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Polymer-derived β -SiAlON:Eu²⁺phosphors

Yang Gao^a, Daiki Hamana^a, Junya Iihama^a, Ryo Iwasaki^a, Sawao Honda^a, Toru Asaka^a, Munni Kumari^b, Tomokatsu Hayakawa^a, Samuel Bernard^b, Philippe Thomas^b and Yuji Iwamoto^{*a}

a. Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan.

b. University of Limoges, CNRS, IRCER, UMR 7315, F-87000 Limoges, France.

- Corresponding author

Yuji Iwamoto:

Department of Life Science and Applied Chemistry, Graduate School of Engineering,
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan

TEL/FAX: +81 52 735 5276

E-mail: iwamoto.yuji@nitech.ac.jp

Abstract (186/200 words maximum)

A series of β -SiAlON:Eu²⁺ phosphors were synthesized from single source precursors, perhydropolysilazane chemically modified with Al(OCH(CH₃)₂)₃, AlCl₃, and EuCl₂. The single source precursors were converted to β -SiAlON:Eu²⁺ phosphors by pyrolysis under flowing N₂ or NH₃ at 1000 °C, followed by heat treatment at 1800 °C under a N₂ gas pressure at 980 kPa. By varying the molar ratio of the chemical modifiers, β -SiAlON:Eu²⁺ with the compositions close to the theoretical ones expressed as Si_{6-z}Al_zO_{z-2y}N_{8-z+2y}:yEu²⁺ were synthesized, where the z values and Eu²⁺ contents were controlled in the ranges of 0.44-0.78 and 0.35-1.48 mol%, respectively. The polymer-derived β -SiAlON:Eu²⁺ phosphors exhibited green emission under excitation at 460 nm attributed to the 4f⁷-4f⁶(7f³)5d¹ transition of dopant Eu²⁺. HAADF-STEM analysis confirmed that the doped-Eu²⁺ existed interstitially within the channels along the c axis of host β -SiAlON. Compared with the conventional powder metallurgy route, the PDC route in this study offers some advantages in grain growth of host β -SiAlON and PL properties in terms of green emission intensity under excitation at 460 nm, and the highest intensity was achieved for the polymer-derived β -SiAlON:Eu²⁺ with z = 0.64 and 0.37 mol% Eu²⁺.

1 Introduction

Along with the progress of human society, people become more aware of the alternative ways of lighting sources because of the several problems of the traditional lighting source, such as the cost, lighting efficiency, and environmental friendship. The light-emitting diodes (LEDs) have immediately spread worldwide to become the most popular fourth-generation illumination source. Classical LEDs are composed of semi-conductive compounds such as gallium arsenide (GaAs), gallium phosphide (GaP), and silicon carbide (SiC), while phosphor-converted white LEDs (pc-wLEDs) have attracted much attention because of their environmental friendliness and great luminescent property. Currently, blue LED-driven white LEDs, which are formed by blending a blue LED chip with a yellow phosphor (one-pc wLEDs), or a green phosphor together with a red phosphor (two-pc wLEDs) have been in practical use [1,2].

As a kind of rare earth (RE) ions which are always utilized to be the activator in luminescent materials, europium (Eu) ions, both divalent and trivalent, have been studied and several Eu-doped luminescent systems have been discovered so far, such as AlN:Eu²⁺ (blue emission centered at 465 nm) [3], M₂Si₅N₈:Eu²⁺ (M= Ca, Sr, Ba) (yellow-orange emission with maxima from 570 to 605 nm) [4] and SiAlON:Eu²⁺ as quite important yellow (M- α -SiAlON:Eu²⁺, M = Ca, Mg) [5,6] and green (β -SiAlON:Eu²⁺) [7] phosphors with high quantum efficiency, low thermal quenching and excellent chemical stability. As an exceptional green phosphor applied for the two-pc wLEDs, β -SiAlON:Eu²⁺ phosphors have been widely reported [8-11]. β -SiAlON is a solid solution of β -silicon nitride (Si₃N₄), where Si-N bonds are partly replaced with

Al-O and Al-N bonds and expressed as $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, in which the z value respects the Al concentration in the system, and in regard to the charge compensation by Eu^{2+} doping, Wang et al. put forward a modified formula of $\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y}\text{N}_{8-z+2y}:\text{yEu}^{2+}$ [8].

According to previous studies, the photoluminescence (PL) properties of β -SiAlON: Eu^{2+} phosphors are governed by several materials factors, in particular chemical composition and related local structure around the dopant Eu^{2+} : Xie et al. reported that both the z value and Eu^{2+} concentration can be the factors that influence the emission intensity [9]. The phase purity and the Eu^{2+} solubility of the host β -SiAlON were improved with lowering the z value, and by taking into account the emission efficiency as well as the phase purity of the host β -SiAlON, it was suggested that the β -SiAlON: Eu^{2+} phosphors with $z = 0.1\text{--}0.5$ are acceptable for practical applications [9]. On the other hand, the critical Eu^{2+} concentration in the host β -SiAlON was suggested approximately 0.7 and 0.5 mol % for $z = 0.1$ and 0.5, respectively [9]. In addition, they found that the solubility of Eu^{2+} decreased continually with the increasing z value of the host β -SiAlON, which was attributed to the structural distortion caused by the introduction of Al and O [9].

Takahashi et al. found that the content of some elements, especially oxygen is closely related to the emission color and intensity [10]. In another work, Li et al. reported that the additional trivalent europium (Eu^{3+}) ions in the matrix, which were called as killer sites, can have a side effect on the emission intensity of β -SiAlON: Eu^{2+} phosphors, and the reduction of Eu^{3+} successfully improved the green-emitting property at 400–450 nm [11]. Wang et al. went for the theoretical cooperation condition of Eu^{2+}

in the β -SiAlON matrix and suggested that the divalent Eu ions formed EuN_9 units with nitrogen ions, and the values of Eu-N bond length of this unit make some effect on the maximum emission wavelength (emission color) [8]. Accordingly, it is evident that strict chemical composition control is essential to develop β -SiAlON:Eu²⁺ as a high-performance green phosphor for two-pc wLEDs.

The design of high-performance functional ceramics based on atomic or molecular units is an ideal way to accurately control chemical composition, morphology/structure and functional properties. An important approach is the synthesis of ceramic-based materials from organometallic precursors [12-18]. Especially, the polymer-derived ceramics (PDCs) route has been known as practicable to produce silicon (Si)-based non-oxide ceramic systems [16-18].

Recently, we have succeeded in the synthesis of β -SiAlON:Eu²⁺ phosphors through the PDCs route for the first time: single source precursors were synthesized by chemical modification of PHPS ((SiH₂-NH)_n) with aluminum triisopropoxide (Al(OCH(CH₃)₂)₃), and europium (II) chloride (EuCl₂), then converted to β -SiAlON:Eu²⁺ phosphors by pyrolysis under flowing N₂ at 1000 °C followed by heat treatment at 1800 °C under a N₂ gas pressure at 980 kPa [19]. Moreover, in this PDCs route, by the partial replacement of the Al(OCH(CH₃)₂)₃ with aluminum trichloride (AlCl₃), the oxygen content in the 1000 °C-pyrolyzed product, amorphous SiAlEuON was successfully controlled independently with the Al content [20], which offers an opportunity to investigate the effect of the chemical composition on the β -SiAlON:Eu²⁺ phosphors formed *in-situ* in more details.

