J Electroceram (2008) 21:370–373
DOI 10.1007/s10832-007-9202-7

Oxynitride/nitride phosphors for white light-emitting diodes (LEDs)

Rong-Jun Xie · Naoto Hirosaki · Mamoru Mitomo

Abstract Oxynitride/nitride phosphors have attracted significant attention recently because they have promising luminescence properties and superior thermal and chemical stabilities which predestinates them for use in white LEDs to generate white light. This paper reports on luminescence spectra of Eu^{2+} or Ce^{3+}-activated α-SiAlON, β-SiAlON, and alkaline earth silicon nitride ($M_2Si_5N_8$, M = Ca, Sr, Ba). A single broad emission band is observed for all samples, and the emission color depends on the type of activators and host lattice: α-SiAlON:Ce^{3+} (blue), α-SiAlON:Eu^{2+} (yellow), β-SiAlON:Eu^{2+} (green), and $M_2Si_5N_8$:Eu^{2+} (red). The excitation spectrum of these oxynitride/nitride phosphors covers a wide range from ultraviolet to visible light, enabling them to be used for white LEDs when an ultraviolet or blue LED chip is combined.

Keywords Oxynitride · Phosphor · Luminescence · White light-emitting diodes

1 Introduction

White light-emitting diodes (LEDs) are attracting significant attention in recent years because they are a new, ultra efficient, low power and environment friendly lighting system [1]. They are supposed to replace traditional incandescent and fluorescent bulbs, and are suitable for backlights for portable electronics, medical and automotive applications. Three general approaches are available for generating white light from LEDs. The first method directly mixes light from red, green and blue (RGB) LEDs to produce a white source. The second technology uses a blue LED to pump one or more visible light-emitting phosphors integrated into the phosphor-converted LED package. The third way uses an ultraviolet LED to pump a combination of red, green and blue phosphors. For white LED lamps that use phosphor down-conversion of blue or UV light, the development of new phosphors is a key requirement to enable improvements in color temperature and color rendering, and to open up new markets for LEDs.

The requirements for phosphors used in white LEDs include that (1) the excitation wavelength of phosphors must match well with the emission wavelength of the LED chips; (2) the phosphor must absorb strongly at the emission wavelength of the LED chips; (3) the phosphors must have high quantum efficiency; and (4) the phosphor must be stable against moisture, temperature and electromagnetic irradiation. At present, commonly used phosphors for white LEDs are mostly based on sulfides and oxides, for example, ZnS:Cu, Al [2, 3], $SrGa_2S_4$:Eu^{2+} [4], YAG:Ce^{3+} [1], and CaS:Eu^{2+} [5]. These phosphors, typically sulfide phosphors, have low thermal or chemical stability, resulting in a strong temperature dependence of chromaticity as well as the degradation in efficiency of white LED devices. On the other hand, most oxide-based phosphors cannot absorb visible light efficiently, making them impossible to combine with blue LEDs to generate white light. Therefore, novel phosphor materials with superior properties are in great demand. Recently, oxynitride/nitride-based phosphors, for example, rare earth-activated α-SiAlON, are reported to have unusual photoluminescence properties [6–11]. In addition, theses phosphors are expected to have excellent chemical and thermal stabilities because their basic crystal

R.-J. Xie (✉) · N. Hirosaki · M. Mitomo
National Institute for Materials Science,
Namiki 1-1, Tsukuba,
Ibaraki 305-0044, Japan
e-mail: xie.rong-jun@nims.go.jp

structure is built on rigid tetrahedral networks, either of the Si–(O, N) or Al–(O, N) type.

