keep residual impurities as low as possible (Table 2) through the 2<sup>nd</sup> heat treated process, luminescence intensity values showed a fairly enhanced result (Fig. 3). Calculated emission intensity was about 117% of YAG: Ce<sup>3+</sup> at the same excitation of 455 nm.

### 3.3 Effect of Eu<sup>2+</sup> ion concentration on luminescence property

The optical reflection spectra of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors with different Eu<sup>2+</sup> ion concentration are shown in Fig. 4. For all samples, two strong absorption bands were presented in the range of the UV to visible spectra region, the first absorption band at 250 - 350 nm was caused by the electronic transition of the Sr/SmSi<sub>5</sub>N<sub>8</sub> host and the second absorption band at 350 - 550 nm can be assigned to the 4f<sup>7</sup> → 4f<sup>6</sup>5d<sup>1</sup> transition of Eu<sup>2+</sup> ion. The absorption becomes stronger and the absorption edges shift to the longer wavelength with increasing Eu<sup>2+</sup> concentration so that the body color of phosphors become gradually distinct reddish.

Dependence of emission intensity and peak emission wavelength on Eu<sup>2+</sup> concentration of the (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor is shown in Fig. 5. With increasing Eu<sup>2+</sup> content, emission intensity of (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor was maximized at a Eu<sup>2+</sup> concentration of around 2 at % (i.e., x=0.02) and then decreased slowly with more Eu<sup>2+</sup> doping. The decrease in emission intensity beyond a critical concentration is ascribed to the concentration quenching which is mainly caused by the energy transfer between two Eu<sup>2+</sup> ions. Meanwhile, the peak

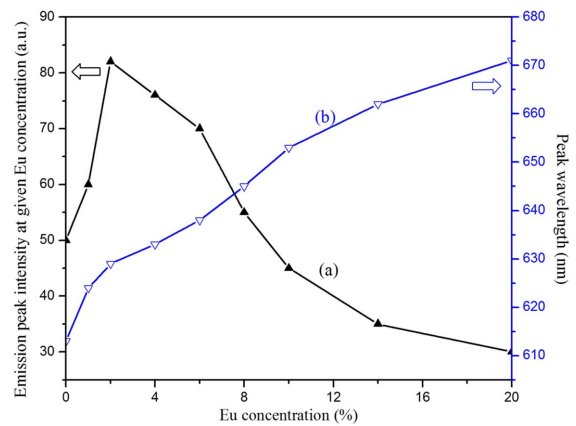


Fig. 5. Dependence of emission intensity (a) and emission peak wavelength (b) as a function of Eu concentration in (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor under 455 nm excitation.

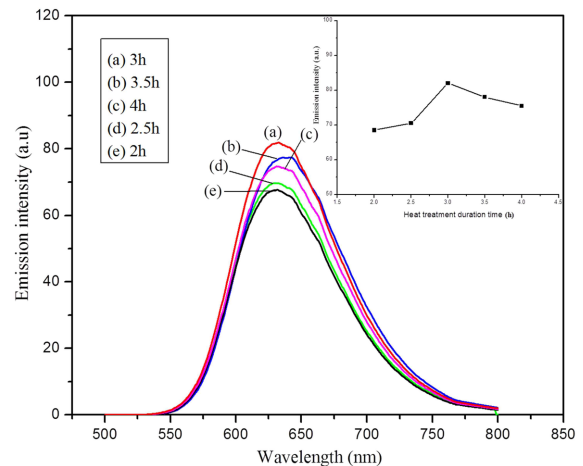


Fig. 6. Emission intensity of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at %) according to heat treatment duration time.

emission of (Sr/Sm<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor shifted to the longer wavelength side (red shift) as Eu<sup>2+</sup> concentration increased from 0 to 20 at %.

### 3.4 Effect of heat treatment condition during 2<sup>nd</sup> heating process on luminescence intensity

Effect of heat treatment time during 2<sup>nd</sup> heating process on emission intensity of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at%) phosphor was shown in Fig. 6. The highest emission intensity was observed at the 3 h heat treatment duration time. This result may be caused by impurities decreasing according to increased holding time for the reaction of carbon with oxygen to more thoroughly produce carbon monoxide, which result in increased emission intensity. However when holding time was increased beyond 3 h treatment, emission intensity showed an obvious decreasing tendency due to powder agglomeration by overheating.

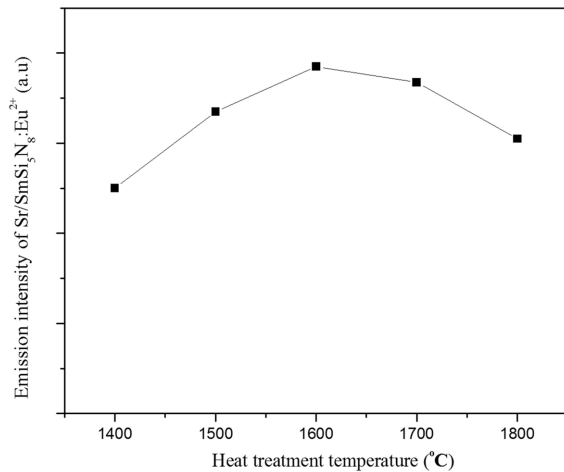


Fig. 7. Emission intensity of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at %) according to heating temperature.