In this study, a series of amorphous SiAlEuON compounds were prepared by N₂ or NH₃-pyrolysis of single source precursors, Al, Eu-modified PHPS in which strictly controlled chemical composition was established at the molecular scale. The polymer-derived amorphous compounds were converted to β -SiAlON:Eu²⁺ phosphors by heat treatment up to 1800 °C under a N₂ gas pressure at 980 kPa. The relationships between the chemical composition, phase purity, morphology, and PL properties of the polymer-derived β -SiAlON:Eu²⁺ samples are discussed based on a set of characterization techniques including X-ray diffraction (XRD), PL spectroscopy, scanning electron microscope (SEM) observations and a high-angle annular dark-field-scanning transmission microscopy (HAADF-STEM) analysis.

2 Experimental

2.1 Materials and methods

Commercial PHPS (AZ NN110-20, 20 wt% xylene solution, AZ Electronic Materials Co., Ltd., Tokyo, Japan), Al(OCH(CH₃)₂)₃ (99.9 %, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), AlCl₃ (99.9 %, Sigma-Aldrich Japan, Tokyo, Japan) and EuCl₂ (99.9 %, Sigma-Aldrich Japan, Tokyo, Japan) were used as-received. The handling of the chemicals and reagents was performed under dry argon (Ar) atmosphere using standard Schlenk techniques. Single source precursor synthesis was conducted according to our established procedures [19, 20].

Here, we describe the synthesis of the **A66E1** sample as a representative of the synthesis process applied in this study: a 300 mL two-neck round-bottom flask

equipped with a magnetic stirrer was charged with PHPS (Si: 67.91 wt%, 10 mL of 20 wt% xylene solution, i.e. Si 48.50 mmol), $\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$ (0.593 g, 2.90 mmol), AlCl_3 (0.387 g, 2.90 mmol) and EuCl_2 (0.108 g, 0.48 mmol), then refluxed for 1 h. After the reaction mixture was cooled down to RT, the solvent was removed under vacuum at RT. The residue of the white solid precursor was subsequently pyrolyzed in a tube furnace (model ARF60–150–31KC, Asahi Rika, Chiba, Japan) under flowing NH_3 at 1000 °C for 1 h with a heating rate of 5 °C min^{-1} . The pyrolyzed powder was further heat-treated in a graphite resistance-heated furnace (model High Multi 5000, Fujidempa Kogyo, Co., Ltd., Osaka, Japan) at 1800 °C for 1 h under a N_2 gas pressure at 980 kPa.

As reference samples, $\beta\text{-SiAlON:Eu}^{2+}$ phosphors were prepared by the conventional powder metallurgy method. Starting powders of $\alpha\text{-Si}_3\text{N}_4$ (Grade SN-E10, Ube Industries, Ltd., Tokyo, Japan), aluminum nitride (AlN , 99.99 % purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), α -aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$, 99.99 % purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) and europium(III) oxide (Eu_2O_3 , 99.99 % purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) were used. A proper amount of mixed powder with the composition equivalent to the nominal composition of the **A63E1** ($\text{SiAl}_{0.09}\text{O}_{0.18}\text{N}_{1.00}\text{Eu}_{0.01}$) [20] was prepared by mixing the starting powders using an agate mortar and pestle with a small amount of ethanol (reagent grade, 99.5 %, Kishida Chemical Co. Ltd., Osaka, Japan). The mixed powder was heat-treated at 1800 °C for 1 h in the same manner as applied for the polymer-derived samples. In addition, a longer heat treatment at 1800 °C for 8 h was also performed on this mixed powder. The resulting $\beta\text{-SiAlON:Eu}^{2+}$ phosphor samples

prepared were labeled as **PMM63-1h** and **PMM63-8h**, respectively. As another reference, a green-emitting β -SiAlON:Eu²⁺ phosphor sample with the composition of Eu_{0.003}Si_{0.414}Al_{0.013}O_{0.004}N_{0.565} was prepared from 94.77 mass % α -Si₃N₄, 2.68 mass % AlN, and 2.55 mass % Eu₂O₃ as reported by Hirosaki et al. [7]. The mixed powder was heat-treated at 1800 °C for 8 h under the same manner mentioned above to afford another β -SiAlON:Eu²⁺ phosphor sample labeled as **PMM-8h**.

2.2 Characterizations

Elemental analyses for oxygen (O), nitrogen (N) (inert-gas fusion method using an oxygen nitrogen hydrogen analyzer, model EMGA-930, Horiba, Kyoto, Japan), and carbon (C) (non-dispersive infrared method using a carbon sulfur analyzer, model CS844, LECO CORPORATION, St. Joseph, USA) were performed on the pyrolyzed and heat-treated samples. The Al and Eu contents in the polymer-derived SiAlON:Eu²⁺ samples were analyzed by the energy dispersive X-ray spectrometer (EDS) mounted on a SEM (model JSM-6010LA, JEOL Ltd., Tokyo, Japan). In this study, EDS element mapping analysis was performed on the powdered sample surfaces observed within a SEM image area of approximately 20 x 25 (μm^2) at the magnification and accelerating voltage of 5000x and 15 kV, respectively to give an atomic percentage for all the constituent elements. For each sample, the Al/Si and Eu/Si ratios were evaluated as an average value of the mapping scans conducted for at least five different areas randomly

selected. Then, chemical composition of the polymer-derived SiAlON-based samples was determined as follows [19, 20]:

$$\text{wt}\% (\text{Si} + \text{Al} + \text{Eu}) = 100 \% - \text{wt} \% (\text{C}) - \text{wt} \% (\text{N}) - \text{wt} \% (\text{O}) \quad (1)$$

XRD measurement was performed on the β -SiAlON:Eu²⁺ phosphor samples by an X-ray diffractometer (model X' Pert-Pro $\alpha 1$, PANalytical, UK) using Cu radiation.

Morphology of the polymer-derived β -SiAlON:Eu²⁺ samples was observed by using a SEM (model JSM-6010LA, JEOL Ltd., Tokyo, Japan). In order to quantify the growth behavior of the host β -SiAlON grains, one hundred single β -SiAlON grains in the SEM image were randomly chosen for the selected samples, and their diameter and length were measured [21]. The average diameter, length, and aspect ratio of the β -SiAlON grains were calculated using software (Igor Pro, WaveMetrics, Inc., Portland, USA). Local structure around the dopant Eu²⁺ was investigated by using a high-angle annular dark-field-scanning transmission microscope (HAADF-STEM) (model JEM-ARM200F, JEOL Ltd., Tokyo, Japan).

The photoluminescence (PL) emission and excitation spectra were recorded at RT using a fluorescence spectrometer (model F-7000, Hitachi, Tokyo, Japan) with a xenon (Xe) lamp. Quantum efficiency was measured with a 60 ϕ integrating sphere (model 5J0-0422, Hitachi, Tokyo, Japan) equipped with Hitachi F-7000 and sodium salicylate was used as a reference.

3. Results and Discussion

3.1 Chemical composition and crystallization of polymer-derived multicomponent amorphous compounds

The single source precursor synthesis in this study was conducted for the **A66E1** and **A69E1** samples listed in Table 1.