In this article, three oxynitride/nitride phosphors are introduced. They are α-SiAlON:RE (RE = Eu^{2+} and Ce^{3+}), β-SiAlON:Eu^{2+}, and alkaline-earth silicon nitride ($M_2Si_5N_8$:Eu^{2+}, M = Ca, Sr, and Ba). The structure of α-SiAlON is derived from α-Si_3N_4 by substitution of Al–O and Al–N for Si–N, and its chemical composition can be written as $M_{m/\nu}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ (M = Ca, Li, Mg, Y and lanthanides with a valence of ν) [12, 13]. α-SiAlON has a hexagonal crystal structure and the P31c space group. The structure of β-SiAlON is derived from β-Si_3N_4 by equivalent substitution of Al–O for Si–N, and its chemical composition can be written as $Si_{6-z}Al_zO_zN_{8-z}$ (z represents the number of Al–O pairs substituting for Si–N pairs and $0<z\leq4.2$) [12, 13]. β-SiAlON has a hexagonal crystal structure and the $P6_3$ space group. Alkaline-earth silicon nitrides are reported by Schnick et al. [14, 15], synthesized by reaction of silicon diimide with metallic calcium, strontium and barium under N_2. $Ca_2Si_5N_8$ has a monoclinic crystal structure with Cc space group. Both $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$ have an orthorhombic structure with $Pmn2_1$ space group. We investigate the photoluminescence properties of these phosphors from a viewpoint of their applications in white LED lamps, and demonstrate that these novel phosphors, excited either by UV or blue LEDs, are suitable for white LED applications.

2 Experimental procedure

Ca-α-SiAlON:RE (RE = Eu^{2+} and Ce^{3+}) samples, with the compositions of $(Ca_{1-2x/\nu}RE_x)_{m/2}Si_{12-m-n}Al_{m+n}O_nN_{16-n}$, were prepared from α-$Si_3N_4$ (SN-E10, Ube Industries, Ube, Japan), AlN (Tokuyama Corp., Type F, Tokyo, Japan), $CaCO_3$ (Kojundo Chemical Laboratory Co. Ltd., Tokyo, Japan), and rare earth oxides (Shin-Etsu Chemical Co. Ltd., Tokyo, Japan). The powder mixture was sintered at 1700 °C for 2 h under 0.5 MPa N_2. The Eu^{2+}-activated β-SiAlON phosphor, starting from Si_3N_4, AlN, and Eu_2O_3, was synthesized at 1900 °C for 8 h under 1.0 MPa N_2. For preparation of $M_2Si_5N_8$:Eu^{2+}, a different method from Schnick's was used. α-Si_3N_4, M_3N_2 (M = Ca, Sr, Ba) (Kojundo Chemical Laboratory Co. Ltd., Tokyo, Japan) and EuN were used as starting materials. EuN was synthesized by nitridation of metallic europium. The $M_2Si_5N_8$:Eu^{2+} phosphors were synthesized at 1600 °C for 2 h under 0.5 MPa N_2.

The photoluminescence spectra were measured at room temperature using a fluorescent spectrophotometer (F-4500, Hitachi Ltd., Tokyo, Japan) with a 150 W Ushio xenon short arc lamp. The emission spectrum was corrected for the spectral response of a monochromater and Hamamatsu R928P photomultiplier tube by a light diffuser and tungsten lamp. The excitation spectrum was also corrected for the spectral distribution of the xenon lamp intensity by measuring rhodamine-B as a reference.

3 Results and discussion

3.1 α-SiAlON:Ce^{3+}, Eu^{2+} phosphors

Figure 1(a) illustrates the luminescence spectra of 10 at% Ce^{3+}-activated α-SiAlON blue phosphors. A broad emission band (400–650 nm) with the peak wavelength located at 485 nm is observed, which is characteristic of the $4f^05d^1$ →