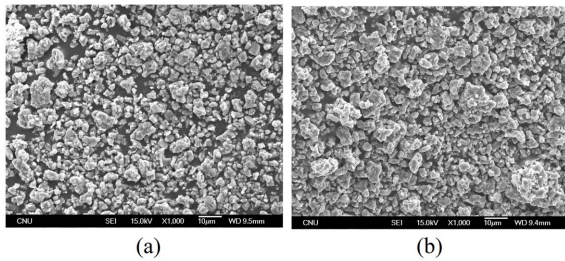


Fig. 8. SEM micrographs according to Temperature effect during 2<sup>nd</sup> heating process (a) 1500°C and (b) 1650°C.

Effect of heat treatment temperature during 2<sup>nd</sup> process on luminescence intensity of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> was shown in Fig. 7. With heat treatment temperature increasing, the emission intensity of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> increased and showed maximum value at 1600°C. But with increasing temperature over 1600°C, emission intensity was decreased obviously. This result can be explained from two contrary factors, namely with temperature increases, reaction of carbon with oxygen would become easy, therefore impurities are reduced effectively which could lead to high luminescence intensity. On the contrary, with the increase of sintering temperature, particle sizes become large and morphologies would become non uniform particles with some part of agglomeration (Fig. 8).

### 3.5 Temperature quenching effect on emission intensity

Phosphors for white LED should have low thermal quenching to avoid changes in chromaticity and brightness of white LED at high temperatures. The temperature-dependent emission intensity of Sr/

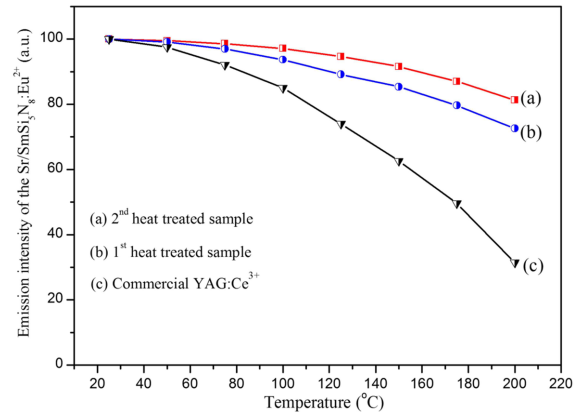


Fig. 9. Temperature quenching of the Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors of the 2<sup>nd</sup> heat treated specimen (a) and the 1<sup>st</sup> heat treated specimen (b) comparing to commercial YAG:Ce<sup>3+</sup> (c).

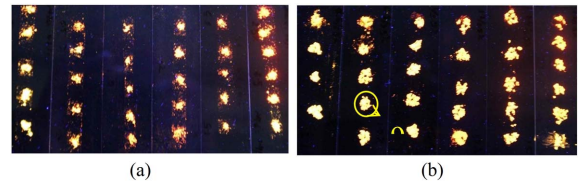


Fig. 10. Emission comparison of 1<sup>st</sup> heat treated phosphor (a) and 2<sup>nd</sup> heat treated phosphor (b).

SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (2 at.%) phosphors and YAG:Ce<sup>3+</sup> phosphors are shown in Fig. 9. and Fig. 10. As the temperature increased from 20 to 200°C, the emission peak of (Sr/Sm<sub>0.98</sub>Eu<sub>0.02</sub>)<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> phosphor was kept at the 628 nm position, but the intensity was decreased by 18% of the initial value, whereas the decrease of YAG:Ce<sup>3+</sup> phosphor was 64%. This result may be due to improved activity of oxygen within the phosphors as temperature increased. According to oxygen content increasing, more decreased emission intensity was observed.

## 4. Conclusion

Red-emitting Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor was successfully prepared by multi-step high frequency induction heat treatment method. XRD analysis showed the single-phase crystal structure of Sr/SmSi<sub>5</sub>N<sub>8</sub>. The excitation spectra of Sr/SmSi<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphors showed broad excitation wavelength range of 300-550 nm with distinct enhanced emission peaks, which means this phosphor is suitable for application of white LED with UV or blue chip. With an increase of Eu<sup>2+</sup> ion concentration, the peak position of emission in spectra was red-shifted from 613 to 671 nm. At 2 at % concentration of Eu<sup>2+</sup> ions in synthesized phosphor, maximum red emission

peak at 628 nm was obtained under 455nm blue light excitation. Through the 2<sup>nd</sup> heat treatment process, luminescence intensity values showed a fairly enhanced result about 117% of YAG: Ce<sup>3+</sup> at the same excitation of 455 nm.

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