Compared with those investigated in our previous studies (**A90E1** [19], **A90E5** [19], and **A63E1** [20]), the Al/Si atomic ratios for the chemical modification of PHPS were increased from 0.09 to 0.12 (**A66E1**) and 0.15 (**A69E1**), respectively by increasing the amount of AlCl_3 . On the other hand, the Eu/Si ratio was fixed at 0.01 so as to control the Eu^{2+} cation concentration in the β -SiAlON as 0.43 mol %, lower than the critical Eu^{2+} concentration (0.5 mol %) previously suggest for the β -SiAlON with $z = 0.5$ [9]. The z values calculated for the **A66E1** and **A69E1** by the theoretical β -SiAlON formula, $\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y}\text{N}_{8-z+2y}:\gamma\text{Eu}^{2+}$ [8] were 0.64 and 0.78, respectively. The resulting nominal chemical composition was expressed by the modified formula, $\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y+\delta}\text{N}_{8-z+2+\gamma}:\gamma\text{Eu}^{2+}$ [19, 20]. The value of differences, δ and γ were also listed in this table.

Table 1 Nominal molar ratios for the synthesis of single source precursors for β SiAlON:Eu²⁺

Name	Si in [SiH ₂ -NH] _n (PHPS)	M/Si ratio			Calculated chemical composition					
					Formula	$\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y+\delta}\text{N}_{8-z+2+\gamma}:\gamma\text{Eu}^{2+}$				Eu ²⁺ (mol%)
		Al(OCH(CH ₃) ₂) ₃	AlCl ₃	EuCl ₂		z	y	δ	γ	
A90E1 [19]	1	0.09	0.00	0.01	$\text{SiAl}_{0.09}\text{O}_{0.27}\text{N}_{1.00}\text{Eu}_{0.01}$	0.50	0.055	1.10	-2.11	0.42
A90E5 [19]	1	0.09	0.00	0.05	$\text{SiAl}_{0.09}\text{O}_{0.27}\text{N}_{1.00}\text{Eu}_{0.05}$	0.50	0.275	1.54	-2.55	2.07
A63E1 [20]	1	0.06	0.03	0.01	$\text{SiAl}_{0.09}\text{O}_{0.18}\text{N}_{1.00}\text{Eu}_{0.01}$	0.50	0.055	0.61	-2.11	0.44
A66E1	1	0.06	0.06	0.01	$\text{SiAl}_{0.12}\text{O}_{0.18}\text{N}_{1.00}\text{Eu}_{0.01}$	0.64	0.054	0.43	-2.11	0.43
A69E1	1	0.06	0.09	0.01	$\text{SiAl}_{0.15}\text{O}_{0.18}\text{N}_{1.00}\text{Eu}_{0.01}$	0.78	0.052	0.26	-2.10	0.43

The chemical compositions of 1000 °C-pyrolyzed samples are listed in Table 2. The Al/Si ratios of **NHA66E1** and **NHA69E1** samples were 0.14 and 0.17, respectively, while Eu/Si ratios of these samples were 0.02-0.03. These values were slightly higher in comparison with the nominal ones calculated based on the composition listed in Table 1, which was due to the volatilization of low molecular fraction of as-received PHPS, monomeric chlorosilanes and oligomers formed *in-situ* during the chemical modification reactions [19, 20]. On the other hand, in spite of the larger amount of AlCl₃ used for the present precursor synthesis, the Cl/Si ratios of the **NHA66E1** and **NHA69E1** samples were measured to be 0.02 and 0.03, and the PDCs route applied in this study was effective to reduce chlorine impurity of the polymer-derived multicomponent SiAlEuON compound as an intermediate for synthesizing SiAlON:Eu²⁺ phosphors through the PDCs route.

Table 2 Chemical compositions of 1000 °C-pyrolyzed samples

Precursor	Pyrolysis atmosphere	Pyrolyzed sample	EDS (molar ratio)			Element analysis (wt%)			Empirical formula
			Al/Si	Eu/Si	Cl/Si	O	N	C	
A90E1 [19]	N ₂	NA90E1 [19]	0.11	0.02	0.02	5.70	22.25	6.25	SiAl _{0.11} O _{0.19} N _{0.84} C _{0.28} Eu _{0.02} Cl _{0.02}
A90E5 [19]	N ₂	NA90E5 [19]	0.10	0.06	0.02	7.12	29.00	4.57	SiAl _{0.10} O _{0.30} N _{1.39} C _{0.25} Eu _{0.06} Cl _{0.02}
A63E1 [20]	N ₂	NA63E1 [20]	0.09	0.02	0.02	4.64	23.34	3.91	SiAl _{0.09} O _{0.15} N _{0.84} C _{0.16} Eu _{0.02} Cl _{0.02}
	NH ₃	NHA63E1 [20]	0.11	0.02	0.01	3.99	30.51	3.01	SiAl _{0.11} O _{0.14} N _{1.20} C _{0.14} Eu _{0.02} Cl _{0.01}
A66E1	NH ₃	NHA66E1	0.14	0.02	0.02	4.90	26.93	3.15	SiAl _{0.14} O _{0.17} N _{1.05} C _{0.14} Eu _{0.02} Cl _{0.02}
A69E1	NH ₃	NHA69E1	0.17	0.03	0.03	4.95	32.33	1.42	SiAl _{0.17} O _{0.19} N _{1.44} C _{0.07} Eu _{0.03} Cl _{0.03}

3.2 Formation of SiAlON:Eu²⁺ phosphors

The 1000 °C-pyrolyzed samples were further heat-treated at 1800 °C under a N₂ pressure at 980 kPa. The chemical compositions of the 1800 °C heat-treated samples

were listed in Table 3. The z values were calculated by using the theoretical β -SiAlON formula, $\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y}\text{N}_{8-z+2y}:\gamma\text{Eu}^{2+}$ [8], and the resulting chemical compositions were expressed as $\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y+\delta}\text{N}_{8-z+2+\gamma}:\gamma\text{Eu}^{2+}$ as mentioned in the experimental section.

Table 3 Chemical compositions of 1800 °C-heated samples

Sample name	EDS (molar ratio)		Element analysis (wt%)			Chemical composition *						β phase ratio (%)
	Al/Si	Eu/Si	O	N	C	Empirical formula	$\text{Si}_{6-z}\text{Al}_z\text{O}_{z-2y+\delta}\text{N}_{8-z+2y+\gamma}:\gamma\text{Eu}^{2+}$				Eu^{2+} (mol%)	
							z	y	δ	γ		
1800°C-NA90E1 [19]	0.10	0.01	2.33	34.37	1.80	$\text{SiAl}_{0.10}\text{O}_{0.07}\text{N}_{1.28}\text{C}_{0.08}\text{Eu}_{0.01}$	0.55	0.055	-0.05	-0.58	0.41	100
1800°C-NA90E5 [19]	0.10	0.04	2.83	34.93	0.13	$\text{SiAl}_{0.10}\text{O}_{0.10}\text{N}_{1.47}\text{C}_{0.01}\text{Eu}_{0.04}$	0.55	0.218	0.44	0.13	1.48	100
1800°C-NA63E1 [20]	0.08	0.01	1.89	39.71	0.19	$\text{SiAl}_{0.08}\text{O}_{0.06}\text{N}_{1.53}\text{C}_{0.01}\text{Eu}_{0.01}$	0.44	0.056	0.00	0.83	0.37	100
1800°C-NHA63E1 [20]	0.10	0.01	3.49	37.65	0.02	$\text{SiAl}_{0.10}\text{O}_{0.12}\text{N}_{1.49}\text{C}_{0.00}\text{Eu}_{0.01}$	0.55	0.055	0.22	0.56	0.37	100
1800°C-NHA66E1	0.12	0.01	3.05	37.44	0.08	$\text{SiAl}_{0.12}\text{O}_{0.11}\text{N}_{1.48}\text{C}_{0.00}\text{Eu}_{0.01}$	0.64	0.054	0.05	0.46	0.37	100
1800°C-NHA69E1	0.15	0.01	4.24	38.01	0.10	$\text{SiAl}_{0.15}\text{O}_{0.15}\text{N}_{1.58}\text{C}_{0.01}\text{Eu}_{0.01}$	0.78	0.052	0.10	0.92	0.35	100

*: Cl content was below the detection limit.

