

In-situ synthesis of multicolor emitting Eu^{2+} -doped α/β -SiAlON composite phosphor

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Generally, the $\text{Ca-}\alpha\text{-SiAlON : Eu}^{2+}$ phosphor emits yellow centered at around 580 nm, while the $\beta\text{-SiAlON : Eu}^{2+}$ phosphor emits green centered at around 530 nm. In this research, multicolor emitting composite phosphors consisting of $\text{Ca-}\alpha\text{-SiAlON : Eu}^{2+}$ and $\beta\text{-SiAlON : Eu}^{2+}$ were in-situ fabricated by gas pressure synthesis. The relationship between photoluminescence characteristics and processing conditions were investigated. Based on the prevailing $\beta\text{-SiAlON}$ phase by compositional design, prolonged soaking time and increased synthesis temperature resulted in the transition of the emission color from dominant yellow to dominant green. Further, improved thermal quenching behavior was achieved for the developed in-situ composite SiAlON phosphor compared to the simple mixture of single phase α - and β -SiAlON phosphor.

Key words: Nitrides, Oxynitride, Sialon, Phosphor, Composite.

Introduction

The (oxy)nitride phosphors have been recently developed and are now at the early stages of commercialization [1–21]. Among the many nitride/oxynitride phosphors, Eu^{2+} -doped SiAlONs were successfully commercialized due to efficient excitation by blue LED and excellent thermal stability [1,7–9, 11, 17–21]. The SiAlON host crystals are modifications of silicon nitride (Si_3N_4) ceramics, and they are made from a raw powder mixture including Si_3N_4 as the main ingredient, and such additives as AlN, rare earth oxides, and alkaline earth oxides [22]. $\alpha\text{-SiAlON}$ has a hexagonal crystal structure and the $P31c$ space group. The stacking sequence of $\alpha\text{-SiAlON}$ is ABCD, which results in two cages in a unit cell as interstitial sites. $\beta\text{-SiAlON}$ has also a hexagonal crystal structure but ABAB staking sequence (space group $P6_3$ or $P6_3/m$). In this structure there are continuous channels parallel to the c -axis. On top of their efficiency and stability, SiAlON phosphors are attractive due to their wide range of emission, covering from green to red [7–9, 11, 17–21]. During the last decade, both the fabrication and analysis of the green-emitting $\beta\text{-SiAlON : Eu}^{2+}$ phosphor [11, 17–19] and yellow-emitting $\text{Ca-}\alpha\text{-SiAlON : Eu}^{2+}$ phosphor [7–9, 20, 21] have been well documented.

In this work, $\alpha/\beta\text{-SiAlON : Eu}^{2+}$ composite phosphors emitting green and yellow simultaneously were synthesized by gas pressure synthesis (GPS). Being different from the research on the monolithic SiAlON phosphor, emphasis was laid on understanding the phase distribution between α - and $\beta\text{-SiAlON}$, together with the preference in accommodation

of the activator Eu into each phase. The relationship between photoluminescence (PL) characteristics and synthesis conditions were also investigated.

Experimental

The compositions studied were located in the so-called SiAlON phase plane with CaO as an $\alpha\text{-SiAlON}$ stabilizer [23]. Based on the equilibrium phase designed as $\beta\text{-SiAlON}$, the concurrent formation of $\text{Ca-}\alpha\text{-SiAlON}$ was pursued by adding incremental CaO ranging from 0 to 0.5 wt% (Table 1). The nominal composition of $\beta\text{-Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z} : \text{Eu}_y$ phosphor with $z = 0.2$ was designed to contain 0.1at% Eu ($y = 0.014$) and 0.3 at% Eu ($y = 0.04$) as an activator. The well-known formula of $\text{Ca}_x\text{Si}_{12-m-n}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n} : \text{Eu}_y$ was adopted as a nominal composition for the $\text{Ca-}\alpha\text{-SiAlON : Eu}^{2+}$ phosphor. The starting materials used for producing $\alpha/\beta\text{-SiAlON : Eu}^{2+}$ composite phosphors were Si_3N_4 (SN-E10, Ube industries, Ltd.), AlN (99.99%,

Table 1. Nomenclatures and compositions of the specimens.

