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# Luminescence properties of red-emitting $M_2Si_5N_8:Eu^{2+}$ (M = Ca, Sr, Ba) LED conversion phosphors

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#### Abstract

The influence of the type of the alkaline-earth ion and the  $Eu^{2+}$  concentration on the luminescence properties of  $Eu^{2+}$ -doped  $M_2Si_5N_8$  (M = Ca, Sr, Ba) has been investigated. XRD analysis shows that  $Eu^{2+}$ -doped  $Ca_2Si_5N_8$  forms a limited solid solution with a maximum solubility of about 7 mol% having a monoclinic lattice. The  $Eu^{2+}$  ion can be totally incorporated into  $Sr_2Si_5N_8$  and  $Ba_2Si_5N_8$  forming complete solid solutions with orthorhombic lattices.  $M_2Si_5N_8$ : $Eu^{2+}$  (M = Ca, Sr) shows typical broad band emission in orange to red spectral range (600–680 nm) depending on the type of M and the europium concentration.  $Ba_2Si_5N_8$ : $Eu^{2+}$  shows yellow to red emission with maxima from 580 to 680 nm with increasing  $Eu^{2+}$  content. The long-wavelength excitation and emission is attributed to the effect of a high covalency and a large crystal-field splitting on the 5d band of  $Eu^{2+}$  in the nitrogen environment. With increasing the europium concentration, the emission band shows a red-shift for all  $M_2Si_5N_8$ : $Eu^{2+}$  compounds due to changing Stokes shift and the reabsorption by  $Eu^{2+}$ . The conversion (i.e. quantum) efficiency increases going from Ca to Ba and Sr under excitation at 465 nm. In particular,  $Sr_2Si_5N_8$ : $Eu^{2+}$  with a quantum efficiency of 75–80% and a thermal quenching of only a few percent at 150 °C, demonstrates to be a highly promising red-emitting conversion phosphor for white-LED applications.

Keywords: Luminescence; Alkaline earth; Silicon nitride; Phosphor; Europium; X-ray powder diffraction; White-light LEDs

## 1. Introduction

A lighting revolution is sweeping all the over world and is stealthily coming in and improving our everyday life. In comparison with incandescent and fluorescent lamps, the InGaN-based white-light-emitting diodes (LEDs) have many advantages in energy efficiency, long lifetime, compactness, environment friendly and designable features [1–3]. Excitingly, the efficiency of white LED lighting has already exceeded that of the incandescent lamps and now is competitive with fluorescent lamps [1–5]. Without doubt, the white LED lighting is setting foot in the lighting industry and greatly challenges the conventional lighting.

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In this solid-state lighting innovation, the wavelength conversion phosphor materials play a crucial role as they once did in fluorescent lamps [6–9]. White LED lighting within a phosphor-LED system can be realized by several approaches: first, a combination of an InGaN-based blue-LED chip (emitting blue light at 465 nm) with a yellow phosphor (i.e.  $YAG:Ce^{3+}$ based materials) [10,11]. Second, a blue-LED chip combined with a green- ( $\sim$ 530 nm) and a red-emitting (>600 nm) phosphor [12] instead of single vellow-emitting phosphor. The two phosphors absorb the blue light from the InGaN chip and convert it into green and red light and then by colour mixing the white light is generated. In addition, by using an UV-LED plus blue-, green- and red-emitting phosphors this purpose can also be reached [12]. Colour mixing of blue, red and green instead of only blue and yellow provides improved colour rendering and a wide range of colour temperatures. The conversion phosphors must strongly absorb UV-blue light (370-450 nm) and efficiently re-emit in the red, green or blue part of the spectrum. However, the well-developed phosphors used for current