The residual chlorine was successfully removed by the high-temperature heat treatment up to 1800 °C, and the resulting chlorine content in each sample was below the detection limit. Both the carbon and oxygen contents in each sample also apparently decreased, which reveals that, alongside the *in-situ* β -SiAlON formation, carbothermal reduction and subsequent nitridation reactions of silica species efficiently proceeded as expected [19, 20].

Fig. 1 presents the XRD patterns of the heat-treated samples, **1800°C-NHA66E1** and **1800°C-NHA69E1** in comparison with those of the **NHA63E1** sample [20], and the reference samples. β -SiAlON ($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, $z=2$: $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$, JCPDS card No. 00-048-1616) is referred to label β -SiAlON phase. All the polymer-derived samples and the reference samples exhibit β -SiAlON single phase.

The diffraction peak position of β -SiAlON shifts towards a lower diffraction angle consistently with the z value due to the lattice expansion by replacing Si-N bond (0.174 nm) with Al-O bond (0.175 nm) or Al-N bond (0.187 nm) [22, 23]. In this study, the shift was clearly observed at the 2θ corresponding to the strongest peak attributed to the (101) plane of β -SiAlON as reported previously [20, 23] (Table 3).

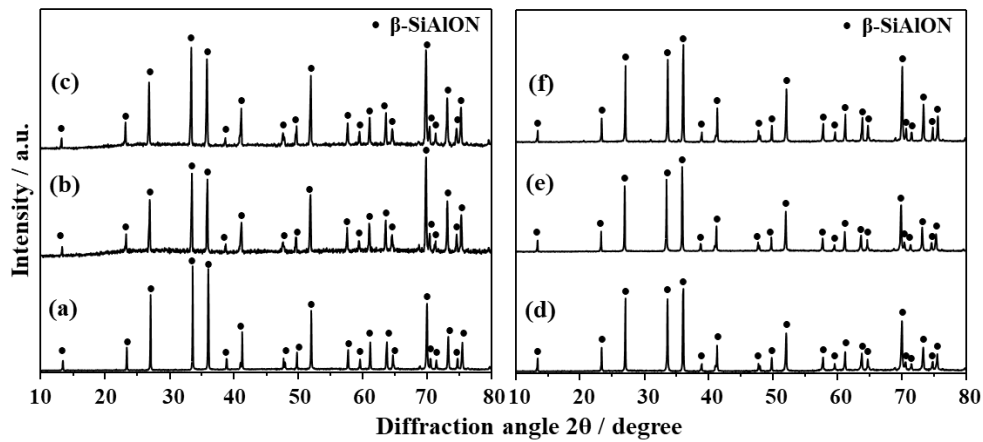


FIGURE 1 XRD patterns of polymer-derived β -SiAlON: Eu^{2+} phosphor samples: (a) **1800°C-NHA63E1** [20], (b) **1800°C-NHA66E1**, (c) **1800°C-NHA69E1** samples and reference samples of (d) **PMM63-1h**, (e) **PMM63-8h** and (f) **PMM-8h**

Table 4 Relation between the z value and X-ray diffraction peak position, 2θ corresponding to (101) plane of the host β -SiAlON identified for the polymer-derived β -SiAlON: Eu^{2+}

z -value	Sample	(101) plane 2θ / degree
0.00	$\beta\text{-Si}_3\text{N}_4^{2)}$	33.666
0.17 ¹⁾	PMM-8h	33.593
0.50 ¹⁾	PMM63-1h	33.557
0.50 ¹⁾	PMM63-8h	33.528
0.55	1800 °C-NHA63E1 [20]	33.510
0.64	1800 °C-NHA66E1	33.507
0.78	1800 °C-NHA69E1	33.421
2.00	$\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6^{3)}$	33.114

1) Calculated based on the nominal composition

2) JCPDS card No. 33-1160

3) JCPDS card No. 00-048-1616

As a typical result, phase evolutions up to 1800 °C of the **NA63E1** sample [20] are shown in Fig. S1. X-ray amorphous **NA63E1** sample crystallizes at 1300 °C and leads to the formation of α -SiAlON (labeled by referring to the data of α -SiAlON, $\text{Ca}_{0.8}\text{Si}_{9.2}\text{Al}_{2.8}\text{O}_{1.2}\text{N}_{14.8}$, JCPDS card No. No. 00-033-0261). At 1400 to 1600 °C, α -SiAlON peaks continue to increase in intensity, while β -SiAlON phase begins to appear at 1400 °C. At 1700 °C, β -SiAlON phase becomes dominant, then appears as a single phase at 1800 °C. Accordingly, in this PDCs route, *in-situ* formation of β -SiAlON from the single source precursor-derived multicomponent amorphous compound can be recognized as follows: 1) nucleation and crystallization of α -SiAlON and 2) subsequent α -/ β -phase transformation promoted by the dissolution, diffusion, and re-precipitation processes through the Si-Al-Eu-O-N transient liquid phase formed *in-situ* [20]. It should be noted that the observed α -/ β -phase transformation was well consistent with that previously suggested: at 1400 to 1800 °C, β -SiAlON precipitates from liquid containing dissolved α -SiAlON [24].

The amount of the transient liquid phase increases consistently with the Al and O contents i.e. the Al/Si ratio in the single source precursor synthesis, and thus a sufficient amount of liquid phase could be formed within the **NHA66E1** and **NHA69E1** samples which allowed the formation of β -SiAlON single phase.

3.3 Morphology of host β -SiAlONs

The 1800°C heat-treated samples exhibited typical rod-like β -SiAlON grains (Fig. 2). The host β -SiAlON grain size distributions of the selected samples were shown in Fig. S2, and their average grain diameter ($D_{av.}$) and length ($L_{av.}$) were plotted and shown in Fig. 3.

