

Paper

High Efficiency Nitride Based Phosphors for White LEDs

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ABSTRACT

In this overview paper, novel rare-earth doped silicon nitride based phosphors for white LEDs applications have been demonstrated. The luminescence properties of orange-red-emitting phosphors ($M_2Si_5N_8:Eu^{2+}$) and green-to-yellow emitting phosphors ($MSi_2N_2O_2:Eu^{2+}$, $M = Ca, Sr, Ba$) are discussed in detail with a focus on the relationship between the properties and structures. With high conversion efficiency in the near UV/blue region, along with high chemical/physical stability, Eu^{2+} - and Ce^{3+} - activated alkaline-earth silicon nitride and oxynitride materials are excellent wavelength-conversion phosphors for white LEDs.

KEYWORDS: nitride, phosphor, luminescence, white LEDs

1. Introduction

Recently, breakthroughs in inorganic light emitting diodes (LEDs) technology^{1,2)} are significantly catalyzing the development of energy-efficient and long lifetime solid-state lighting (SSL). Solid-state lighting technology has now already penetrated in a variety of specialty applications, in effect, LEDs have completely changed the "world of luminance", for example automobile brake lights, traffic signals, liquid crystal displays and mobile backlights, flashlights and all manner of architectural spotlights³⁾. In particular, the invention of high-efficiency blue-emitting InGaN-based LEDs makes realization of efficient, full-spectrum white-light LEDs for general illumination possible by using conversion phosphors, and will bring about a revolution in lighting industry⁴⁾. However, the excitation sources in LEDs are quite different from the traditional sources, such as mercury gas-discharge. Thus only a very limited number of present phosphors can meet the minimum requirements for white-light LED applications. Most traditional phosphors can't be efficiently excited above 400 nm. In order to obtain high efficiency and better color rendering LEDs, the development of suitable green, yellow and red-emitting phosphors is the great challenge. As a conversion phosphor for white phosphor-converted LEDs, a strong absorption in the blue or near-UV region and a highly efficient conversion for re-emission into the green, yellow and red light are required. Therefore, to modify existing and explore new phosphor materials with improved properties for use in white LEDs is extremely urgent.

Fortunately, a new class of inorganic phosphors, viz. rare-earth-doped-silicon-nitride based materials, has been

invented and attracted much attention in recent years due to their high chemical and thermal stability, as well as their unusual luminescence properties compared to oxide, sulphide and halide based phosphors or their combinations. It is just the presence of nitrogen in the host lattice that makes the rare-earth ions exhibit unique optical properties because of their high covalency (nephelauxetic effect) and large crystal field splitting⁵⁾.

In this paper, we will describe some of our research projects on novel rare-earth activated silicon nitride based materials with an emphasis on the luminescence properties of Eu^{2+} - and Ce^{3+} -doped alkaline-earth silicon nitride and oxynitride phosphors for white-LED applications.

2. Experimental approaches

Rare earth doped silicon nitride, oxynitride and carbide-nitride materials were synthesized starting from alkaline-earth metals and/or oxides, silicon nitride, aluminum nitride, silicon carbide and rare-earth nitrides or oxides by a solid-state reaction at high temperature ranging from 1300-1650 °C in a N_2/H_2 atmosphere. The phase composition and crystal structure were determined by the powder X-ray diffraction techniques. Photoluminescence properties were measured at room temperature by a Perkin Elmer LS 50B spectrophotometer equipped with a Xe flash lamp. 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 the standard phosphors (yellow-orange-emitting $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_y\text{SiO}_4:\text{Eu}^{2+}$ and red-emitting $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}^{2+}$) with known quantum efficiency. Temperature dependent efficiency measurements were performed by heating the sample holder up till about 250 °C at maximum under blue light ($\lambda_{\text{exc}} = 450 - 460 \text{ nm}$).