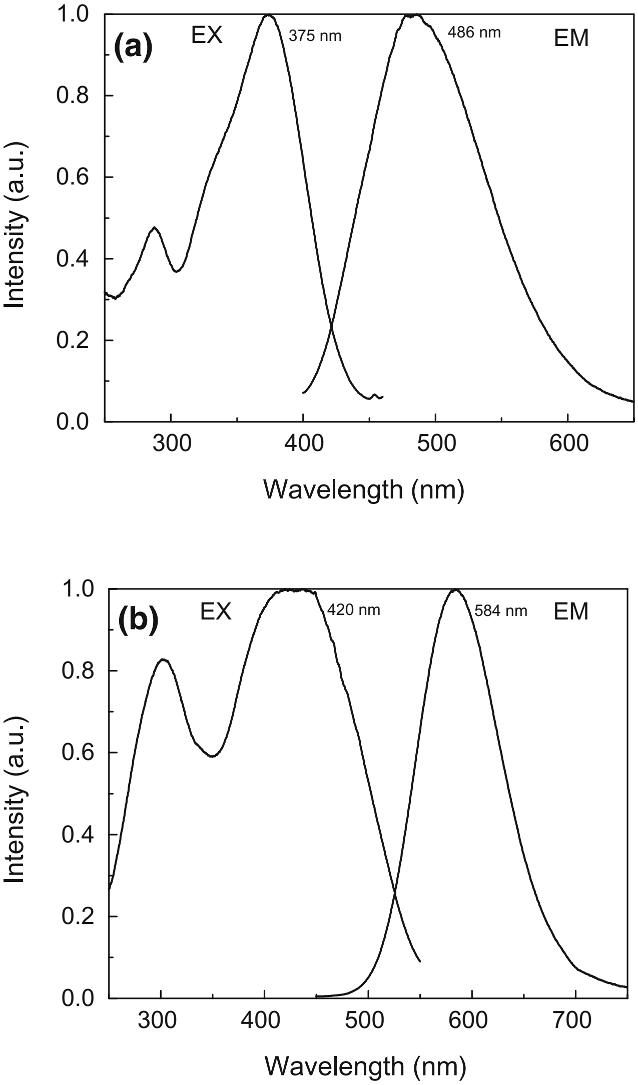

Fig. 1 Excitation and emission spectra of (**a**) 10 at% Ce^{3+}-activated α-SiAlON (m=1, n=0.5). The excitation spectrum was monitored at λ_{em}=485 nm and the emission spectrum was recorded at λ_{ex}=375 nm; (**b**) 7.5 at% Eu^{2+}-activated α-SiAlON (m=2.5, n=1.25). The excitation spectrum was monitored at λ_{em}=584 nm and the emission spectrum was recorded at λ_{ex}=420 nm

$4f^1$ Ce^{3+} emission. The full width of half maximum is 109 nm. The excitation spectrum shows several peaks with the maximum one around 375 nm. This means the blue α-SiAlON:Ce^{3+} phosphor can be excited efficiently by ultraviolet LEDs with the primary emission wavelength of 365–380 nm. The optimal concentration of Ce^{3+} at which the emission intensity is strongest is about 25 at% [16].

Figure 1(b) shows the excitation and emission spectra of 7.5 at% Eu^{2+}-activated α-SiAlON yellow phosphors. Like Ce^{3+}, the Eu^{2+} emission, due to the $4f^65d^1 \rightarrow 4f^7$ electronic transitions, also displays a broad band covering from 500 to 750 nm, the maximum peak value being located at 584 nm. The full width of half maximum is 94 nm. The excitation spectrum of Eu^{2+} has two broad bands with peaks at 300 and 420 nm, respectively. The excitation spectrum flattening is clearly seen at 400–450 nm, which matches well with the emission of near ultraviolet (390–410 nm) or blue (450–470 nm) LEDs. Compared to commonly used YAG:Ce^{3+} yellow phosphor, the α-SiAlON:Eu^{2+} phosphor has a longer emission wavelength, and is suitable for generating warm white light when coupled to a blue LED chip [9, 17].

Both the emission of Ce^{3+} and Eu^{2+} in α-SiAlON can be varied in a wide range by controlling the composition of the host matrix [10, 16]. It implies that the emission color of α-SiAlON phosphors is tunable, which is of great importance for phosphor design and practical applications.

3.2 β-SiAlON:Eu^{2+} green phosphor

Recently Hirosaki et al. [18] have reported that strong green emission can be observed in β-SiAlON when doped with dilute divalent europium. Figure 2 show the luminescence spectra of Eu^{2+} activated β-SiAlON phosphors. The broad emission spectrum has a maximum peak at 538 nm with a full width of half maximum of 55 nm. Two well-resolved broadbands centered at 303 and 400 nm are observed in the excitation spectrum. The broad excitation rang enables the β-SiAlON:Eu^{2+} phosphor to emit strongly under near UV (390–410 nm) or blue (450–470 nm) light excitation. Compared to ZnS:Cu, Al and $Y_3Al_5O_{12}$:Ce^{3+} green phosphors, the β-SiAlON:Eu^{2+} phosphor has better color saturation and thermal stability [18].