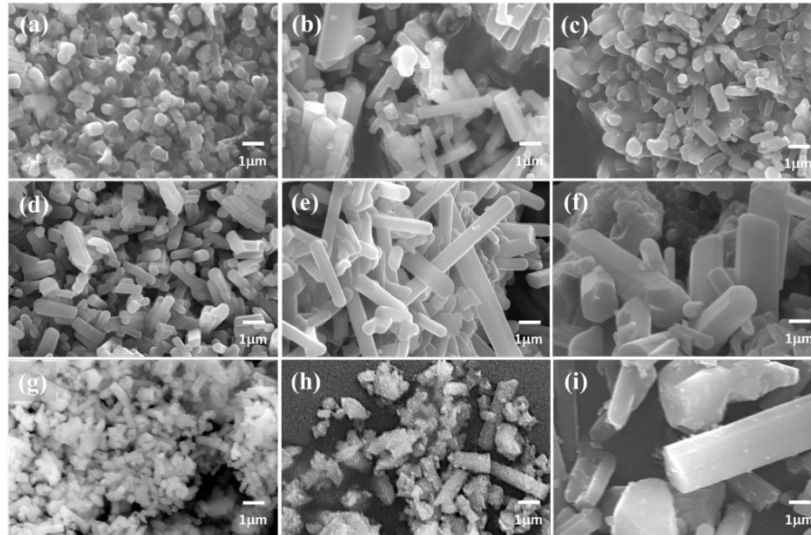


FIGURE 2 SEM images showing morphology of polymer-derived β -SiAlON: Eu^{2+} phosphor samples: (a) 1800°C-NA90E1 [19], (b) 1800°C-NA90E5 [19], (c) 1800°C-NA63E1 [20], (d) 1800°C-NHA63E1 [20], (e) 1800°C-NHA66E1, (f) 1800°C-NHA69E1 and reference samples fabricated through the conventional powder metallurgy route: (g) PMM63-1h, (h) PMM63-8h and (i) PMM-8h

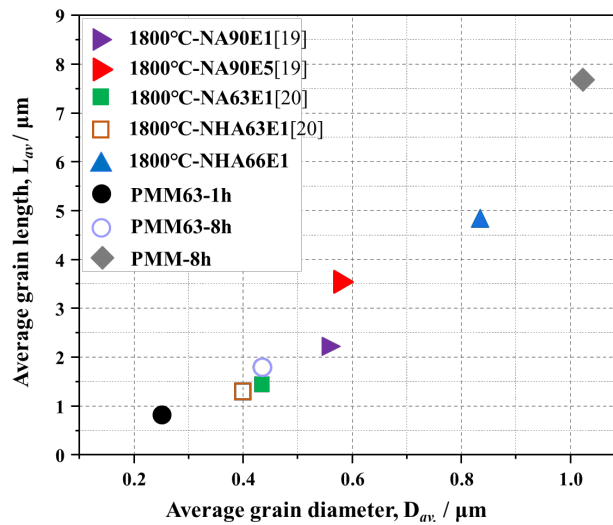


FIGURE 3 Average grain size of the host β -SiAlON evaluated for the β -SiAlON: Eu^{2+} phosphors investigated in this study

Compared with the **1800°C-NA90E1** sample (Fig. 2(a)), the **1800°C-NA90E5** sample showed courser grains (Fig. 2(b)): the D_{av} almost unchanged, while the L_{av} increased from 2.18 to 3.53 μm and the resulting average aspect ratio (R_{av}) reached 6.26 (Figs. S2 and 3). **1800°C-NA63E1** (Fig. 2(c)) and **1800°C-NHA63E1** (Fig. 2(d)) samples exhibited a similar morphology of microstructure composed of fine rod-like grains of approximately 0.3-0.7 μm in diameter and less than 4 μm in length. The effect of the z value on the morphology of the polymer-derived β -SiAlON was significant: with an increase in the z value from 0.55 (**1800°C-NHA63E1** sample, Fig. 2(d)) to 0.64 (**1800°C-NH66E1** sample, Fig. 2(e)) or 0.78 (**1800°C-NH69E1** sample, Fig. 2(f)), the β -SiAlON grain growth was apparently accelerated during a short period of 1 h at 1800 °C, *i.e.* the D_{av} and L_{av} of the **1800°C-NH66E1** sample reached 0.84 and 4.77 μm , respectively, which were more than twice as large as those of the **1800°C-NH63E1** sample. In addition, the R_{av} evaluated for the rod-like β -SiAlON grains increased from 3.40 to 5.82 (Fig. S2). During the 1800 °C-heat treatment, the amount of the transient liquid phase increased consistently with the z value, *i.e.* the Al and O contents, which facilitated the *in-situ* formation of β -SiAlON single phase and the subsequent rod-like β -SiAlON grain growth via the dissolution, diffusion, and precipitation processes.

On the other hand, the D_{av} and L_{av} of the reference sample, **PMM63-1h** (Fig. 2(g)) were apparently smaller and measured to be 0.25 and 0.83 μm , respectively (Figs. S2 and 3). After the longer heat treatment for 8 h at 1800 °C, these values got to be close to those of the **1800°C-NA63E1** sample (Fig. 3). The longer heat treatment was also found as effective to

increase the grain size of another reference sample [7], the D_{av} and the L_{av} of the **PMM-8h** sample (Fig. 2(i)) reached 1.0 and 7.6 nm, respectively (Figs. S2 and 3).

These results suggest that the *in-situ* formation of β -SiAlON through the PDCs route investigated in this study can offer some advantages in grain growth of host β -SiAlON with a low z value below 0.8 during the short heat treatment of 1 h at 1800 °C.

3.3 PL properties of polymer-derived β -SiAlON:Eu²⁺ phosphors

The effect of the chemical composition on the green emission properties of the polymer-derived β -SiAlON phosphors was conducted by measuring PL spectra. Fig. 4(a) shows the room temperature excitation spectra of the polymer-derived β -SiAlON:Eu²⁺ phosphor samples monitored at appropriate maximum emission wavelengths of each sample shown in Fig 4(b).

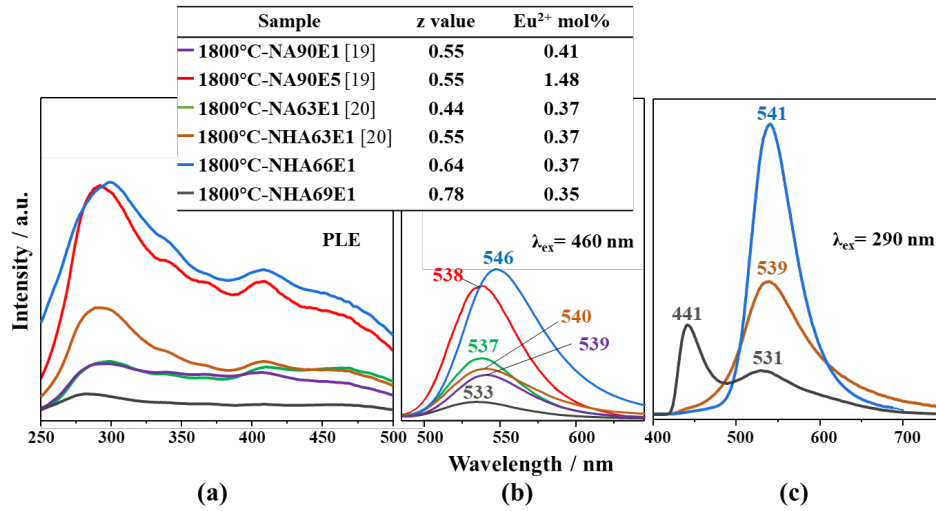


FIGURE 4 PL properties of **1800°C-NHA66E1** and **1800°C-NHA69E1** samples along with **1800°C-NA90E1** [19], **1800°C-NA90E5** [19], **1800°C-NA63E1** [20] and **1800°C-NHA63E1** [20] samples. (a) Excitation spectra monitored at appropriate maximum emission wavelengths shown in (b), and emission spectra under excitation at (b) 460 nm, and (c) 290 nm

These samples exhibited a similar excitation spectrum with a broad peak centered around 300 nm and several peaks around 410 to 500 nm attributed to the absorptions of host lattice and the $4f^7-4f^65d^1$ transitions of the dopant Eu^{2+} cations, respectively [9]. The polymer-derived $\beta\text{-SiAlON:Eu}^{2+}$ phosphors exhibit a typical green emission under blue light excitation ($\lambda_{\text{ex}}=460$ nm) ascribed to the $4f^7-4f^65d^1$ transition of the dopant Eu^{2+} cations (Fig. 4(b)).

