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Properties of SiAlON powder phosphors for white LEDs

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Abstract

Three kinds of Eu^{2+}-doped oxynitride powder phosphors, including green β-SiAlON, yellow Ca-α-SiAlON and newly developed orange Ca-α-SiAlON were prepared by gas pressure sintering, which emit the fluorescent light with emission peak at 540 nm, 585 nm and 597 nm, respectively. Emission intensity more than 90% can be kept in the range of temperature from 30 °C to 200 °C. Emission characteristics are stable after long-term exposure testing for 6000 h at temperature of 85 °C and in humidity of 85%. A white LED device composed of a blue LED chip, β-SiAlON and orange Ca-α-SiAlON phosphors exhibits a modest colour rendering index of 72.
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Keywords: SiAlON; Optical property; Phosphor

1. Introduction

White light-emitting diodes (LEDs) are increasingly used as backlights, automobile headlamps and architecture lightings to replace the conventional incandescent and fluorescent lamps because of low energy consumption, long lifetime and because they are mercury-free.[1,2] White LEDs comprising a blue LED chip and yellow phosphor are widely used. This type white light exhibits high brightness. It does not have green and red colour, therefore, the colour rendering is low, and the colour reproduction region is small. The alternative method of white LEDs is coupling a blue LED chip with green and red phosphors. Its white light has low brightness, while exhibiting high colour rendering and a large colour reproduction region. Ce^{3+}-doped YAG and Eu^{2+}-doped silicate as yellow phosphors and Eu^{2+}-doped silicate as green phosphor are used conventionally for white LEDs.[3] These conventional phosphors exhibit large temperature dependency of emission intensity. Furthermore, silicate phosphors have poor chemical stability, therefore, the brightness of white LEDs decrease and shift colour for long time operation.

In recent years, rare-earth doped oxynitride or nitride phosphors have been investigated.[4–20] Ca-α-SiAlON[4–9] and β-SiAlON[10–12] phosphors are expected to have high thermal and chemical properties because of strong chemical bonding of SiAlON. M-α-SiAlON (M represents cations such as Li, Mg, Ca, or some rare earths) is derived from α-Si_3N_4 by substitution of Al–N, Al–O chemical bond for Si–N. There are two interstitial sites per unit cell, and Ca^{2+} ion is doped in compensation for charged balance, The general formula of Ca-α-SiAlON can be written as $Ca_{m/2}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ (m and n represent the number of Al–N pairs and Al–O pairs substituting for Si–N pairs, respectively). Ca-α-SiAlON yellow phosphor can be prepared by Eu^{2+}-activator dope at interstitial sites as well as Ca^{2+} ion. By substitution of Al–O chemical bond for Si–N of β-Si_3N_4, β-SiAlON with the general formula as $Si_{6-z}Al_zO_zN_{8-z}$ (z represents the number of Al–O pairs substituting for Si–N pairs) is derived. Within crystal structure of β-SiAlON, there are continuous channels parallel to the c direction. Kimoto et al. reported that they have succeeded in direct observation of single Eu^{2+}-dopant in continuous channels using scanning transmission electron microscopy (STEM).[11]

In the present study, powder phosphors such as Eu^{2+}-doped green β-SiAlON, yellow Ca-α-SiAlON and newly developed orange Ca-α-SiAlON have been fabricated. The photoluminescence properties of these powder phosphors were investigated and compared with conventional phosphors. And durability tests were performed. Furthermore, a white LED device was demonstrated.

2. Experimental procedures

Raw materials such as Si_3N_4, AlN, Al_2O_3, Eu_2O_3, $CaCO_3$ and Ca_3N_2 were used for preparation of β-SiAlON and Ca-α-SiAlON powder phosphors. The starting powders were mixed