unit: wt%.					
	specimen	Si_3N_4	AlN	CaCO_3	Eu_2O_3
0.1Eu series	0.1Eu-0CaO	96.22	2.91	0	0.87
	0.1Eu-0.01CaO	96.20	2.91	0.02	0.87
	0.1Eu-0.05CaO	96.13	2.91	0.09	0.87
	0.1Eu-0.1CaO	96.05	2.91	0.18	0.87
	0.1Eu-0.5CaO	95.37	2.89	0.88	0.86
0.3Eu series	0.3Eu-0CaO	94.57	2.86	0	2.56
	0.3Eu-0.01CaO	94.56	2.86	0.02	2.56
	0.3Eu-0.05CaO	94.49	2.86	0.09	2.56
	0.3Eu-0.1CaO	94.40	2.86	0.18	2.56
	0.3Eu-0.5CaO	93.74	2.84	0.88	2.54

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grade B, H.C. Starck), CaCO_3 (99.9%, Kojundo Chemicals), and Eu_2O_3 (99.99% Aldrich). The dry-mixed powder (approximately 10 g) were loosely packed into BN crucibles and fired at 1800–2000 °C for 1–4 h under nitrogen pressure of 0.9 MPa. The phases of the synthesized phosphors were identified by X-ray diffractometer (D/Max 2200, Rigaku) using Cu K α radiation operating at 36 kV and 26 mA. The PL spectra were measured using fluorescent spectrophotometers (Darsa Pro-5200, PSI Ltd.) equipped with 200 W Xe-lamp as an excitation source. The microstructure was examined by scanning electron microscopy (JSM-6700F, Jeol).

Results and Discussion

The PL characteristics of the SiAlON phosphors by varied synthesis temperature and soaking time are plotted in Fig. 1–4. The normalized PL intensity of all the phosphors by the intensity of 0.1Eu-0.5CaO sample synthesized at T18t4 condition (1800 °C–4 h) is given in the legend of each figure.

The mildest synthesis condition in this paper was conducted at 1800 °C for 1 h, abbreviated as T18t1 (Fig. 1). For the 0.1Eu series marked as open symbols, yellow-dominant emission was detected for the 0.5CaO specimen (0.1Eu-0.5CaO), while the other specimens emitted the typical green color. All the emissions from the specimens of the 0.3Eu series marked as solid symbols were characterized as yellow-dominant.

Figure 2 is the measured PL spectra of the SiAlON phosphors synthesized at 1800 °C for 4 h (T18t4). For the 0.1Eu series, green emission was detected for 0–0.1CaO specimens, while a non-Gaussian shape of multicolor emission composed of green and yellow was acquired for the 0.5CaO specimen. For the 0.3Eu series, all the compositions except for the 0CaO specimen emitted multicolor. It is noted that prolonged soaking time from 1 h to 4 h for synthesis at 1800 °C

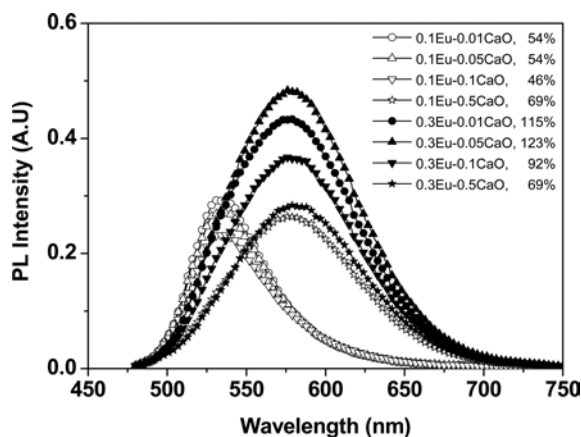


Fig. 1. PL spectra of the T18t1 phosphors synthesized at 1800 °C for 1 h soaking. Normalization of the PL intensity was based on the 0.1Eu-0.5CaO specimen with T18t4 condition.

