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Characterization and properties of green-emitting β-SiAlON:Eu^{2+} powder phosphors for white light-emitting diodes

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This letter reports a β-SiAlON:Eu^{2+} green phosphor with the composition of $Eu_{0.00296}Si_{0.41395}Al_{0.01334}O_{0.0044}N_{0.56528}$. The phosphor powder exhibits a rod-like morphology with the length of ~4 μm and the diameter of ~0.5 μm. It can be excited efficiently over a broad spectral range between 280 and 480 nm, and has an emission peak at 535 nm with a full width at half maximum of 55 nm. It has a superior color chromaticity of $x=0.32$ and $y=0.64$. The internal and external quantum efficiencies of this phosphor is 70% and 61% at $\lambda_{ex}=303$ nm, respectively. This newly developed green phosphor has potential applications in phosphor-converted white LEDs. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1935027]

White light-emitting diodes (LEDs), the so-called next-generation solid-state lighting, offer benefits in terms of reliability, enegy-saving, maintenance and safety, and therefore are gaining much attention. The availability of white LEDs should open up a great number of exciting new application fields: white light sources to replace traditional incandescent and fluorescent lamps, backlights for portable electronics, medical, and architecture lightings, etc. The first commercially available white LED based on phosphors was produced in 1996, which is combining a blue light emitting InGaN with a yellow $(Y_{1-a}Gd_a)_3(Al_{1-b}Ga_b)O_{12}:Ce^{3+}$(YAG:Ce) phosphor.[1] However, this type of white light has poor color rendering caused by the color deficiency in the red- and blue-green of the phosphor. The alternative ways to achieve white light are using an UV LED with RGB (red, green, and blue) phosphors,[2–4] or coupling a blue LED to RG phosphors,[5] for a high color rendering index (CRI) and a high power output. For this, both of these methods require efficient green phosphors that should have the excitation wavelength matching with the emission wavelength of the UV LEDs (λ_{em} =350–410 nm) or the blue LEDs (λ_{em}=450–470 nm). Currently, the green phosphors used for white LEDs are mostly based on sulfides, for example, ZnS:Cu, Al,[2,3] or $SrGa_2S_4:Eu^{2+}$.[4] However, the sulfide-based phosphors have low chemical stabilities, causing the strong temperature dependence of chromaticity and degradation of the luminous efficiency of the white LEDs. Therefore, it is necessary to develop alternative green phosphors with comparable or superior performance to the sulfides.

Rare-earth doped oxynitride or nitride phosphors have been found to have longer excitation and emission wavelengths compared to their oxidic counterparts.[6–9] The luminescence is attributable to the strong nephelauxetic effect and large crystal field splitting as the activator ions are coordinated to nitrogen. Besides this, the oxynitride or nitride phosphors are expected to have high thermal and chemical stabilities because the crystal structure of the host lattice is built on stiff frameworks consisting of Si–N or Al–N tetrahedra. We have developed a yellow oxynitride phosphor based on Eu^{2+}-doped Ca-α-SiAlON, which absorbs strongly over a broad range from UV to visible spectral region.[9–11] A warm white LED device has been developed by using this yellow phosphor and a blue LED chip.[12]

In this letter, we will report a green oxynitride phosphor which is suitable for use in white LEDs: Eu^{2+}-activated β-SiAlON. 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 $0<z\leqslant 4.2$).[13,14] β-SiAlON has a hexagonal crystal structure and the $P6_3$ space group. In this structure there are continuous channels parallel to the c direction. The Eu^{2+}-activated β-SiAlON phosphor, with the composition of $Eu_{0.00296}Si_{0.41395}Al_{0.01334}O_{0.0044}N_{0.56528}$, was prepared from 94.77 mass % Si_3N_4, 2.68 mass % AlN, and 2.55 mass % Eu_2O_3. The powder mixture was then synthesized at 1900 °C

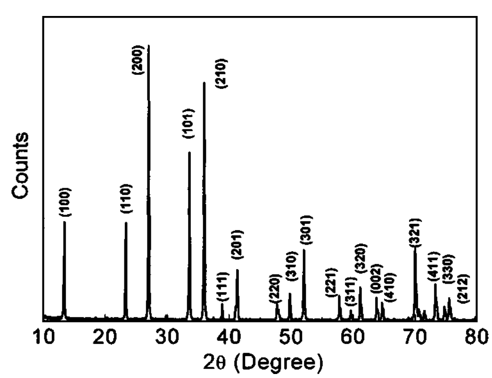

FIG. 1. X-ray diffraction pattern of Eu^{2+}-doped β-SiAlON.