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according to the α or β SiAlON composition in a ball milling using ethanol and β-Si_3N_4 balls. β-SiAlON had z value varied from 0.20 to 0.25, m and n of Ca-α-SiAlON were varied from 0.5 to 4.0 and from 0 to 1.5, respectively. The europium content was varied from 0.3 to 2.5 wt%. The firing was performed using a carbon resistance furnace in a boron nitride crucible by gas pressure sintering method at the temperature of 1800–2000 °C under 0.6–0.9 MPa nitrogen pressure. The sintered powders were milled and passed through a 330 mesh sieve, then green β-SiAlON, yellow and orange Ca-α-SiAlON powder phosphors were prepared, and the mean particle sizes measured by laser light diffraction method (LS230, Beckman Coulter, USA) are 20.7 μm, 22.5 μm and 10.9 μm, respectively. The photoluminescence spectra and emission peak intensity were measured by a fluorescence spectrometer (F4500, Hitach, Japan). Chromaticity coordinates and quantum efficiency were measured by a multi channel photo detector (MCPD7000, Otsuka denshi, Japan). Temperature dependence of emission integrated intensity was evaluated using a multi channel photo detector and compared with conventional phosphors. Luminescence decay curves were measured under the excitation wavelength of 266 nm using Nd:YAG pulse laser. High temperature high humidity durability tests as well as UV irradiation and heating tests have been performed. In addition, a white LED device using a blue LED chip and SiAlON phosphors was fabricated.

3. Results and discussion

Fig. 1 shows photoluminescence spectra of synthesized Eu^{2+}-doped powder phosphors. Green Eu^{2+}-β-SiAlON, yellow Eu^{2+}-Ca-α-SiAlON and orange Eu^{2+}-Ca-α-SiAlON can be excited by blue light with wavelength of 455 nm and emit the fluorescent light with emission peak at 540 nm, 585 nm and 597 nm, respectively. The full width at half-maximum (FWHM) of emission spectra for these phosphors is 55 nm, 91 nm and 84 nm, respectively. In particular, β-SiAlON exhibits narrow emission spectrum, which is suitable for the application of backlight because pure colour of green can be obtained. As shown in excitation spectrum monitored at emission peak, these phosphors can be excited over a broad spectral range in the UV or visible light region. Upon varying the excitation wavelength, there is no significant changes in emission spectrum expect the emission intensity. Fig. 2 depicts chromaticity coordinates of Eu^{2+}-doped green β-SiAlON, yellow and orange Ca-α-SiAlON powder phosphors. As compared to yellow YAG phosphor (P46Y3, Kasei-Optnix, Japan), β-SiAlON is yellowish green and yellow Ca-α-SiAlON is red shifted. By tuning m and n, newly developed orange SiAlON could be prepared. Photoluminescence properties and quantum efficiency of SiAlON powder phosphors are shown in Table 1. Relative peak intensity which is the height of emission peak, compared to that of YAG phosphor (P46Y3), β-SiAlON, yellow and orange Ca-α-SiAlON phosphors is 199%, 143% and 168%, respectively. External quantum efficiency of these phosphors is 49.8%, 55.9% and 58.8%, respectively. At early stage of development, the external quantum efficiency exited by blue light for β-SiAlON

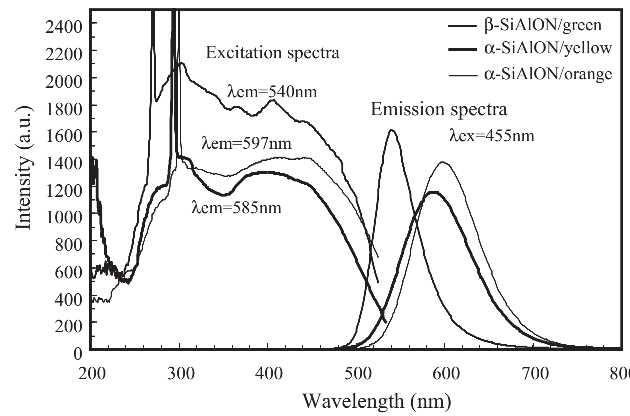

Fig. 1. Photoluminescence spectra of β-SiAlON and Ca-α-SiAlON powder phosphors.

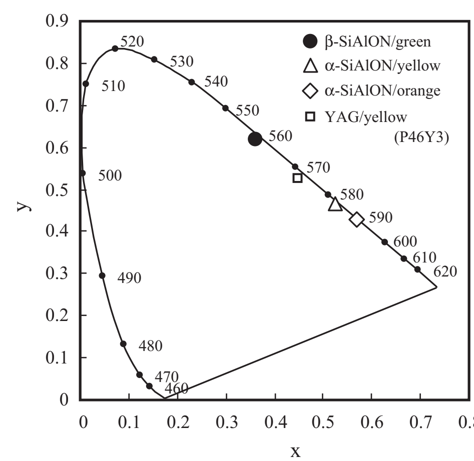

Fig. 2. Chromaticity coordinates of β-SiAlON and Ca-α-SiAlON powder phosphors.