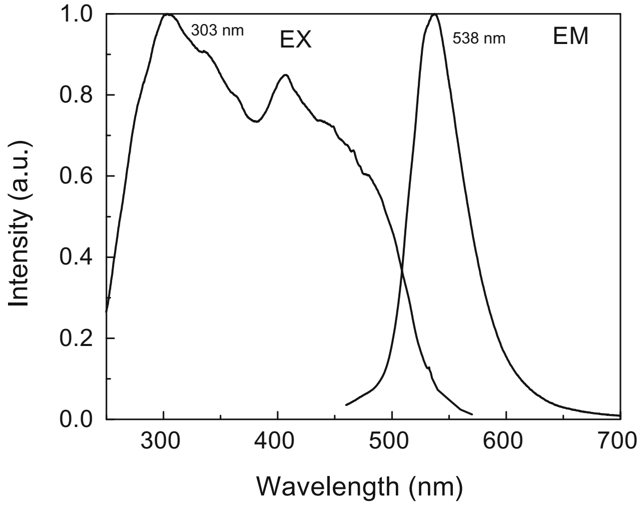

Fig. 2 Excitation and emission spectra of 0.3 at% Eu^{2+}-activated β-SiAlON (z=0.17). The excitation spectrum was monitored at λ_{em}= 538 nm and the emission spectrum was recorded at λ_{ex}=303 nm

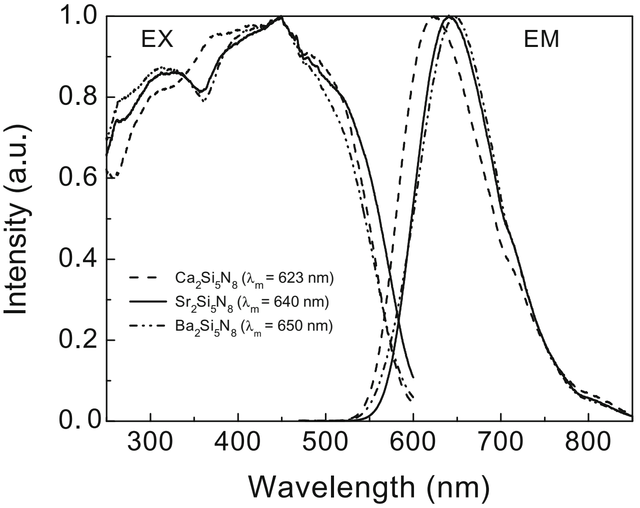

Fig. 3 Excitation and emission spectra of 10 at% Eu^{2+}-activated $M_2Si_5N_8$ (M = Ca, Sr, Ba). The excitation spectrum was monitored at λ_{em}=623, 640 and 650 nm for Ca, Sr, and Ba, respectively, and the emission spectrum was recorded at λ_{ex}=450 nm

3.3 $M_2Si_5N_8$:Eu^{2+} red phosphors

The luminescence of $Ba_{2-x}Eu_2Si_5N_8$ prepared by reaction of silicon diimide and metallic barium and europium has been reported by Hoppe et al. [6]. In our case, alkaline earth silicon nitride was prepared by a solid state reaction between metallic nitrides. Figure 3 shows the luminescence spectra of $M_2Si_5N_8$:$10Eu^{2+}$ (M = Ca, Sr and Ba) phosphors. A single emission band is centered at 623, 640 and 650 nm for Ca, Sr, and Ba, respectively. A red-shift of emission wavelength is observed with increasing the ionic size of alkaline earth metals. The excitation spectrum extensively shifts to long-wavelength side, with the peak located at

Table 1 Characteristics of oxynitride/nitride phosphors.

Phosphors	EX (nm)	EM (nm)	Emission color
α-SiAlON:Ce^{3+}	375	485	Blue
α-SiAlON:Eu^{2+}	420	584	Yellow
β-SiAlON:Eu^{2+}	303	538	Green
$M_2Si_5N_8$:Eu^{2+} (M = Ca, Sr, Ba)	450	620–650	Red

450 nm for all samples. It is due to the fact that the Eu^{2+} ions are coordinated to nitrogen only, which causes strong nephelauxetic effect. The excitation spectrum resembles each other, indicating the chemical environment of Eu^{2+} in these materials is very similar. It is seen from the PL spectra that red $M_2Si_5N_8:Eu^{2+}$ phosphors can be used in both ultraviolet (360–410 nm) and blue (450–470 nm) LEDs to generate white light.