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mercury gas-discharge fluorescent lamps cannot be directly applied to white LED lighting because of a very low absorption in the UV-blue range (370–450 nm). So far, only a limited number of phosphors is available, for example, yellow-emitting YAG:Ce<sup>3+</sup> [1,13], green-emitting SrGaS<sub>4</sub>:Eu<sup>2+</sup> and red-emitting Sr<sub>1-x</sub>Ca<sub>x</sub>S:Eu<sup>2+</sup> based phosphors [12]. With respect to the above mentioned phosphor materials, either they have low luminous efficacy (i.e. YAG:Ce<sup>3+</sup>) [3] or low stability against humid, thermal and radiative environments (i.e. Sr<sub>1-x</sub>Ca<sub>x</sub>S:Eu<sup>2+</sup>) [3,12] which significantly reduces the quality of the output light and the service lifetime of LEDs [14]. Therefore, it is urgent to develop novel conversion phosphors with improved properties to be used for white LED lighting for general illumination.

Among the various phosphors, the red-emitting phosphors are the most urgent ones to be improved. Apart from  $Sr_{1-x}Ca_xS:Eu^{2+}$  based phosphors, traditional powerful redemitting phosphors with line emission, i.e. Y2O3:Eu3+, cannot serve this function in white LED lighting [1,15]. Recently, the invention of a new class of red-emitting nitride phosphors  $M_2Si_5N_8$ :Eu<sup>2+</sup> (M = Ca, Sr, Ba) [16,17] has triggered a renewal in the field of luminescent materials. Subsequently, a number of new nitride-based phosphors has been found and investigated in most recent years [3,16,18–24]. For  $M_2Si_5N_8:Eu^{2+}$  (M = Ca, Sr, Ba), van Krevel [17] reported unusual long-wavelength Eu<sup>2+</sup> emission (620-660 nm) with absorption bands in the visible range. The long-wavelength emission is attributed to a large covalency and crystal-field splitting effect on the Eu<sup>2+</sup> 5d band due to the presence of coordinating nitrogen [17]. Later, Höppe et al. [24] studied the luminescence properties in a series of  $Ba_{2-x}Eu_xSi_5N_8$  compounds which revealed two emission maxima peaking at about 600 nm, corresponding to two crystallographic Ba(Eu) sites in the Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> host lattice. The emission maxima shift to longer wavelength with increasing Eu content due to reabsorption processes of  $Eu^{2+}$  [24]. With respect to the above mentioned investigations, there still remains a number of questions, for example, in order to further improve the luminescence properties, the solubility of Eu<sup>2+</sup> should be clarified. Moreover, the influence of the type of M ion and the Eu concentration on the luminescence properties are important issues.

Therefore, in the present study, we focus on the investigation of the solubility of  $Eu^{2+}$  in the  $M_2Si_5N_8$  host lattice and the influence of the type of the M ion and the  $Eu^{2+}$  concentration on the luminescence properties and conversion efficiency of  $M_2Si_5N_8:Eu^{2+}$ .

## 2. Experimental

#### 2.1. Starting materials

The binary nitride precursors SrN<sub>x</sub> ( $x \approx 0.6-0.66$ ), BaN<sub>x</sub> ( $x \approx 0.6-0.66$ ) and EuN<sub>x</sub> ( $x \approx 0.94$ ) were pre-prepared by the reaction of the pure strontium metal (Aldrich, 99.9%, pieces), barium metal (Aldrich, 99.9%, pieces) and Eu metal (Csre, 99.9%, lumps) under flowing dried nitrogen at 800, 550 and 800 °C, respectively, for 8–16 h in horizontal tube furnaces. In addition, calcium nitride powder Ca<sub>3</sub>N<sub>2</sub> (Alfa, 98%) and  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder (Permascand, P95H,  $\alpha$  content 93.2%; oxygen content ~1.5%) are used as the as-received raw materials.