Table 1
Photoluminescence properties and quantum efficiency of SiAlON powder phosphors.

Sample	Colour	Photoluminescence property			Quantum efficiency		
		Relative peak intensity	Chromaticity coordinates		Absorption efficiency	Internal quantum efficiency	External quantum efficiency
			x	y			
β-SiAlON	Green	199%	0.361	0.618	68.2%	73.0%	49.8%
Ca-α-SiAlON	Yellow	143%	0.526	0.468	74.6%	74.9%	55.9%
Ca-α-SiAlON	Orange	168%	0.569	0.428	83.4%	70.5%	58.8%

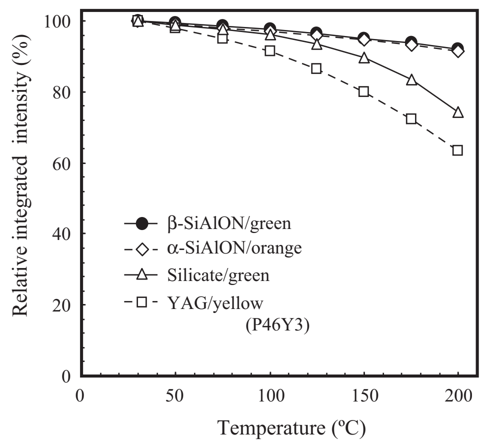

Fig. 3. Relative integrated intensity of powder phosphors as a function of temperature.

powder phosphor was the low value of 33%.[10] We have succeeded in the improvement of emission efficiency by optimizing conditions of composition and sintering temperature for synthesis. Fig. 3 plots relative integrated emission intensity excited by blue light as a function of temperature. Relative emission intensity for green β-SiAlON, and orange Ca-α-SiAlON phosphors measure at 200 °C is 92.2% and 91.5%, respectively. As compared to conventional phosphors such as silicate and YAG, green β-SiAlON and orange Ca-α-SiAlON powder phosphors have much smaller thermal quenching, which is owing to stiff frameworks of SiAlON as host crystal. For the application of LCDs backlight, it is required that the decay time is short. Luminescence decay time was measured for β-SiAlON powder phosphor. Fig. 4 shows luminescence decay curve. Emission peak intensity is decreasing significantly as time passed. The decay time $\tau_{1/10}$ is about 1.7 μs. This value is small enough for the application of backlight.

Reliability tests of SiAlON powder phosphors were performed. The results of high temperature and high humidity test for β-SiAlON and orange Ca-α-SiAlON phosphors are shown in Fig. 5. Emission peak intensities under the excitation with wavelength of 455 nm are stable after long-term exposure testing for 6000 h at temperature of 85 °C and in humidity of 85%. Intense UV light with peak wavelength of 365 nm and 120 mW/cm^2 was irradiated to β-SiAlON phosphor for long time. As shown in Fig. 6, there is no change of emission peak intensity for more than 8000 h. Fig. 7 shows thermal stability of β-SiAlON powder phosphor as function of aging time. Emission peak intensity is stable after 2500 h heating at temperature of 150 °C.

A white LED device which consists of a blue LED chip, green β-SiAlON and orange Ca-α-SiAlON phosphors was demonstrated. In order to emit white light, the composition of

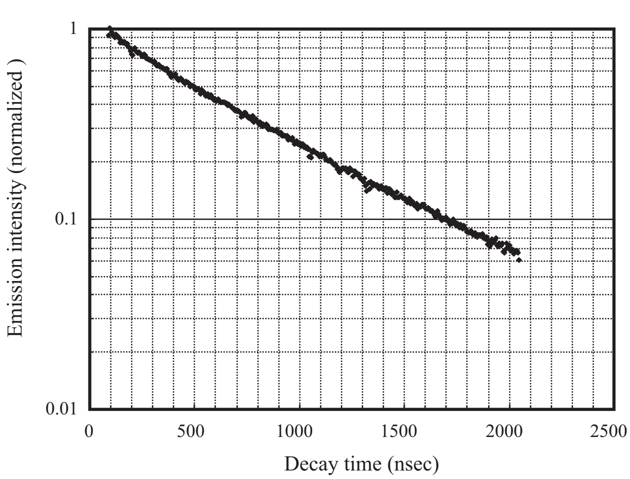

Fig. 4. Emission intensity of β-SiAlON powder phosphor as a function of decay time.