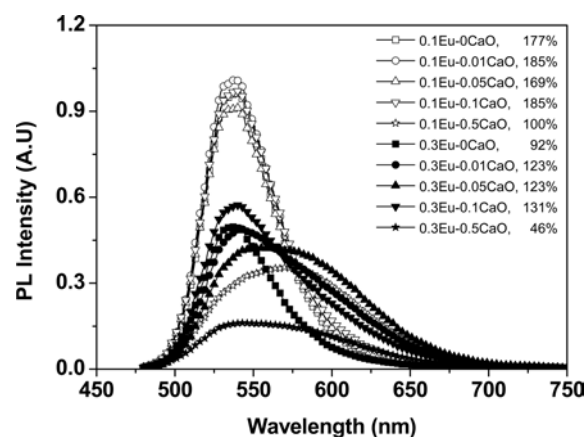


Fig. 2. PL spectra of the T18t4 phosphors synthesized at 1800 °C for 4 h soaking. Normalization of the PL intensity was based on the 0.1Eu-0.5CaO specimen with T18t4 condition.

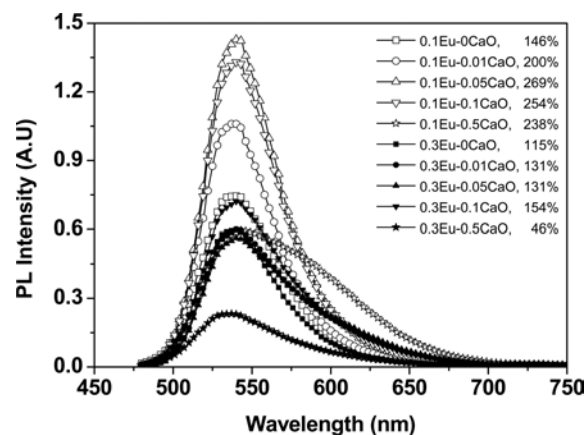


Fig. 3. PL spectra of the T19t4 phosphors synthesized at 1900 °C for 4 h soaking. Normalization of the PL intensity was based on the 0.1Eu-0.5CaO specimen with T18t4 condition.

caused the preferred enhancement in green emission. Increase in the synthesis temperature to 1900 °C (T19t4 in Fig. 3) and 2000 °C (T20t4 in Fig. 4) with fixed 4 h soaking time also led to strengthened green emission over yellow emission. Further, it is manifest that both increased temperature and prolonged soaking time contributed to an increase in overall PL intensity.

XRD analysis for the synthesized phosphors prepared in the T18t4 condition confirmed the concurrent formation of α - and β -SiAlON phase (Fig. 5). Si was partially coated onto the surface of the flattened specimen powder in the XRD holder as a standard material for the correction of the peak position [24, 25]. The minor α -SiAlON phase is marked by a solid circle and the other peaks are all indexed as a β -SiAlON phase. For the 0.1Eu series in Fig. 5(a), 0–0.1 wt% addition of CaO yielded a single phase β -SiAlON, while the 0.5 wt% CaO specimen was composed of major β -SiAlON phase and minor α -SiAlON phase. On the other hand, all the compositions except for 0CaO were analyzed to be a mixture of α - and β -SiAlON phase for the 0.3Eu series, in Fig. 5(b). The composite mode of the phases present in the developed phosphors matches well

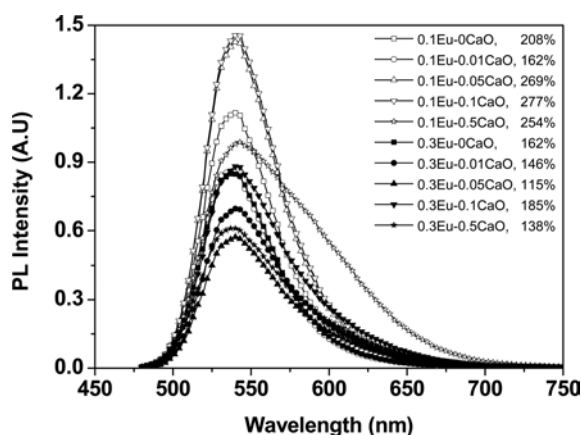


Fig. 4. PL spectra of the T20t4 phosphors synthesized at 2000 °C for 4 h soaking. Normalization of the PL intensity was based on the 0.1Eu-0.5CaO specimen with T18t4 condition.

with the PL spectra in Fig. 2. That is, compositions containing single phase β -SiAlON emitted green only, while composites of α/β -SiAlON emitted a multicolor comprised of yellow and green. As designed by the starting compositions, the amount of the β -SiAlON phase calculated by XRD peak ratio exceeded several times that of the α -SiAlON phase. However, in spite of the substantial difference in the content of each phase, a comparable PL intensity between yellow emission and green emission was measured. The reason for the preferred incorporation of activator Eu ion into the α -SiAlON crystal is related to the difference in the interstitial sites of the α - and β -SiAlON phase, which

will be explained together with Fig. 6 and 7.