#### 2.2. Synthesis of undoped and $Eu^{2+}$ -doped $M_2Si_5N_8$

Polycrystalline  $M_{2-x}Eu_xSi_5N_8$  ( $0 \le x \le 0.2$  for M = Ca,  $0 \le x \le 2.0$  for M = Sr, Ba) powders were prepared by a solid-state reaction method at high temperature. The  $Ca_3N_2$ ,  $SrN_x$ ,  $BaN_x$  and  $EuN_x$  as well as  $\alpha$ -Si\_3N\_4 powders were weighed out in the appropriate amounts and subsequently mixed and ground together in an agate mortar. The powder mixtures were then transferred into molybdenum crucibles. All processes were carried out in a purified-nitrogenfilled glove box. Subsequently, those powder mixtures were fired twice (with a medium grinding in between) in a horizontal tube furnace at 1300–1400 °C for 12 and 16 h, respectively, under flowing 90% N<sub>2</sub>–10% H<sub>2</sub> atmosphere. After firing, the samples were gradually cooled down in the furnace. There was no apparent reaction of the prepared nitrides with the Mo crucibles.

#### 2.3. X-ray diffraction data collection and unit cell refinement

All measurements were performed on finely ground samples, which were analyzed by X-ray powder diffraction (Rigaku, D/MAX-B) using Cu K $\alpha$  radiation at 40 kV and 30 mA with a graphite monochromator.

The phase formation of undoped and Eu<sup>2+</sup>-doped M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> materials was examined using a routine scan (2 °/min). Lattice parameters determination was carried out by the least-squares method from X-ray diffraction data collected in step scan with a step size of 0.01° in 2 $\theta$  and a count time of 10 s between 10° and 90° 2 $\theta$  using silicon powder as an internal standard.

#### 2.4. Optical measurements

The diffuse reflectance, emission and excitation spectra of the samples were measured at room temperature with a Perkin-Elmer LS 50B spectrophotometer equipped with a Xe flash lamp. The reflection spectra were calibrated with the reflection of black felt (reflection 3%) and white barium sulfate (BaSO<sub>4</sub>, reflection ~100%) in the wavelength region of 230–700 nm. The excitation and emission slits were set at 5 nm. The emission spectra were corrected by dividing the measured emission intensity by the ratio of the observed spectrum of a calibrated W-lamp and its known spectrum from 300 to 900 nm. Excitation spectra were automatically corrected for the variation in the lamp intensity by a second photomultiplier and a beam-splitter. All the spectra were measured with a scan speed of 100 nm/min.

For 465 nm excitation, the relative luminescence intensity was determined as the area under the emission curve of the sample. The conversion (i.e. quantum) efficiency of the luminescence was estimated by dividing the luminescence intensity by the measured absorption of 465 nm radiation, and comparing the result with the value correspondingly determined for a standard phosphor (yellow-orange-emitting  $Sr_{2-x-y}Ba_xCa_ySiO_4:Eu^{2+}$  (Sbcose) and red-emitting  $Ca_{1-x}Sr_xS:Eu^{2+}$  (Sarnoff)) with known quantum efficiency. Temperature dependent efficiency measurements were performed by heating the sample holder up till about 250 °C at maximum.

### 3. Results and discussion

# 3.1. Phase formation and the solubility of $Eu^{2+}$ in $M_2Si_5N_8$ (M = Ca, Sr, Ba)

The X-ray powder diffraction patterns show that undoped and Eu-doped M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> (M = Ca, Sr, Ba) compounds are formed as nearly single-phase materials. Fig. 1 shows the unit cell volume dependence on the fraction *x* in M<sub>2-x</sub>Eu<sub>x</sub>Si<sub>5</sub>N<sub>8</sub>. For Ca<sub>2-x</sub>Eu<sub>x</sub>Si<sub>5</sub>N<sub>8</sub>, as expected, the unit cell expands with increasing the Eu<sup>2+</sup> concentration in the range of x = 0-0.14 (i.e. 0-7 mol% with respect to Ca), which is consistent with the fact that Eu<sup>2+</sup> (1.17 Å, CN = 6) is significantly larger (about 15%) in size than Ca<sup>2+</sup> (1.00 Å, CN = 6) [25]. When the *x* value surpasses 0.14, the unit cell volume keeps constant corresponding to the appearance of impurity phases. This implies that the maximum



Fig. 1. The relationship between the unit cell volume of  $M_{2-x}Eu_xSi_5N_8$  and the *x* value. The inset shows the enlarged part for M = Ca.