3. Results and discussion

3.1 $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Ca, Sr, Ba)

$\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Ca, Sr, Ba)^{6,8)} is a class of orange-red emitting phosphors. The crystal structures are different with the type of M, i.e., monoclinic system for M = Ca, and orthorhombic system for M = Sr, Ba. Therefore, the incorporation of Eu^{2+} into $\text{M}_2\text{Si}_5\text{N}_8$ forms a limited solid-solution with a maximum solubility about 7 mol% for the Ca- and complete solid-solutions for the Sr- and Ba-compounds (Fig. 1) because they are isostructural with $\text{Eu}_2\text{Si}_5\text{N}_8$. Accordingly, the position of the emission bands of $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Sr, Ba) can be easily tailored by Eu concentrations in comparison with $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ⁸⁾.

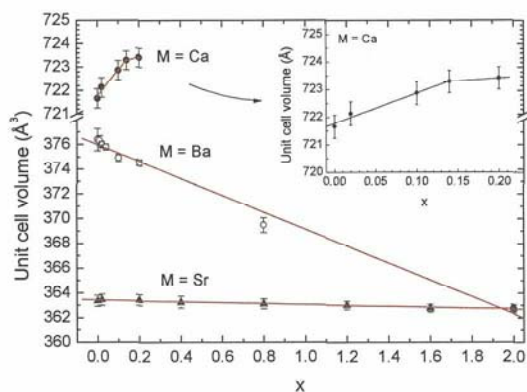


Figure 1 Relationship between the unit cell volume of $\text{M}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ and x

It can be seen that there is a broad and strong absorption band in the visible range around 370 - 500 nm, perfectly matching with the radiation of blue InGaN-based LEDs (Fig. 2). Further, these absorption bands can be enhanced by adjusting the Eu concentration. Under excitation in the Eu absorption band (i.e., blue spectral range $\sim 450 \text{ nm}$), $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ shows highly efficient orange to red emission, which is originating from the $4f^65d \rightarrow 4f$ transition of Eu^{2+} . The emission bands center at about 610 nm and range from 500 to 860 nm (Fig. 3), depending on the type of M. In addition, the emission band also can be shifted from 590 to 680 nm with increasing Eu concentrations. Furthermore, the exact position of the emission band can also be modified by partial replacement of M by another alkaline-earth ion, for example, Sr by Ca. In this way, $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ exhibits a

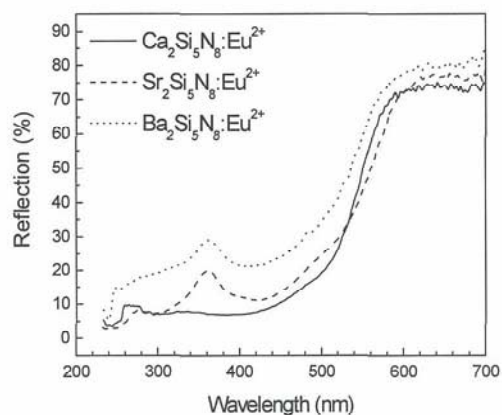


Figure 2 Reflection spectra of $\text{M}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ (M = Ca, Sr, Ba, $x = 0.10$)

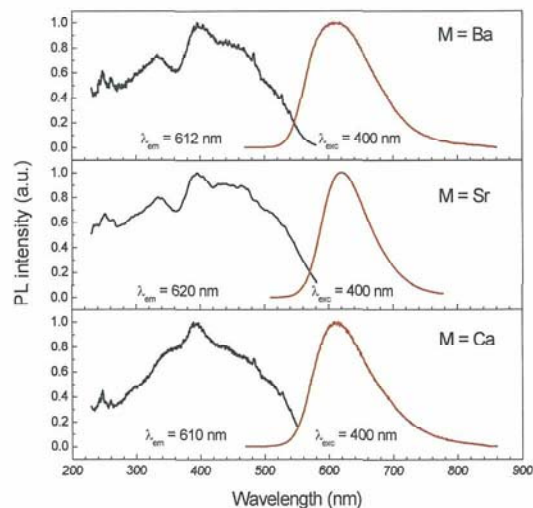


Figure 3 Excitation and emission spectra of $\text{M}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ ($x = 0.10$)

significant red shift of the emission band from about 620 to 643 nm (Fig. 4), while the conversion efficiency and the temperature dependence almost remain at the same levels of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$.