For the compositions showing multicolor emission in Fig. 1-Fig. 4, the evolution of PL spectra with varied synthesis temperature and soaking time for 0.1Eu-0.5CaO and 0.3Eu-0.05CaO is compared in Fig. 6(a) and Fig. 6(b), respectively. A preferred increase (decrease) in PL intensity for green (yellow) emission is evident in the order of T18t1, T18t4, T19t4, and T20t4. These phenomena are quite rational considering the phase stability mentioned in Fig. 5. That is, a phase transformation from the meta-stable α -SiAlON to equilibrium β -SiAlON takes place with the escalating synthesis condition.

Except for the single emission of yellow by the T18t1 specimen in Fig. 6(a) and (b), multicolor emitting spectra were successfully decomposed by the peak fitting method, and were comprised of green emission centered at 538-540 nm (DWL_g) and yellow emission centered at 575-586 nm (DWL_y). The sizes of the full width at half maximum (FWHM) of a decomposed emission match well with those of the typical values of the single phase α - and β -SiAlON phosphor (Table 2). The validity of the curve fitting for the decomposition of the multicolor emission into two monicolor emissions is self-sustained by the similarity in the values in Table 2 with the typical parameters of the SiAlON phosphor. A quantitative analysis of green intensity (B_g) and yellow intensity (B_y) was conducted by comparing the area integral of the decomposed monicolor emission, which confirmed the preferred strengthening of the green emission with increased

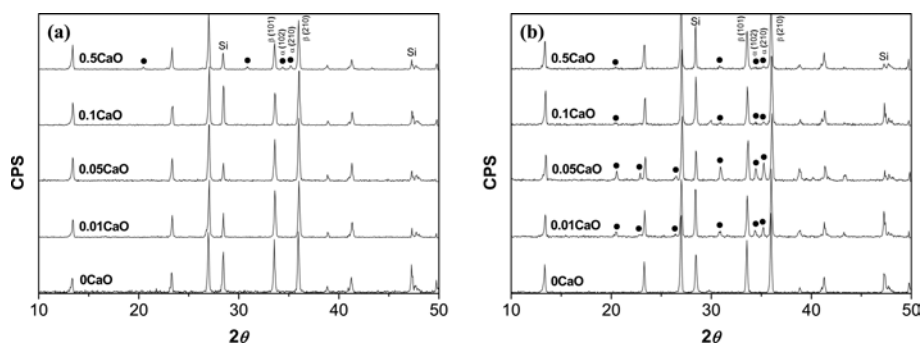


Fig. 5. XRD patterns of (a) 0.1Eu series and (b) 0.3Eu series by T18t4 condition. (Si: silicon, ● α -SiAlON, non-marked others: β -SiAlON)

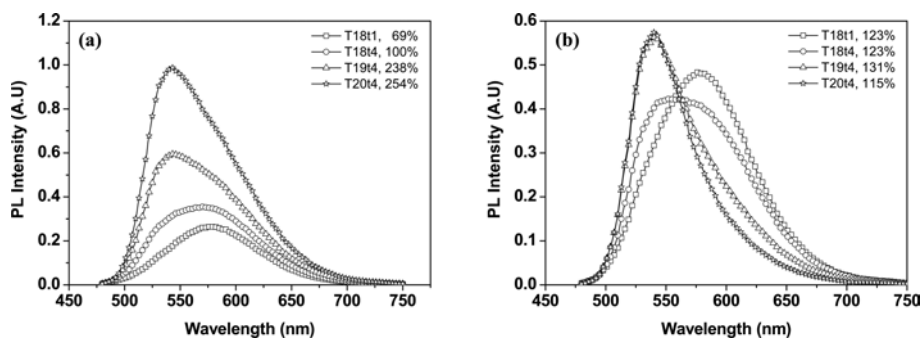


Fig. 6. PL spectra of (a) 0.1Eu-0.5CaO and (b) 0.3Eu-0.05CaO by various synthesis conditions. Preferred strengthening in green emission is seen in the order of T18t1, T18t4, T19t4, and T20t4.