solubility of  $Eu^{2+}$  in  $Ca_2Si_5N_8$  is around x = 0.14 (i.e. 7 mol%) (Fig. 1). The limited solubility is due to the fact that the two end members  $Ca_2Si_5N_8$  and  $Eu_2Si_5N_8$  have different crystal structures (i.e. monoclinic versus orthorhombic crystal system). In contrast, the unit cell volume of  $M_{2-x}Eu_xSi_5N_8$  (M = Sr, Ba) nearly linearly decreases with an increase of *x* due to the replace-

ment of  $Sr^{2+}$  or  $Ba^{2+}$  with the smaller  $Eu^{2+}$  ion [25], perfectly following Vegard's law in the two systems (Fig. 1). In addition, the lattice shrinkage for  $Ba^{2+}$  is significantly larger than that for  $Sr^{2+}$  when  $Eu^{2+}$  is incorporated as a consequence of  $Ba^{2+}$  being larger in size than  $Sr^{2+}$  [25]. The  $M_2Si_5N_8$  (M=Sr, Ba) and  $Eu_2Si_5N_8$  compounds are isostructural with orthorhombic crystal system [26], from which the formation of a complete solid solution between  $Sr_2Si_5N_8$ – $Eu_2Si_5N_8$  and  $Ba_2Si_5N_8$ – $Eu_2Si_5N_8$ can be understood. Furthermore, the above mentioned conclusions are confirmed by their luminescence properties (see sections below).

## 3.2. Diffuse reflection spectra

Fig. 2 shows the diffuse reflection spectra of undoped and  $Eu^{2+}$ -doped  $M_2Si_5N_8$  (M = Ca, Sr, Ba). All undoped  $M_2Si_5N_8$  compounds show a drop in reflection in the UV range around 300 nm with an estimated band gap of about 250 nm for M = Ca, 265 nm for M = Sr and 270 nm for M = Ba, corresponding to the valence-to-conduction band transitions of the  $M_2Si_5N_8$  host lattice. The intense reflection in the visible spectral range is in agreement with the observed grey-white daylight colour of undoped  $M_2Si_5N_8$ . Obviously, two broad absorption bands can be seen from the reflection spectra of low Eu concentration



Fig. 2. Diffuse reflection spectra of  $M_{2-x}Eu_xSi_5N_8$ : (a) M = Ca, (b) M = Sr and (c) M = Ba.

samples (Fig. 2). Due to the absence of such a band in undoped  $M_2Si_5N_8$ , the very broad absorption band (370–490 nm) is attributed to the absorption by the Eu<sup>2+</sup> ions. In agreement with this assignment the intensity of this absorption increases for higher Eu concentration (Fig. 2). Apart from this main absorption band in the visible range, a short-wavelength absorption band centered at about 300 nm is observable in  $M_2Si_5N_8$ :Eu<sup>2+</sup> which is also ascribed to the absorption of Eu<sup>2+</sup> because with increasing  $Eu^{2+}$  concentration the intensity of this absorption band increases. In contrast to the undoped samples, the daylight colour of Eu<sup>2+</sup>-doped M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> is orange to red for M = Ca, Sr and yellow to red for M = Ba, varying with the Eu concentration as a result of a strong absorption in the visible range around 370-490 nm. Additionally, the onset of the reflection drop significantly shifts to a longer wavelength as the Eu concentration increases indicating that the absorption range can be tailored by the Eu content (Fig. 2). The absorption edge continuously shifts over the whole range  $0 < x \le 2$  to longer wavelength from 490 to 608 nm for  $Sr_2Si_5N_8:Eu^{2+}$  (Fig. 2b) and 460-608 nm for Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (Fig. 2c) in agreement with the conclusion that Eu is totally incorporated into the Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> and Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> lattices. For Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup>, however, the red-shift of the absorption edge is found to be negligible for x = 0.2 as compared to x = 0.14 (Fig. 2a), in agreement with the solubility limit at  $x \approx 0.14$ .