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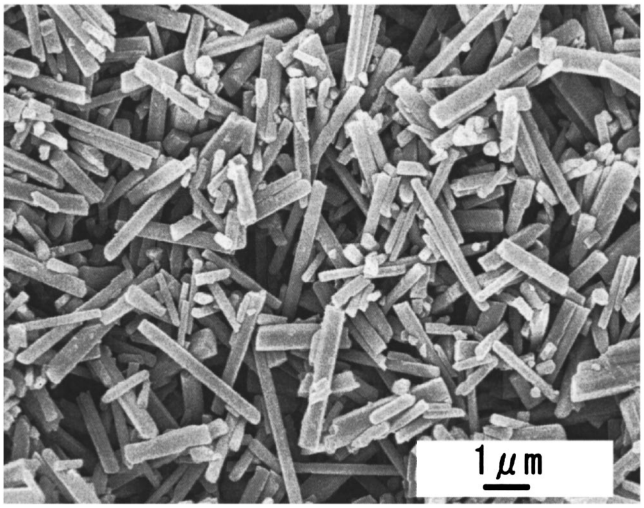

FIG. 2. Scanning electron microscopy image of Eu^{2+}-doped β-SiAlON particles.

for 8 h in a 10 atm nitrogen atmosphere. The product phase was identified by x-ray diffraction (Model RINT2500, Rigaku, Tokyo, Japan) using Cu $K\alpha$ radiation. The chemical composition of the sample was measured by an induction coupled plasma method (ICP) and an oxygen-nitrogen analyzer (TC-436, LECO). The photoluminescence spectra of the powder phosphor were measured by a fluorescence spectrophotometer (Model F-4500, Hitachi) at room temperature. The cathodoluminescence study was performed with an electron beam of 5 kV and 200 pA at room temperature.

Figure 1 shows the x-ray diffraction pattern of the synthesized sample. Obviously, the product is a single phase of β-Si_3N_4 or β-SiAlON and free of secondary phases. The well-defined sharp diffraction peaks imply that the particles have high crystallinity. The lattice parameters calculated from the XRD measurement are a=7.6090 Å and c =2.9115 Å for this phase. The lattice constants are larger than those of β-Si_3N_4 (a=7.5950 Å and c=2.9023 Å),[15] suggesting that the synthesized powder is a solid solution of β-Si_3N_4, i.e., β-SiAlON. Quantitative analysis of the sample shows the constituent elements in mass percent of 2.16 for Eu, 55.6 for Si, 1.64 for Al, 38.0 for N, and 2.1 for O. This gives the composition of the synthesized powder of $Eu_{0.0029}Si_{0.40427}Al_{0.0121}O_{0.02679}N_{0.55391}$. In comparison with the nominal composition, the measured composition has

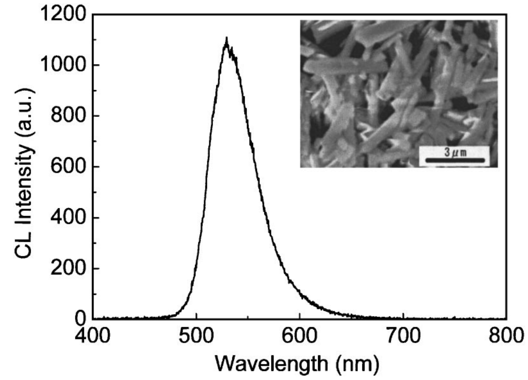

FIG. 4. Cathodoluminescence (CL) spectrum of Eu^{2+}-doped β-SiAlON. The upper-right inset shows its monochromatic CL image.

comparable Eu, Si, Al, and N contents but possesses extremely high oxygen content. The high oxygen content arises from the inherent surface oxides in the Si_3N_4 and AlN starting powders. The z value for the measured composition is calculated as 0.17 using the Si/Al ratio, which is close to 0.14 determined from the lattice constants.