Among the red-emitting phosphor of $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Ca, Sr, Ba), $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ shows the best performance not only in quantum efficiency but also in its thermal stability (Fig. 5) which is comparable with $\text{YAG}:\text{Ce}^{3+}$.

It is worth noting that the choice of Eu^{2+} concentration in $\text{M}_2\text{Si}_5\text{N}_8$ should be carefully taken, although an increasing Eu^{2+} concentration can enhance the absorption and quantum efficiency. Because of a strong interaction between the Eu^{2+} ions, a higher Eu^{2+} concentration also can significantly decrease the thermal stability of $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, which results in a high thermal quenching rate, as shown in Fig. 6 for the case of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$. Therefore, substitution for each M ion with other alkaline-

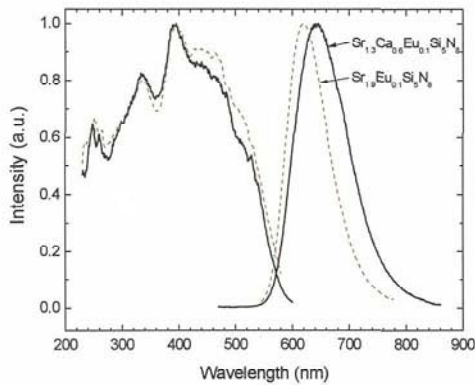


Figure 4 Excitation and emission spectra of $\text{Sr}_{1.3}\text{Ca}_{0.6}\text{Eu}_{0.1}\text{Si}_5\text{N}_8$ ($\lambda_{\text{em}} = 642 \text{ nm}$, $\lambda_{\text{exc}} = 400 \text{ nm}$) and $\text{Sr}_{1.9}\text{Eu}_{0.1}\text{Si}_5\text{N}_8$ ($\lambda_{\text{em}} = 620 \text{ nm}$, $\lambda_{\text{exc}} = 400 \text{ nm}$)

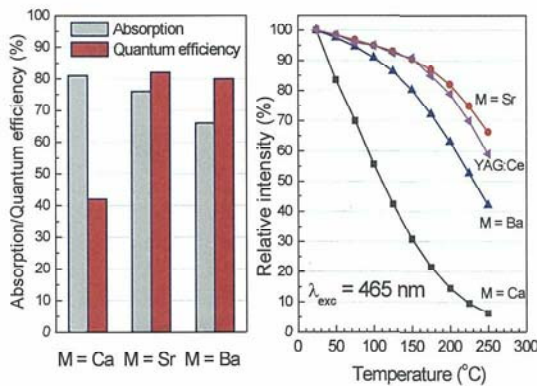


Figure 5 Quantum efficiency and temperature dependence of $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (5 mol%)

earth ions could be a wise way to achieve the purpose of tuning the emission spectrum (see Fig. 4).

Ce^{3+} -doped and Ce^{3+} , Li^+ or Na^+ co-doped $\text{Sr}_2\text{Si}_5\text{N}_8$ are also highly efficient green-emitting phosphors with a broad emission band at about 540 nm corresponding to $4f^05d^1 \rightarrow 4f^1$ transitions of Ce^{3+} . Excitation and emission spectra of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Ce},\text{Na}$ (5 mol%) with two different excitation monitoring wavelengths (400 and 430 nm) are shown in Fig. 7. Evidently, with the dominant excitation band changing from short to long wavelength, the corresponding emission band shifts in the opposite direction, i.e. from long wavelength to short wavelength, which indicates that Ce^{3+} occupies two different Sr sites in $\text{Sr}_2\text{Si}_5\text{N}_8$. Since there is a strong absorption and excitation band in the range of 370 – 450 nm (Fig. 7), perfectly matching with the blue light source of (In,Ga)N-based LED chips, in combination with other phosphors (blue- and red-emitting phosphors), $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Ce}^{3+}$ is capable of generating white-light, in particular as a green-emitting phosphor for use in near UV white LEDs.