## 3.3. Photoluminescence properties of $Eu^{2+}$ in $M_2Si_5N_8$

In the excitation spectra of  $M_2Si_5N_8:Eu^{2+}$  (M = Ca, Sr, Ba) approximately five broad bands can be distinguished (Table 1 and insets in Fig. 3). The position of these excitation bands is almost independent of the type of the M ion, the Eu concentration and the crystal structure, peaking at about 250, 300, 340, 395 and 460 nm (Fig. 3). Only a small variation for various M ions can be observed, in agreement with the observed diffuse reflection spectra. The first excitation band at ~250 nm is readily assigned to the host lattice excitation (e.g. transition from the valence to conduction band for the  $M_2Si_5N_8$  host lattices). The remaining excitation of Eu<sup>2+</sup>. The most intense 5d excitation band of Eu<sup>2+</sup> is located at about 395 nm in  $M_2Si_5N_8:Eu^{2+}$ .

Table 1

Luminescence data for Eu-doped  $M_{2-x}Eu_xSi_5N_8$  (M = Ca, Sr, Ba)

The lowest energy levels of the 5d excitation band (very broad at about 420–520 nm) seem to be further decomposed into two or three sub-bands, especially for M = Sr and Ba at higher Eu concentrations. The position of the 5d excitation band of the  $Eu^{2+}$  ions at low energy (>400 nm) is attributed to the influence of highly covalent bonding of Eu<sub>M</sub>-N and a large crystal-field splitting due to the presence of nitrogen [17,18]. In addition, with increasing  $\mathrm{Eu}^{2\bar{+}}$  concentration these sub-bands at longer wavelength become more intense corresponding to a decline of the dominant excitation band at about 395 nm. Moreover, the absence of significant changes in the position and shape of the excitation band suggests that the covalency of the Eu-N bonds and the crystal-field strength around the Eu<sup>2+</sup> ions are very similar in the M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> series (Table 1). For Eu<sup>2+</sup> ions occupying two M sites with low point symmetry more than four 5d excitation bands are expected to be observed. However, the appearance of only four obvious 5d excitation bands of Eu<sup>2+</sup> implies that they do seriously overlap at room temperature and possibly some of them are hidden in the conduction band of the M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> host lattice, similar to the case of  $Ce^{3+}$ -doped  $M_2Si_5N_8$  [23].

Here, it is worth noting that  $M_2Si_5N_8:Eu^{2+}$  not only has high absorption but also efficient excitation in the same spectral region of 400–470 nm (see Fig. 3), perfectly matching with the radiative blue light from the InGaN-based LEDs (~465 nm).

It is clear that Eu is present as divalent ion in all Eu-doped M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> samples due to the absence of sharp f-f transition lines of Eu<sup>3+</sup> in the excitation spectrum and the presence of broad band emission characteristic (Fig. 3). As a result, this red broad band emission is essentially assigned to the  $4f^{6}5d^{1} \rightarrow 4f^{7}$  transition of the  $Eu^{2+}$  ion [6]. The position of the  $Eu^{2+}$  emission band is strongly dependent on the type of M ion and the Eu concentration (see colour point in Fig. 4). Among M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup>, the colour coordinates of Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> are most close to those of the Sarnoff reference sample  $(Sr_{1-x}Ca_xS:Eu^{2+})$  (Fig. 4). For Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup>, the emission maximum shifts to long wavelength from 605 to 615 nm with increasing the Eu concentration (Fig. 3a). This red-shift terminates at about x = 0.14(i.e.  $7 \mod \% Eu^{2+}$ ) in agreement with the maximum solubility of Eu<sup>2+</sup> (~7 mol%) in Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> (Fig. 1). A very small redshift ( $\sim 10$  nm) of the emission band is fairly consistent with a small amount of Ca<sup>2+</sup> replacement by Eu<sup>2+</sup>. For M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup>