Compared with the **1800°C-NA90E1** sample [19], the green emission intensity of the **1800°C-NA63E1** and the **1800°C-NAH63E1** samples [20] slightly increased by reducing the carbon impurity in the intermediate amorphous compound synthesized by the 1000 °C-pyrolysis (Table 2). On the other hand, the green emission intensity of the **1800°C-NA90E5** sample [19] was apparently improved by increasing the amount of the dopant Eu^{2+} from 0.41 to 1.48 (Table 3), and as shown in Fig. 4, the present **1800°C-NHA66E1** sample ($z=0.64$) shows a significant increase in the intensity of the overall excitation spectrum and exhibits the highest green emission intensity under blue light excitation at 460 nm. However, a further increase in the z -value to 0.78 (**1800°C-NHA69E1** sample) of the present polymer-derived $\beta\text{-SiAlON:Eu}^{2+}$ sample resulted in the apparent degradation of the PL properties (Figs. 4(a) and 4(b)).

Fig. 8 (c) shows the emission spectra excited at 290 nm. Both **1800°C-NHA63** and **1800°C-NHA66** samples revealed a single green emission peak around 540 nm, while the **1800°C-NHA69** sample exhibited a broad peak centered at 441 nm as a dominant emission peak, which reveals the different coordination environment of the dopant Eu^{2+} cations in the **1800°C-NHA69** sample.

The results of the thermogravimetry-mass spectrometry (TG-MS) analysis (model STA7200, Hitachi, Tokyo, Japan) for the single source precursors performed in our previous studies [19, 20] revealed that, at around 744 °C, the EuCl_2 began to melt accompanied by Cl^- elimination, which triggered Eu-N bond formations with silylamino moiety derived from PHPS associated with the elimination of HCl up to 1000 °C. This reaction was clearly observed by detecting a total ion current chromatogram (TICC) peak composed mainly of mass fragments at the m/z ratios of 38 and 36 assigned to HCl [19, 20]. Results of the TG-MS analysis for the present **A66E1** and **A69E1** samples were shown and compared with the **AE63E** sample [19] in Fig. S3. The **AE63E** sample exhibited a distinct TICC peak around 850 °C. The **A66E1** sample also showed a broad TICC peak around 850 to 1000 °C, however, such a peak was not detected for the **A69E1** sample. Accordingly, the 1000 °C-pyrolyzed sample (**NHA69E1**) was a quaternary SiAlON amorphous compound physically mixed with the thermally decomposed products of EuCl_2 (i.e. without the Eu-N bond formation) which led to the phase separation to afford the X-ray amorphous secondary phase to offer the Eu^{2+} cation site attributed to the blue emission at 441 nm, or essentially, the solubility of the Eu^{2+} was lower due to the higher z value of the **1800°C-NHA69E1** sample (0.78), which promoted the formation of Eu^{2+} -doped secondary glassy phase at the 0.35 mol % Eu-doping.

As a typical result, the amplified excitation spectrum ($\lambda_{\text{em}} = 537$ nm) of the **1800°C-NA63E1** sample is shown in Fig. 5. The $4f^7-4f^65d^1$ transition energy levels detected as a minor peak and/or shoulder correspond well with the $7F_J$ ($J=1-6$) energy levels of Eu^{3+} cation [25], which is consistent with previous results obtained by the extremely low

temperature (6 K) PL measurements of β -SiAlON:Eu²⁺ phosphors performed by Takahashi et al. [26] and suggests that chemical bonding between the Eu²⁺ and the host atoms in the β -SiAlON is ionic, i.e. the crystal field strength around the Eu²⁺ is weak, which allows the 5d¹ level to exhibit the 4f-electronic structure [26].

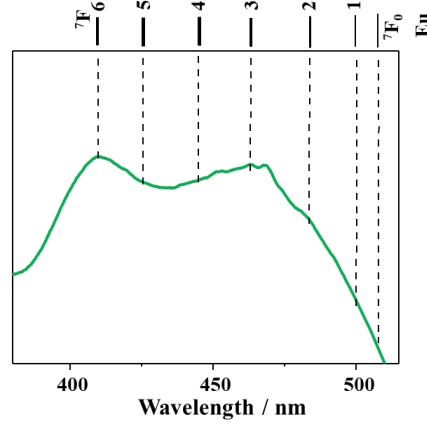


FIGURE 5 Amplified excitation spectrum of the **1800°C-NA63E1** sample [20] with the ⁷F_J (J=1-6) energy levels of Eu³⁺ cation

To study the Eu²⁺ cation site in the present polymer-derived β -SiAlON in more detail, the HAADF-STEM analysis was performed on the **1800°C-NA63E1** sample. As a typical local structure of the host β -SiAlON, six-membered rings composed of Si and Al which partially replace Si [11] can be seen clearly in Fig. 6(a). Moreover, further analysis of the line profile of the Z contrast on the HAADF-STEM image resulted in the detection of an additional metal cation ascribed to Eu²⁺ (Fig. 6(b)): the Z contrast profile along with the A-B line across the atomic channel shown in Fig. 6(a) exhibits an additional peak (marked by a red arrow) corresponding to the center position of the six-membered ring along the *c* axis of the host β -SiAlON lattice (marked by a red arrow in Fig. 6(a)). These results reveal that Eu²⁺ in the present polymer-derived host β -

SiAlON is located interstitially within the channels along the c axis, and thus the crystal field strength around the Eu^{2+} is suggested as weak as discussed above. In addition, this observation result is well consistent with those previously offered both experimentally [27] and theoretically [8] for the $\beta\text{-SiAlON}:\text{Eu}^{2+}$ phosphors fabricated by the conventional powder metallurgy method.

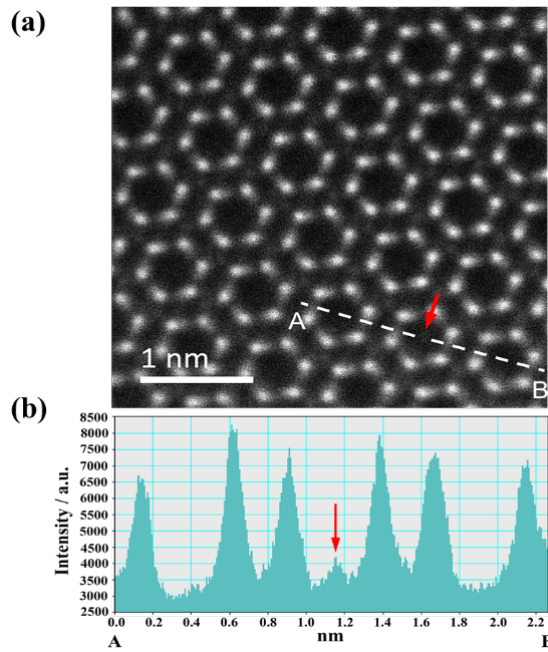


FIGURE 6 (a) HAADF-STEM image of **1800°C-NA63E1** sample [20] showing (a) typical six-membered rings of $\beta\text{-SiAlON}$ and (b) the Z contrast profile along with the A-B line across the atomic channel shown in (a).