Figure 2 shows the scanning electron microscopy (SEM) image of the β-SiAlON powder phosphor. The powder consists of rod-like crystals which have a uniform size of 4 μm in length and 0.5 μm in diameter. The fine structure of the β-SiAlON crystal was further analyzed by high-resolution transmission electron microscopy (HRTEM) as shown in Fig. 3(a). The marked interplanar d spacing (0.3 nm) corresponds to that of the (100) lattice plane of β-SiAlON. An ultrathin amorphous layer, with the thickness of 0.7 nm, is observed on its surface. Analyzed by TEM-EELS [Fig. 3(b)], Eu atoms are homogeneously distributed both near the edge and at the center of the β-SiAlON particles. It suggests that the Eu atoms are not segregated on the amorphous surface layer or on the crystals defect sites but coordinated on a specific atomic site (e.g., the channels) in the β-SiAlON structure.

The luminescence properties of the powder phosphor, especially its uniformity, can be characterized by means of CL.[16] A typical CL spectrum of the β-SiAlON phosphor is shown in Fig. 4. A broadband emission centered at 530 nm is observed. To elucidate the variation of the luminescence intensity among different particles, the monochromatic CL image was taken (wavelength=530 nm), as shown in the insert in Fig. 3. The particles are seen as rods with uniform bright-

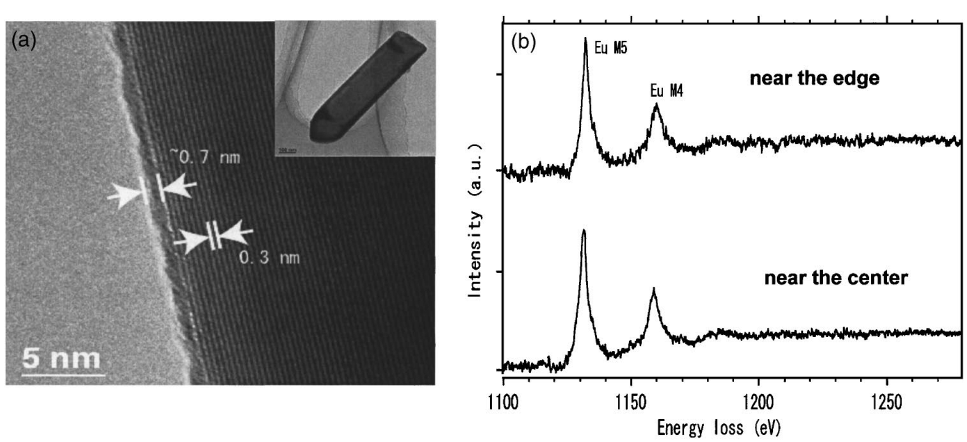

FIG. 3. (a) High-resolution transmission electron microscopy (HRTEM) image of β-SiAlON crystals and (b) the distribution of Eu near the edge and in the center of β-SiAlON.

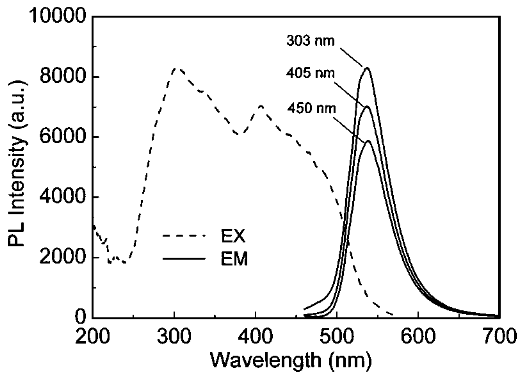

FIG. 5. Photoluminescence spectra of Eu^{2+}-doped β-SiAlON (λ_{em} =535 nm for excitation and λ_{ex}=303, 405, and 450 nm for emission).