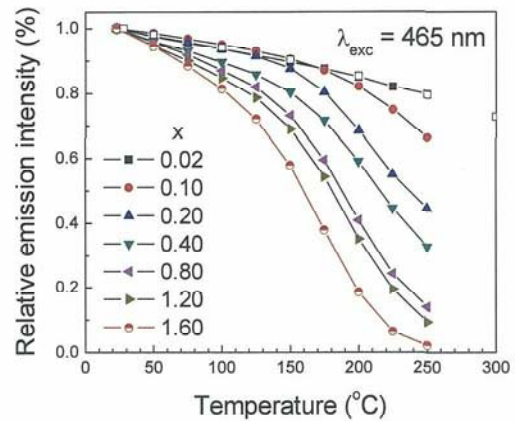


Figure 6 Relative intensity of $\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ as a function of temperature and Eu^{2+} concentration

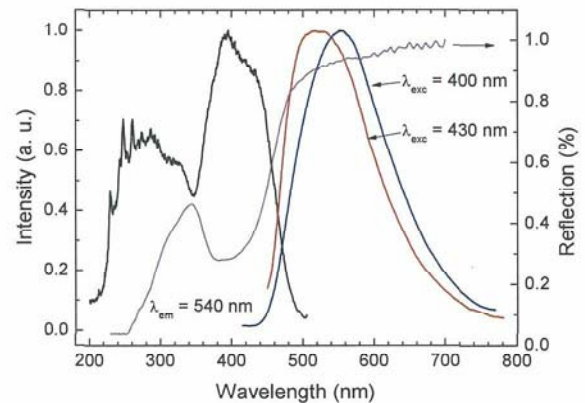


Figure 7 Reflection, excitation and emission spectra of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Ce}^{3+}, \text{Na}^+$

3.2 $\text{MSi}_2\text{N}_2\text{O}_2:\text{Eu}^{2+}$ (M = Ca, Sr, Ba)

Alkaline-earth silicon oxynitride phosphors, $\text{MSi}_2\text{N}_2\text{O}_2:\text{Eu}^{2+}$ (M=Ca, Sr, Ba)⁹, crystallize in the monoclinic crystal system with layered crystal structures, in which the alkaline-earth ion M is located in between layers of interconnected $\text{Si}(\text{O},\text{N})_4$ tetrahedra. In contrast to red-emitting $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Ca, Sr, Ba), as the oxygen ion takes part in the formation of the chemical bonding with the activator ions (Eu^{2+} or Ce^{3+}), with varying types of M, $\text{MSi}_2\text{N}_2\text{O}_2:\text{Eu}^{2+}$ shows blue-green to greenish-yellow emission, which can be efficiently excited in near UV to UV/blue region (370-470 nm), as shown in Fig. 8. $\text{CaSi}_2\text{N}_2\text{O}_2:\text{Eu}^{2+}$ shows a greenish-yellow emission at around 560 nm with the largest full-width half-maximum (FWHM ~ 95 nm) emission bands under near UV to blue light excitation (Fig. 8 (a)). Going from Ca to Sr and Ba, with an increase of the ionic size, $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}^{2+}$ yields efficient green to yellowish-green emission peaking at about 540 nm. While, $\text{BaSi}_2\text{N}_2\text{O}_2:\text{Eu}^{2+}$ emits strong blue-green light in the range of 490 – 505 nm with the