To study the Eu^{2+} solubility at the interstitial site of the **1800°C-NHA66E1** sample which showed the best green emission performance, the Eu/Si ratio was increased from 0.01 to 0.03 and 0.05 in the single source precursor synthesis and converted to $\beta\text{-SiAlON}:\text{Eu}^{2+}$ phosphors in the same manner. As shown in Fig. S4(a), the excitation spectra monitored at appropriate

maximum emission wavelengths shown in Fig. S4(b) revealed that the intensities corresponding to the $4f^7-4f^65d^1$ transitions around 410 to 500 nm decreased by increasing the Eu/Si ratio. Under the blue light excitation at 460 nm, the green emission peak intensity was decreased and the peak top shifted toward a shorter wavelength with increasing the Eu/Si ratio (Fig. S4(b)), in addition, under excitation at 290 nm, another emission peak appeared around 474 nm on the left shoulder of the green emission peak (Fig. S4(c)), and the appropriate excitation spectra ($\lambda_{em} = 474$ nm) exhibited a broad peak centered around 280 nm (Fig. S4(d)). These results suggest that the Eu^{2+} cation-doping at the Eu/Si ratio > 0.01 leads to the promoted formation of the Eu^{2+} cation-doped secondary glassy phase by exceeding the Eu^{2+} solubility of the $\beta\text{-SiAlON}$ with $z = 0.64$.

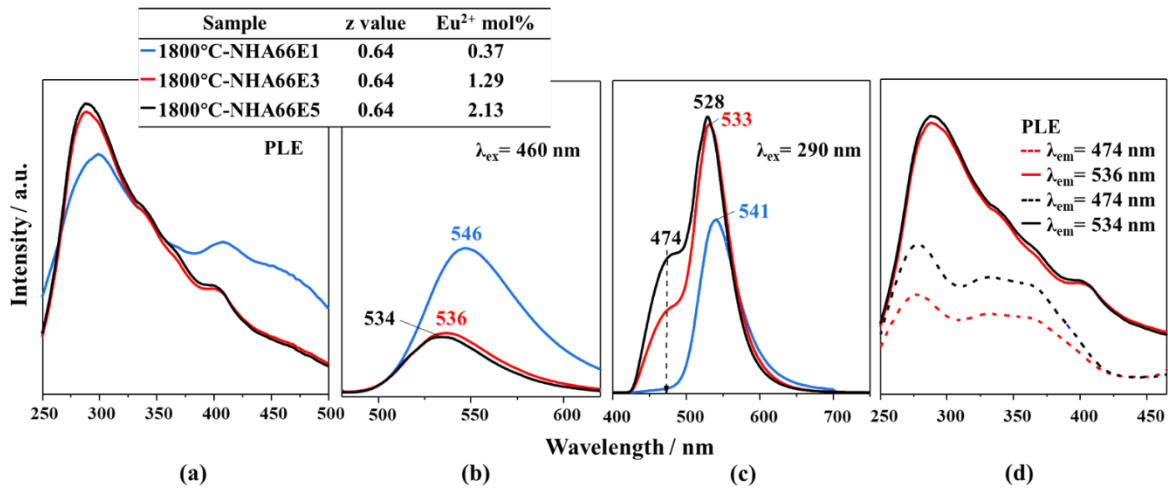


FIGURE S4 (a), (d) excitation and (b), (c) emission spectra of 1800°C-NHA66E1, 1800°C-NHA66E3, and 1800°C-NHA66E5 samples

Fig. 7 shows the comparison of PL properties between the polymer-derived samples (1800°C-NA63E1 and 1800°C-NHA66E1) and the reference samples (PMM63-1h, PMM63-8h, and PMM-8h) fabricated by the conventional powder metallurgy method.

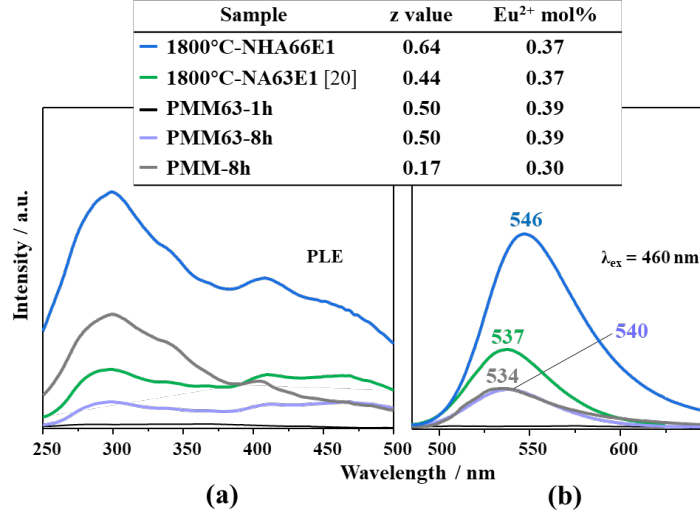


FIGURE 7 (a) Excitation and (b) emission spectra of **1800°C-NA63E1 [20]**, **1800°C-NHA66E1** samples along with the reference samples fabricated through the conventional powder metallurgy route.

The chemical composition of the **1800°C-N63AE1** sample ($z = 0.44$, $\text{Eu}^{2+}\text{mol}\% = 0.37$) is compatible with **PMM63-1h** and **PMM63-8h** samples, while the **PMM-8h** has another composition of $\text{Eu}_{0.00296}\text{Si}_{0.41395}\text{Al}_{0.01334}\text{O}_{0.0044}\text{N}_{0.56528}$ ($z=0.17$, nominal $\text{Eu}^{2+}\text{mol}\% = 0.3$) reported by Hirosaki et al. [7].

The internal quantum efficiency ($\eta_{\text{int.}}$) and external quantum efficiency ($\eta_{\text{ex.}}$) of the selected samples are plotted and shown as a function of excitation wavelength in Fig. 8. For the $\beta\text{-SiAlON:Eu}^{2+}$ with z value below 0.8, the present PDC route offers some advantages to achieve higher intensity of the green emission, especially under blue light excitation at 460 nm ascribed to the $4f^7\text{-}4f^6(^7f_3)5d^1$ transition of dopant Eu^{2+} ions, and the $\eta_{\text{int.}}$ and η_{ex} of the **1800°C-NHA66E1** ($z= 0.64$, Eu^{2+} 0.37 mol%) sample were measured to be 11.6 and 7.2 %, respectively.