$M_{2-x}Eu_xSi_5N_8$	M = Ca	M = Sr	M=Ba
Crystal system	Monoclinic Cc	Orthorhombic <i>Pmn</i> 2 <sub>1</sub>	Orthorhombic Pmn2 <sub>1</sub>
Maximum solubility of Eu <sup>2+</sup>	x = 0.14	x = 2.0	x = 2.0
5d Excitation band (nm) <sup>a</sup>	297, 355, 394, 460, 496	294, 334, 395, 465, 505	295, 334, 395, 460, 504
Emission band (nm)	605-615	609–680	570-680
Center of gravity $(cm^{-1})^{a,b}$	25800	26000	26100
Crystal-field splitting (cm <sup>-1</sup> ) <sup>a,c</sup>	13500	14200	14100
Stokes shift (cm <sup>-1</sup> ) <sup>a,d</sup>	3800	3700	3500
Conversion efficiency <sup>e</sup> (%)	50-55	75–80	75–80

<sup>a</sup> x = 0.10.

<sup>b</sup> Center of gravity calculated from averaging the energies of the observed 5d excitation levels of Eu<sup>2+</sup>.

<sup>c</sup> Crystal-field splitting estimated from the energy difference between highest and lowest observed 5d excitation levels of Eu<sup>2+</sup>.

<sup>d</sup> Stokes shift calculated from the energy difference between the lowest 5d excitation band and emission band of Eu<sup>2+</sup>.

e x = 0.02.



Fig. 3. Excitation (inset) and emission spectra of  $M_{2-x}Eu_xSi_5N_8$ : (a) M = Ca, (b) M = Sr and (c) M = Ba.



Fig. 4. CIE colour coordinates of the emission spectrum of  $M_{2-x}Eu_xSi_5N_8$  ( $\lambda_{exc} = 465$  nm).

(M = Sr, Ba), the emission band of  $Eu^{2+}$  successively shifts from orange for M = Sr and yellow for M = Ba at low Eu concentration to the red spectral region for high Eu concentration up to a maximum wavelength of ~680 nm, which perfectly agrees with a linear decrease of the unit cell volume with increasing Eu content for both M = Sr and Ba (Fig. 3b and c). The red-shift in Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (~107 nm) is larger than in Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (~71 nm) also in agreement with a more significant shrinkage of the unit cell of Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> as compared to Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> due to the incorporation of Eu<sup>2+</sup>.

In  $M_2Si_5N_8$  (M = Ca, Sr, Ba), there are two crystallographic M sites [27,28]. Therefore, two emission bands are expected to be observed for the Eu ions occupying two M sites. However, the presence of only a single broad emission band suggests that the environment of both  $Eu^{2+}$  ions is very similar or the  $Eu^{2+}$  ions are not very sensitive to the changes of the local structure, eventually resulting in large overlap of the two emission bands of  $Eu^{2+}$  in  $M_2Si_5N_8:Eu^{2+}$ , especially for higher Eu content (Fig. 3). This is consistent with the fact that varying the excitation wavelength yields similar emission spectra. However, after Gaussian deconvolution on an energy scale, these broad emission bands can be well decomposed into two Gaussian components for  $M_2Si_5N_8:Eu^{2+}$  (5 mol%) as typical examples (Fig. 5). Our results are consistent with the observation



Fig. 5. Observed (solid) and fitted (dashed) emission spectra and decomposed Gaussian components (dotted) of  $M_2Si_5N_8$ :Eu (5 mol%): (a) M = Ca, (b) M = Sr and (c) M = Ba ( $\lambda_{exc} = 395$  nm).

of Höppe et al. [24], they observed two maxima in the emission spectrum of  $Ba_{1.89}Eu_{0.11}Si_5N_8$  corresponding to the two  $Eu_{Ba}$  centers in  $Ba_2Si_5N_8$  [24]. Evidently, for  $Ba_2Si_5N_8:Eu^{2+}$  the emission band is significantly broadened (FWHM ~ 125 nm) due to the large difference between the two  $Eu_M$  sites as compared to  $Ca_2Si_5N_8:Eu^{2+}$  (FWHM ~ 104 nm) and  $Sr_2Si_5N_8:Eu^{2+}$  (FWHM ~ 88 nm) (Fig. 5).