smallest FWHM of about 31 nm. In addition, the Stokes shift decreases in the sequence of Ca > Sr > Ba, correspondingly, the quantum efficiency of $\text{MSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ shows the same tendency under excitation at 405 and 460 nm (Fig. 9) which differs from $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ (M = Ca, Sr, Ba) (see Fig. 5). It is found that the emission bands can be mainly modified by changing the Eu concentration and by mixing Ba, Sr and Ca as well as slightly by the variation of the N/O ratio. For example, the position of the emission band of $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ can be shifted from about 530 to 545 nm by increasing the Eu concentration (Fig. 10) with a lower N/O ratio. In contrast, the emission band of $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ can be further extended to longer wavelengths ranging from 560 to 580 nm for a higher N/O ratio, yielding a yellow emission of Eu^{2+} under nitrogen-rich environment.

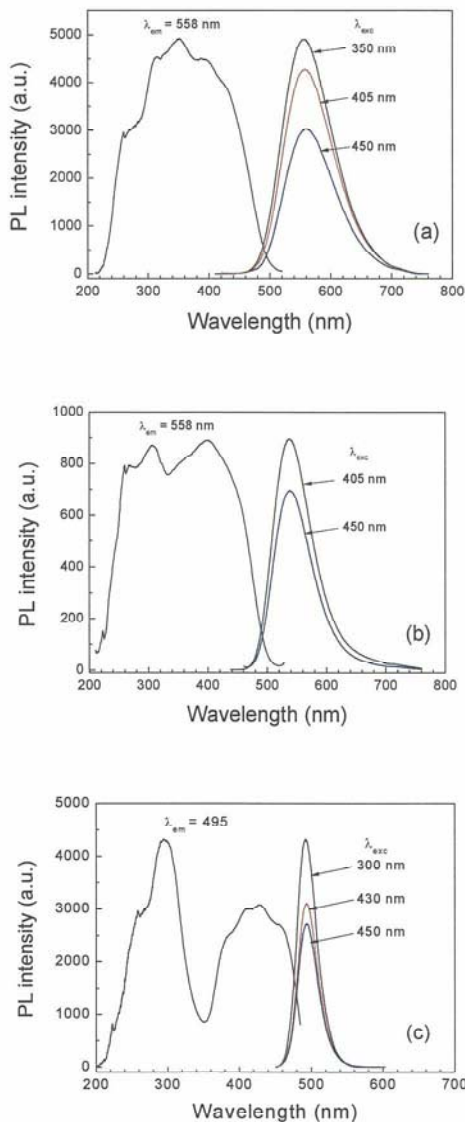


Figure 8 Excitation and emission spectra of $\text{MSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ (2 mol% Eu), (a) M = Ca, (b) M = Sr, (c) M = Ba

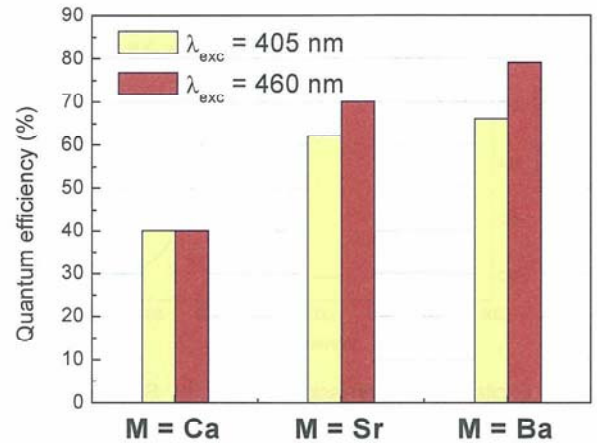


Figure 9 Quantum efficiency of $\text{MSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ at the excitation wavelength of 405 and 460 nm, respectively