Table 2. Various parameters of the decomposed emissions.

	0.1Eu-0.5CaO						0.3Eu-0.05CaO					
	PWL _g (nm)	PWL _y (nm)	FWHM _g (nm)	FWHM _y (nm)	B _g (%)	B _y (%)	PWL _g (nm)	PWL _y (nm)	FWHM _g (nm)	FWHM _y (nm)	B _g (%)	B _y (%)
T18t1	—	—	—	—	—	—	—	—	—	—	—	—
T18t4	539	584	42	79	18.5	81.5	540	586	38	78	22.4	77.6
T19t4	538	583	38	78	29.1	70.9	539	582	37	74	45.2	54.8
T20t4	539	583	38	76	34.6	65.4	538	575	36	66	52.7	47.3

(PWL: peak wavelength, FWHM: full width at half maximum, B: PL intensity).

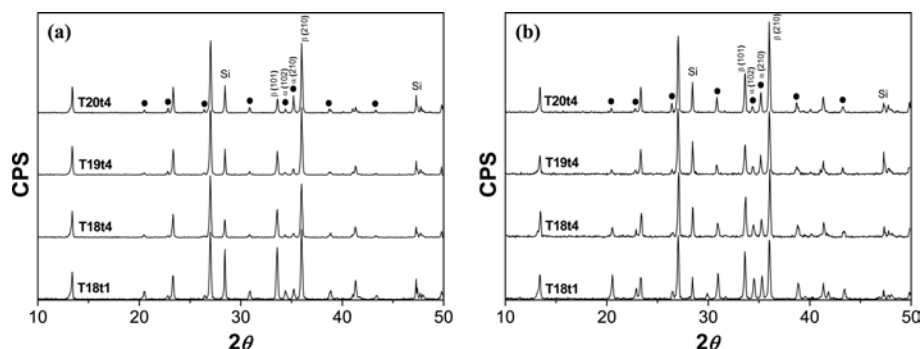


Fig. 7. XRD patterns of (a) 0.1Eu-0.5CaO and (b) 0.3Eu-0.05CaO by various synthesis conditions. (Si: silicon, ● α -SiAlON, non-marked others: β -SiAlON)

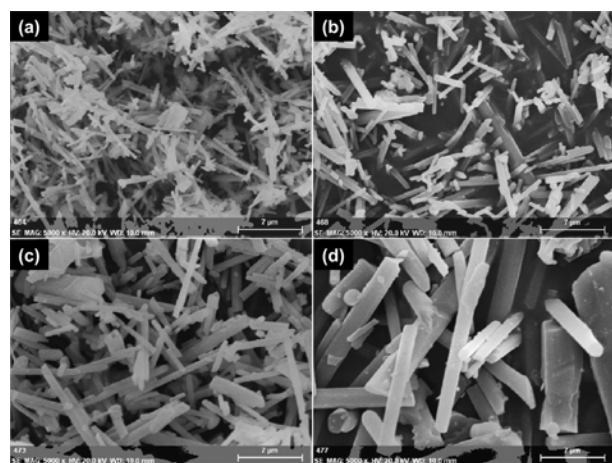


Fig. 8. SEM micrographs of 0.1Eu-0.5CaO phosphors synthesized by various conditions. (a) T18t1, (b) T18t4, (c) T19t4, (d) T20t4.

synthesis temperature and time. The authors were able to control the wide range of the combination between B_g and B_y by adjusting the composition and processing variables. B_g and B_y for 0.1Eu-0.5CaO ranged from 18.5 and 81.5% to 34.6 and 65.4%, respectively. Those of 0.3Eu-0.05CaO covered from 22.4 and 77.6% to 52.7 and 47.3%, respectively. Implications of the current results are that homogeneously mixed α/β -SiAlON composite phosphors emitting green and yellow at the same time can be fabricated by in-situ process.