Although the excitation spectra are almost independent of the M type, the position of the emission bands is strongly dependent on it. For example, the emission bands of  $M_2Si_5N_8:Eu^{2+}$  (1 mol%) peak at about 605, 610 and 574 nm for M = Ca, Sr and

Ba, respectively. Therefore, the shift in emission band is due to a difference in Stokes shift, which gradually increases in the sequence Ca>Sr>Ba (Table 1) as expected for the relaxation in the  $4f^{7}5d$  excited state of  $Eu^{2+}$  becoming less restricted when the size of the alkaline-earth ion decreases [29].

The Stokes shift increases for higher Eu concentrations in all cases. The changes of the Stokes shift as function of the Eu concentration are about 300, 1200 and 2100 cm<sup>-1</sup> for M = Ca, Sr and Ba, respectively. Based on the fact that the center of gravity and crystal-field splitting do not show a significant change, therefore, the observed red-shift of the emission band of  $M_2Si_5N_8:Eu^{2+}$  with increasing the Eu concentration can be mainly ascribed to an increase of the Stokes shift for M = Sr and Ba (Fig. 3). Here we also cannot exclude some contribution from the reabsorption by Eu<sup>2+</sup>.

For excitation with 465 nm the relative luminescence intensities of the  $M_{1.98}Eu_{0.02}Si_5N_8$  samples are 71% (M = Ca), 87% (M = Sr) and 84% (M = Ba). The highest conversion (i.e. quantum) efficiency is measured for  $Sr_2Si_5N_8:Eu^{2+}$ , viz. 75–80%. This compound also shows the least thermal quenching: at 150 °C the decrease in quantum efficiency is only a few percent, while the efficiency of  $Ca_2Si_5N_8:Eu^{2+}$  has already dropped to about 40% of its room temperature value. The strong thermal quenching effect of  $Ca_2Si_5N_8:Eu^{2+}$  is expected from its Stokes shift being somewhat larger than that of  $M_2Si_5N_8:Eu^{2+}$ (M = Sr, Ba), and in agreement with the relationship reported by Blasse for several alkaline-earth host lattices between a higher quenching temperature and a larger alkaline-earth ion [30,31].

According to the above mentioned properties,  $Sr_2Si_5N_8:Eu^{2+}$  has the highest potential as a red-emitting conversion phosphor for white LED applications as just recently confirmed by first tests of  $Sr_2Si_5N_8:Eu^{2+}$  in real white-emitting phosphor-conversion LEDs [32].

## 4. Conclusions

Undoped and  $Eu^{2+}$ -doped  $M_2Si_5N_8$  (M = Ca, Sr, Ba) materials were obtained by a solid-state reaction of  $MN_x$ ,  $EuN_x$  and  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder at 1300–1400 °C under an N<sub>2</sub>-H<sub>2</sub> (10%) atmosphere. The maximum solubility of Eu<sup>2+</sup> is about 7 mol% in the Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> lattice. In contrast, Eu<sup>2+</sup> can be completely incorporated into the  $M_2Si_5N_8$  (M = Sr, Ba) lattice because the  $M_2Si_5N_8$ (M = Sr, Ba) compounds are isostructural with Eu<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>. Eudoped M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> shows a typical broad band emission of Eu<sup>2+</sup> in the spectral range from orange to red (570-680 nm) due to the  $4f^{6}5d \rightarrow 4f^{7}$  transition. With increasing Eu concentration, the emission band shifts to longer wavelength depending on the type of M ion and the Eu concentration which is found to be proportional to the changes of the unit cell volume for M = Srand Ba. This red-shift is related to an increase of the Stokes shift and possibly can also be attributed to some reabsorption by  $Eu^{2+}$ . The absorption and excitation bands of M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> materials ranging from 370 to 460 nm perfectly match with the emission of InGaN-based LEDs making them attractive as conversion phosphors for white-LED applications. The highest potential is shown by  $Sr_2Si_5N_8:Eu^{2+}$  with a conversion (i.e. quantum) efficiency of 75–80% for 465 nm excitation combined a very favourable thermal quenching behaviour.

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