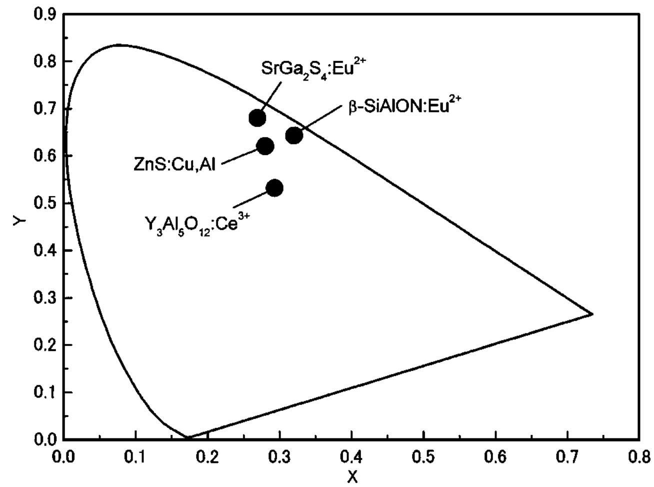

FIG. 6. Chromaticity coordinates of Eu^{2+}-doped β-SiAlON phosphors.

ness. Even for each rod-like particle the luminescence intensity is also uniform. Moreover, this confirms that the doped β-SiAlON particle itself gives the green emission.

The PL spectra of the powder phosphor are shown in Fig. 5. The phosphor exhibits an intense green emission upon UV or visible light excitation. The emission spectrum consists of a single broadband with a maximum at 535 nm, which can be ascribed to the allowed $4f \rightarrow 5d$ transitions of Eu^{2+}. The full width at half maximum of the emission band is about 55 nm. Upon varying the excitation wavelength there is no significant changes in the emission spectrum except the emission intensity. It indicates the presence of only one kind of Eu^{2+} site. Two well-resolved broadbands centered at 303 and 400 nm and a number of shoulders are observed in the excitation spectrum. The structure in the excitation spectrum is due to the crystal field splitting of the 5d level of the Eu^{2+} ions.

External (η_0) and internal (η_i) quantum efficiencies (QEs) were calculated by using the following equations:[17]

$$\eta_0 = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda E(\lambda) d\lambda}$$

$$\eta_i = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda [E(\lambda) - R(\lambda)] d\lambda},$$

where $E(\lambda)/h\nu$, $R(\lambda)/h\nu$, and $P(\lambda)/h\nu$ are the number of photons in the spectrum of excitation, reflectance, and emission of the phosphor, respectively. The reflection spectrum of Spectralon diffusive white standards is used for calibration (the reflectivity is nearly 100% in the range of 200–900 nm). At current synthesis conditions, the internal quantum efficiency of the β-SiAlON:Eu^{2+} phosphor is 70%, 54%, and 50% at the excitation wavelength of 303, 405, and 450 nm, respectively, and the corresponding external quantum efficiency is 61%, 41%, and 33%.

Figure 6 shows the Commission International de l'Eclairage (CIE) chromaticity coordinates of the β-SiAlON:Eu^{2+} phosphor. The chromaticity coordinates of the β-SiAlON:Eu^{2+} phosphor are x=0.32 and y=0.64. It is significantly better than that of $Y_3Al_5O_{12}$:Ce^{3+}, and is superior to ZnS:Cu, Al in color saturation. As seen in the PL spectra, the β-SiAlON:Eu^{2+} phosphor has strong green emission under the UV (350–410 nm) or blue (450–470 nm) light excitation. It means the β-SiAlON:Eu^{2+} phosphor could be a good green phosphor candidate for creating white light in phosphor-converted white LEDs, when combined with a UV LED and RB phosphors or with a blue LED and a red phosphor. The development of a white LED device using this green phosphor is under the way, and it will be reported elsewhere.

In conclusion, a green oxynitride phosphor, with a nominal composition of $Eu_{0.00296}Si_{0.41395}Al_{0.01334}O_{0.0044}N_{0.56528}$ (β-SiAlON:Eu^{2+}), has been reported. Its microstructural characterization, PL spectra, quantum efficiencies, and chromaticity are presented. It is superior to the commercially available green phosphors YAG:Ce^{3+} and ZnS:Cu, Al, and has the internal and external quantum efficiencies of 70% and 61% at λ_{ex}=303 nm, respectively. Preliminary studies have shown that this phosphor may find applications in white LEDs.

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