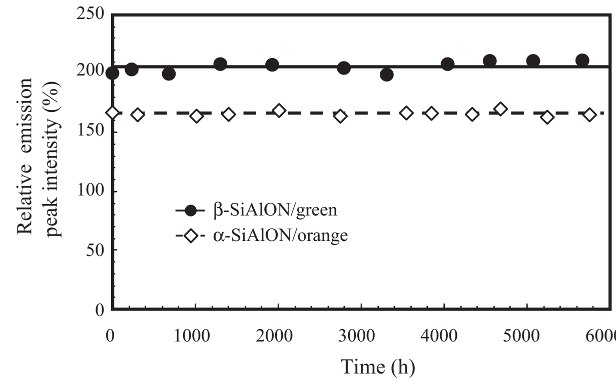

Fig. 5. Relative emission peak intensity of β-SiAlON and Ca-α-SiAlON powder phosphors as a function of time: at temperature of 85 °C, in humidity at 85%RH.

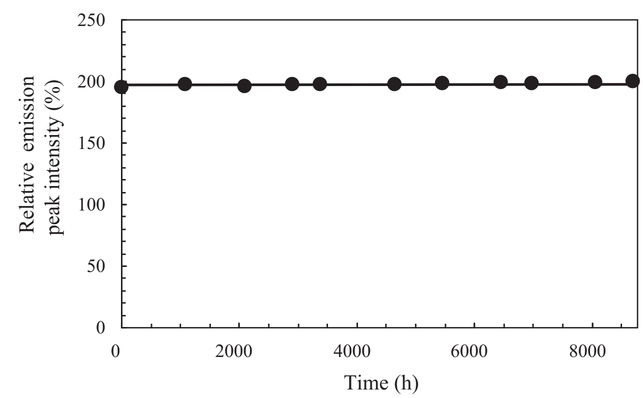

Fig. 6. Relative emission peak intensity of β-SiAlON powder phosphor as a function of time: UV irradiation test.

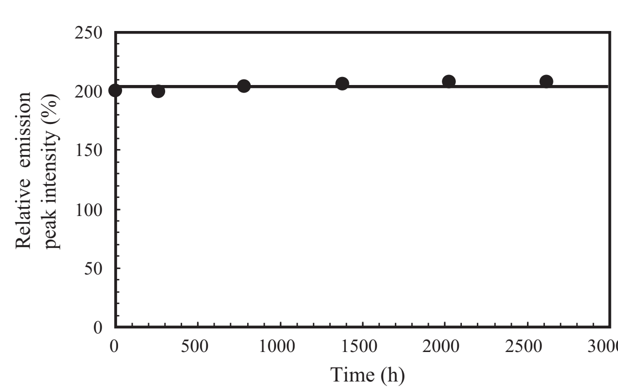

Fig. 7. Relative emission peak intensity as a function of time of β-SiAlON powder phosphor: heating at 150 °C.

Table 2
Luminescence properties of a white LED consists of a blue LED chip and SiAlON powder phosphors.

Composition (wt%)			Chromaticity coordinates		Colour temperature (K)	Rendering index/Ra
β-SiAlON (Green)	Ca-α-SiAlON (Orange)	Resin	*x*	*y*		
4.8	0.8	94.4	0.331	0.321	5553	72

phosphors dispersed in the silicone resin was tailored. Table 2 presents luminescence properties of a fabricated white LED. The CIE1931 chromaticity coordinates (x, y) are (0.331, 0.321), and the colour temperature is 5553 K. It exhibits a modest rendering index of 72.

4. Conclusions

Eu^{2+}-doped green β-SiAlON, yellow Ca-α-SiAlON and newly developed orange Ca-α-SiAlON powder phosphors were fabricated, which exhibit fluorescent emission peak at 540 nm, 585 nm and 597 nm, respectively, under UV or blue light excitation. They have small temperature dependency of emission intensity in comparison with conventional phosphors such as Ce^{3+}-doped YAG and Eu^{2+}-doped silicate for white LEDs. Integrated emission intensity measured at 200 °C is over 90% of that measured at 30 °C. As results of reliability test, β-SiAlON and Ca-α-SiAlON phosphors exhibit excellent durability. No change of emission characteristics was observed after high temperature at 85 °C and high humidity of 85% testing for 6000 h. The manufacture of a white LED device was attempted using green β-SiAlON and orange Ca-α-SiAlON phosphors excited by a blue LED chip with colour temperature of 5553 K and a modest rendering index of 72.

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