Corresponding XRD patterns for the emissions in Fig. 6 are illustrated in Fig. 7. It is evident that both the 0.1Eu-0.5CaO specimens and 0.3Eu-0.05CaO specimens

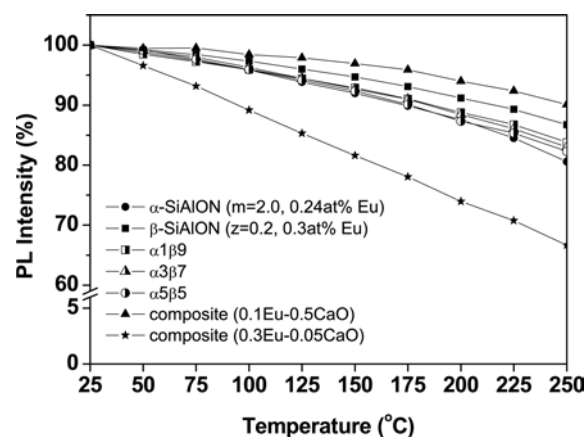


Fig. 9. The measurement of the thermal quenching behavior. Comparison was made between the developed composite phosphor, single phase phosphor, and simple mixture of the single phase phosphor.

consist of α - and β -SiAlON phase over the entire synthesis conditions of the current research. It should be noted that only yellow emission was detected for the T18t1 condition in spite of the larger peak for β -SiAlON phase. The discrepancy between XRD patterns and PL spectra is ascribed to the solubility of the Eu ion into the α - and β -SiAlON crystal. Activator Eu ion is not solved into the SiAlON crystal as a substitution but only by an interstitial [7, 8, 11, 17, 19, 26]. To incorporate the Eu ion into the β -SiAlON crystal requires a higher temperature owing to its smaller interstitial site compared with the α -SiAlON crystal, because the diameter of a continuous channel along the c-axis of the β -SiAlON crystal is smaller than the size of the interstitial site in the

α -SiAlON crystal [7, 8, 11, 17]. It is postulated that the incorporation of the Eu ion in the β -SiAlON crystal was not sufficient for green emission for the T18t1 synthesis condition. Decreasing (increasing) the amount of metastable α -SiAlON (equilibrium β -SiAlON) phase with increased synthesis temperature and time is the direct cause of the blue-shifted PL spectra in Fig. 6. Further, the increased peak ratio of (210)/(101) for α -SiAlON and (210)/(101) for β -SiAlON was caused by the texturing of phosphor particles for XRD sample preparation, which will be discussed in detail in Fig. 8.

Photographs in Fig. 8 are the particle morphologies of 0.1Eu-0.5CaO observed by SEM. An elongated particle shape is typical to SiAlONs and the particle growth is a well expected result with increasing temperature and soaking time. A similar trend was observed for the 0.3Eu-0.05 Series. Particle growth from T18t1 to T20t4 is the cause of the change in the XRD peak ratio in Fig. 7. In the course of the flattening treatment of the phosphor powders on the XRD specimen holder using the slide glasses, the degree of texturing increases with proportion to the particle size and aspect ratio. That is, elongated large particles are preferentially oriented with the c-axis parallel to the holder surface, so the peak for the (210) plane parallel to c-axis gets stronger [25, 27]. Though it is difficult to discern each SiAlON phase from the SEM image, it was revealed by the EBSD (electron beam scattered diffraction) that each phase grows as a separate particle.

A thermal quenching property of the in-situ composite SiAlON phosphors was compared to single phase SiAlON and a simple mixture of them. One of the developed in-situ composite phosphors, 0.1Eu-0.5CaO, exhibited superior thermal stability to those of both single phase and simple mixture of single phase. Further research is required to reveal the relation between thermal quenching and the composite phosphor.

Conclusions

Multicolor emitting in-situ Eu²⁺-doped α/β -SiAlON composite phosphors were developed. Controlled emission with a varying ratio of yellow to green was achieved by adjusting the composition and synthesis condition. Designing the β -SiAlON as a dominant phase, the blue-shift of the emitted PL spectra with increased synthesis temperature and soaking time was revealed to be caused by strengthened green emitting β -SiAlON phosphor. The monicolor yellow emission was obtained by the mildest synthesis condition (T18t1), while dominantly green emission was produced by the harshest synthesis condition (T20t4). The multicolor emission was successfully decomposed into green and yellow, which was confirmed by the similarity in the various parameters between the developed multicolor emission and typical monicolor emission. Further, enhanced thermal stability of the SiAlON phosphor can

be acquired through the formation of the in-situ composite α/β -SiAlON phosphors.

Acknowledgments

This work was supported by the KIMS Academy Lab Program of the Korea Institute of Materials Science, Korea.

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