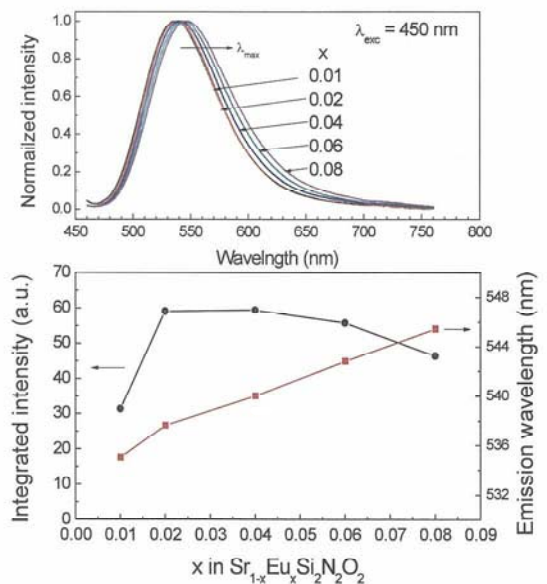


Figure 10 Influence of Eu concentration on emission spectra and integrated emission intensity and emission wavelength of $\text{Sr}_{1-x}\text{Eu}_x\text{Si}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ as a function of x

Similar to $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ (M = Ca, Sr, Ba), the emission intensity of $\text{MSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$ phosphors show exactly the same decreasing tendency against temperature and the thermal quenching rate decreases in the order of Ca < Ba < Sr, as shown in Fig. 11. This probably can be partially explained by more relaxation in the excited state of Eu^{2+} becoming less restricted when the size of the alkaline earth ion decreases¹⁰, in particular for Ca^{2+} , whose ionic size is significantly smaller than that of Eu^{2+} . Moreover, with increasing the temperature the emission band shows

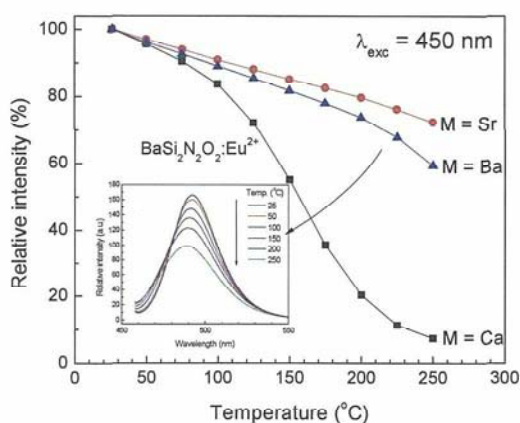


Figure 11 Temperature dependence and emission spectra as a function of temperature (inset) of $MSi_2N_2O_2:Eu^{2+}$ (1 mol% Eu)

a blue shift for all M, which also strongly depends on the type of M, i.e., 3.4, 1.7 and 11 nm for Ba, Sr and Ca, respectively, for Eu concentration of 1 mol%.

3.3 $M_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$ (M = Ca, Y, x = m/valence)

Closely related to the α - Si_3N_4 structure, $Ca_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}:Eu^{2+}$ (α -Sialon)¹¹⁻¹² and $Ca_{x/2}Si_{12-x}Al_xN_{16}:Eu^{2+}$ show highly efficient yellow-to-orange emission peaking from 580 to 595 nm with varying Eu concentration and the composition of the host lattice (i.e., x, m and n) in the excitation range of 370 - 450 nm (Fig. 12). Apart from a good thermal stability, the quantum efficiency can reach up to about 80%. With a decrease of oxygen content in Ca- α -Sialon, although the crystal structure slightly deviates from a regular hexagonal system, the luminescence properties of $Ca_{x/2}Si_{12-x}Al_xN_{16}:Eu^{2+}$ are similar to that of oxygen-rich Ca- α -Sialon: Eu^{2+} due to their strongly similar crystal structure/local environment around Eu^{2+} . As a yellow-emitting phosphor, similar to YAG: Ce^{3+} , $M_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}:Eu^{2+}$ itself can produce white light combined with a blue-emitting LED chip.