3.4 Applications

Table 1 summarizes the luminescence properties and emission colors of oxynitride/nitride phosphors described above. It is possible to develop three kinds of white LED lamps by using these phosphors: (1) α-SiAlON:Ce^{3+} (blue), β-SiAlON:Eu^{2+} (green) and $M_2Si_5N_8:Eu^{2+}$ (red) phosphors excited by an ultraviolet LED; (2) a yellow α-SiAlON:Eu^{2+} phosphor combined to a blue LED (bi-chromatic LED). A warm white LED lamp has been reported by Sakuma et al. [17], which has a luminous efficacy of 42 lm/W, a color rendering index (CRI) of 56, and a corrected color temperature of 2700 K, operated at a forward-bias current of 20 mA at room temperature; (3) β-SiAlON:Eu^{2+} (green) and $M_2Si_5N_8:Eu^{2+}$ (red) phosphors excited by a blue LED, this kind of white LED is supposed to have a higher color rendering index.

4 Conclusion

Several oxynitride/nitride phosphors, α-SiAlON:Ce^{3+} (blue), α-SiAlON:Eu^{2+} (yellow), β-SiAlON:Eu^{2+} (green) and $M_2Si_5N_8:Eu^{2+}$ (red), were prepared by a solid-state reaction, and their luminescence properties were investigated. These novel phosphors can be excited efficiently either by ultraviolet or blue light radiation, and are suitable for white LEDs to generate white light when combined with ultraviolet or blue LED chips.

References

1. S. Nakamura, G. Fasol, *The Blue Laser Diode: GaN Based Light Emitters and Lasers*. (Springer, Berlin, 1997)
2. Y. Sato, N. Takahashi, S. Sato, Jpn. J. Appl. Phys. **35**, L838 (1996)
3. Y. Narukawa, I. Niki, K. Izuno, M. Yamada, Y. Murazaki, T. Mukai, Jpn. J. Appl. Phys. **41**, L371 (2002)
4. Y.D. Huh, J.H. Shim, Y. Kim, Y.R. Do, J. Electrochem. Soc. **150**, H57 (2003)
5. N. Yamashita, O. Harada, K. Nakamura, Jpn. J. Appl. Phys. **34**, 5539 (1995)
6. H.A. Hoppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, J. Phys. Chem. Solids, **61**, 2001 (2000)
7. R.J. Xie, M. Mitomo, K. Uheda, F.F. Xu, Y. Akimune, J. Am. Ceram. Soc. **85**, 1229 (2002)
8. R.J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, N. Ohashi, J. Am. Ceram. Soc. **87**, 1368 (2004)
9. R.J. Xie, N. Hirosaki, K. Sakuma, Y. Yamamoto, M. Mitomo, Appl. Phys. Lett. **84**, 5404 (2004)
10. R.J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T. Suehiro, K. Sakuma, J. Phys. Chem. B **108**, 12027 (2004)
11. R.J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T. Suehiro, T. Sekiguchi, J. Phys. Chem. B **109**, 9490 (2005)
12. G.Z. Cao, R. Metselaar, Chem. Mater. **3**, 242 (1991)
13. T. Ekstrom, M. Nygren, J. Am. Ceram. Soc. **75**, 259 (1992)
14. T. Schlieper, W. Schnick, Z. Anorg. Allg. Chem. **621**, 1037 (1995)
15. T. Schlieper, W. Milius, W. Schnick, Z. Anorg. Allg. Chem. **621**, 1380 (1995)
16. R.J. Xie, N. Hirosaki, M. Mitomo, T. Suehiro, X. Xin, H. Tanaka, J. Am. Ceram. Soc. **88**, 2883 (2005)
17. K. Sakuma, K. Omichi, N. Kimura, M. Ohashi, D. Tanaka, N. Hirosaki, Y. Yamamoto, R.J. Xie, T. Suehiro, Opt. Lett. **29**, 2001 (2004)
18. N. Hirosaki, R.J. Xie, K. Kimoto, T. Sekiguchi, Y. Yamamoto, T. Suehiro, M. Mitomo, Appl. Phys. Lett. **86**, 211905 (2005)