3.4 Carbide-nitride phosphors

Rare-earth silicon carbide-nitrides, with an ideal formula $Ln(I)Ln(II)Si_4N_6C$ (Ln = Y, Ce, La, Eu and Tb), have a special local structure in its network. An unusual long-wavelength 4f-5d excitation band of Ce^{3+} is observed when doped in $Ln(I)Ln(II)Si_4N_6C$ due to the highly covalent silicon-nitride-carbide network and strong crystal field strength on the dopant Ln sites¹³. Ce^{3+} -doped $Y_2Si_4N_6C$ shows a strong blue-green color in daylight. In the reflection spectra of Ce^{3+} -doped $Y_2Si_4N_6C$, there are two obvious absorption bands centered at about 380 nm and 427 nm which are definitely related to the Ce^{3+} absorption because no absorption band in this range can

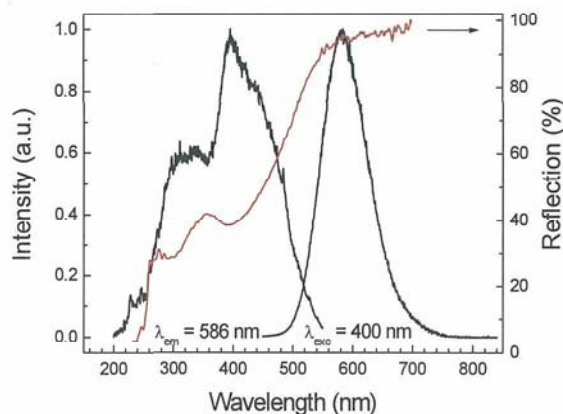


Figure 12 Excitation, emission and reflection spectra of $CaAl_2Si_{10}N_{16}:Eu^{2+}$ (4 mol% Eu)

be found for undoped $Y_2Si_4N_6C$. In addition, a weak absorption shoulder at about 495 nm can possibly also be assigned to the Ce^{3+} ions, because with increasing Ce^{3+} concentration this absorption shoulder becomes stronger (Fig. 13). Ce^{3+} -doped $Y_2Si_4N_6C$ shows a green emission with maxima in the range of 530 - 560 nm depending on the Ce^{3+} concentration (not shown in Fig. 13). The broad emission band in the range of 450 - 800 nm is ascribed to the transition from the lowest energy crystal field splitting component of the 5d level to the 4f ground state of Ce^{3+} . As $Y_2Si_4N_6C:Ce^{3+}$ can be efficiently stimulated in the UV/blue range (370 - 450 nm), it shows high promise for use as a conversion phosphor for white LEDs.

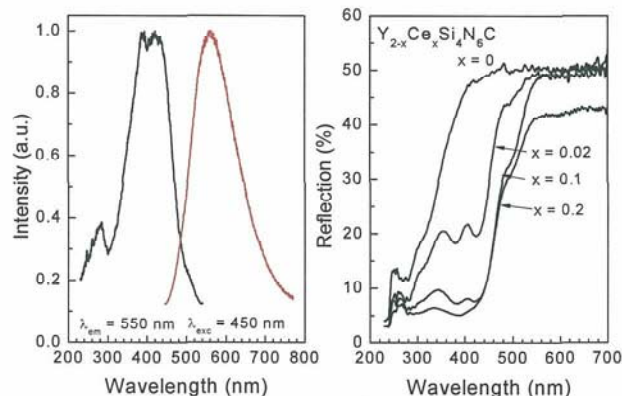


Figure 13 Excitation, emission and reflection spectra of $Y_2Si_4N_6C:Ce^{3+}$ (1-10 mol%)

Conclusions

Eu^{2+} - and Ce^{3+} -doped alkaline-earth-silicon-nitride based materials, in particular with Eu^{2+} as an activator, can be efficiently stimulated by near-UV and blue-LED radiation, converting the absorbed radiation in green, yellow and red emission, covering the whole visible

spectral range. Given the high quantum efficiency, high chemical and thermal stability in the near-UV/blue region, along with good compatible composition, orange-red emitting $M_2Si_5N_8:Eu^{2+}$ ($M = Ca, Sr, Ba$) and green-emitting $MSi_2N_2O_2:Eu^{2+}$ ($M = Ba, Sr$) have turned out to be good candidate conversion phosphors for use in both near UV- and blue-LEDs. In addition, many new ternary and multinary nitride based phosphors with unconventional or improved properties are expected to be discovered in the near future for white LEDs.

References

- (1) TASO, J.Y., Ed. :Light emitting diodes (LEDs) for general illumination, Update2002, Optoelectronics Industry Development Association, Washington, DC (2002).
- (2) Zukauskas, A., Shur, M.S. and Gaska, R.: Introduction to Solid-State Lighting, John Wiley & Sons, Inc., New York (2002).
- (3) NARUKAWA, Y.: White light LEDs, Optic & Photonics News, No.4, pp.25-29 (2004).
- (4) NAKAMURA, S.: Candela-class high-brightness InGaN/AlGaIn double-heterostructure blue-light-emitting diodes, Appl. Phys. Lett., Vol.64(13), pp 1687-1689 (1994).
- (5) van KREVEL, J.W.H., HINTZEN, H.T., METSELAAR, R. and MEIJERINK, A.: Long wavelength Ce^{3+} emission in Y-Si-O-N materials, J. Alloys Comp., Vol. 268(6), pp.272-277 (1998).
- (6) van KREVEL, J.W.H.: On new rare-earth doped M-Si-Al-O-N materials: Luminescence properties and oxidation resistance, PhD thesis, Eindhoven University of Technology (2000).
- (7) HÖPPE, H.A., LUTZ, H., MORYS, P., SCHNICK, W. and SEILMEIER, A.: Luminescence in Eu^{2+} doped $Ba_2Si_5N_8$: fluorescence thermoluminescence, and upconversion, J. Phys. Chem. Solids, Vol.61, pp.2001-2006 (2000).
- (8) LI, Y.Q., van STEEN, J.E.J., van KREVEL J.W.H., BOTTY, G., DELSING, A.C.A., DISALVO, F.J., de WITH G. and HINTZEN, H.T.: Luminescence properties of red-emitting $M_2Si_5N_8:Eu^{2+}$ ($M = Ca, Sr, Ba$) LED conversion phosphors, J. Alloys Comp. Vol.417(1-2), pp.273-279 (2006).
- (9) LI, Y.Q., DELSING, A.C.A., de WITH, G. and HINTZEN, H.T.: Luminescence properties of Eu^{2+} -activated alkaline-earth silicon-oxynitride $MSi_2O_2\delta N_{2+2\delta}$ ($M = Ca, Sr, Ba$): a promising class of novel LED conversion phosphors, Chem. Mater., Vol.17(12), pp.3242-3248 (2005).
- (10)BLASSE, G. and GRABMAIER, B.C.: Luminescent Materials, Springer-Verlag, Berlin (1994).
- (11)van KREVEL, J.W.H., van RUTTEN, J.W.T., MANDAL, H., HINTZEN, H.T. and METSELAAR, R.: Luminescence properties of terbium-, cerium-, or europium-doped α -SiAlON materials, J. Solid State Chem., Vol.165, pp.19-24, (2002).
- (12)XIE, R.J., MITOMO, M. UHEDA, K., XU, F.F. and AKIMUNE, Y.: Preparation and luminescence spectra of calcium- and rare-earth- ($R = Eu, Tb, \text{ and } Pr$) codoped α -SiAlON ceramics, J. Am. Ceram. Soc., Vol.85(5), pp.1229-1234 (2002).
- (13)Li, Y.Q.: Structure and luminescence properties of novel rare-earth doped silicon nitride based materials, Ph.D. thesis, Eindhoven University of Technology (2005).

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