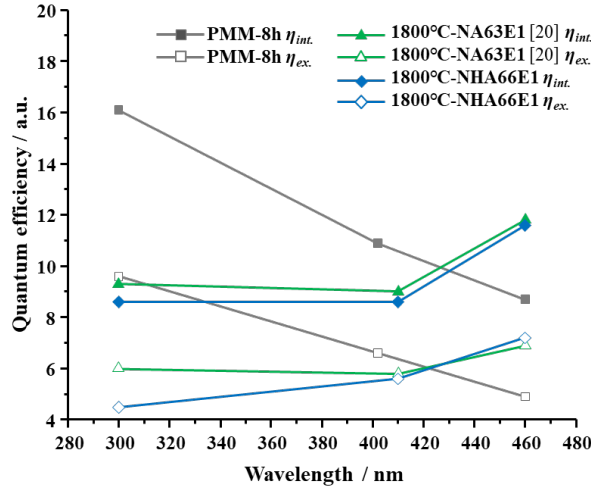


FIGURE 8 The internal quantum efficiency (η_{int}) and external quantum efficiency (η_{ex}) of the selected samples as a function of excitation wavelength

4. Conclusions

A series of β -SiAlON:Eu²⁺ phosphors with z values and Eu²⁺ contents in the ranges of 0.44-0.78 and 0.35-1.48 mol%, respectively were synthesized through the PDCs route: high-purity single source precursors in which strictly controlled chemical composition was established at the molecular scale by chemical modification of a commercially available PHPS with Al(OCH(CH₃)₂)₃, AlCl₃ and EuCl₂. The single source precursors were successfully converted to β -SiAlON:Eu²⁺ phosphors by pyrolysis at 1000 °C under flowing N₂ or NH₃ followed by heat treatment at 1800 °C under a N₂ gas pressure at 980 kPa. The polymer-derived β -SiAlON:Eu²⁺ phosphors exhibited green emission under excitation at 460 nm attributed to the 4f⁷-4f⁶(⁷f₃)5d¹ transition of dopant Eu²⁺ ions. The findings of our present study are summarized as follows:

1. HAADF-STEM analysis confirmed that the doped-Eu²⁺ cation existed interstitially within the channels along the c axis of the host β -SiAlON, which was consistent

with previous reports on the β -SiAlON:Eu²⁺ phosphors fabricated by the conventional powder metallurgy method.

2. The critical Eu²⁺ concentration in the polymer-derived host β -SiAlON was estimated at approximately 1.48 and 0.37 mol % for $z = 0.55$ and 0.64 , respectively.
3. Compared with the conventional powder metallurgy route, the PDC route investigated in this study offers some advantages in grain growth of host β -SiAlON with z value below 0.8 during the short period of 1 h-heat treatment at $1800\text{ }^{\circ}\text{C}$.
4. The polymer-derived β -SiAlON:Eu²⁺ phosphors exhibited better PL properties in terms of green emission intensity under excitation at 460 nm , and the highest intensity was achieved for the polymer-derived β -SiAlON:Eu²⁺ with $z = 0.64$ and $0.37\text{ mol\% Eu}^{2+}$. The internal and external quantum efficiencies were measured to be 11.6 and 7.2 \% , respectively.

Single source precursor-derived multicomponent amorphous compounds are highly homogeneous at the molecular scale. Moreover, the content of excess oxygen existed as silica species can be finely controlled by selecting the $\text{Al}(\text{OCH}(\text{CH}_3)_2)_3/\text{AlCl}_3$ molar ratio in the precursor synthesis, which leads to the formation of a sufficient amount of homogeneous transition liquid phase upon heating to $1800\text{ }^{\circ}\text{C}$ to afford β -SiAlON:Eu²⁺ composed of well-grown rod-like host β -SiAlON grains. On the other hand, the excess oxygen was finally spent out for the carbothermal reduction and subsequent nitridation reactions to afford β -SiAlON:Eu²⁺ having a composition close to the theoretical one. In addition, an increase in the critical Eu²⁺ concentration in the host β -SiAlON was also suggested as one of the potential advantages of this route.

These results revealed that the PDCs route investigated in this study is promising for developing high-performance β -SiAlON:Eu²⁺ green phosphors for two-pc wLEDs

using a blue LED tip. Further study on the improvement of the green emission properties is in progress by applying higher heat treatment temperatures at 1900 °C or higher under high N₂ pressure above 980 kPa.

Conflicts of interest

There are no conflicts to declare.

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Author contributions

Y.G. conceived and planned this study, and drafted the manuscript; Y.G., D.H., J.I., R.I. and M.K. contributed to the evaluation of samples; S.H. T.A. and T.H. contributed to Formal analysis; S.B. and P.T. reviewed the draft; Y.I. conceived, reviewed, and supervised this work. All authors have read and agreed to the published version of the manuscript.

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Figure captions

FIGURE 1 XRD patterns of polymer-derived β -SiAlON: Eu²⁺ phosphor samples: (a) **1800°C-NHA63E1** [20], (b) **1800°C-NHA66E1**, (c) **1800°C-NHA69E1** samples and reference samples of (d) **PMM63-1h**, (e) **PMM63-8h** and (f) **PMM-8h**

FIGURE 2 SEM images showing morphology of polymer-derived β -SiAlON: Eu²⁺ phosphor samples: (a) **1800°C-NA90E1** [19], (b) **1800°C-NA90E5** [19], (c) **1800°C-NA63E1** [20], (d) **1800°C-NHA63E1** [20], (e) **1800°C-NHA66E1**, (f) **1800°C-NHA69E1** and reference samples fabricated through the conventional powder metallurgy route: (g) **PMM63-1h**, (h) **PMM63-8h** and (i) **PMM-8h**

FIGURE 3 Average grain size of the host β -SiAlON evaluated for the β -SiAlON: Eu²⁺ phosphors investigated in this study

FIGURE 4 PL properties of **1800°C-NHA66E1** and **1800°C-NHA69E1** samples along with **1800°C-NA90E1** [19], **1800°C-NA90E5** [19], **1800°C-NA63E1** [20] and **1800°C-NHA63E1** [20], samples. (a) Excitation spectra monitored at appropriate maximum emission wavelengths shown in (b), emission spectra under excitation at (b) 460 nm and (c) 290 nm

FIGURE 5 Amplified excitation spectrum of the **1800°C-NA63E1** sample [20] with the ⁷F_j (J=1-6) energy levels of Eu³⁺ cation

FIGURE 6 (a) HAADF-STEM image of **1800°C-NA63E1** sample [20] showing (a) typical six-membered rings of β -SiAlON and (b) the Z-contrast profile along with the A-B line across the atomic channel shown in (a)

FIGURE 7 (a) Excitation and (b) emission spectra of **1800°C-NHA63E1** [20], **1800°C-NHA66E1** samples along with the reference samples fabricated through the conventional powder metallurgy route

FIGURE 8 The internal quantum efficiency ($\eta_{\text{int.}}$) and external quantum efficiency ($\eta_{\text{ex.}}$) of the selected samples as a function of excitation wavelength

Supplementary Information

Polymer-derived β -SiAlON:Eu²⁺ phosphors

Yang Gao^a, Daiki Hamana^a, Junya Iihama^a, Ryo Iwasaki^a, Sawao Honda^a, Toru Asaka^a, Munni Kumari^b, Tomokatsu Hayakawa^a, Samuel Bernard^b, Philippe Thomas^b and Yuji Iwamoto^{*a}

a. Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan.

b. University of Limoges, CNRS, IRCER, UMR 7315, F-87000 Limoges, France.

- Corresponding author

Yuji Iwamoto:

Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan

TEL/FAX: +81 52 735 5276

E-mail: iwamoto.yuji@nitech.ac.jp

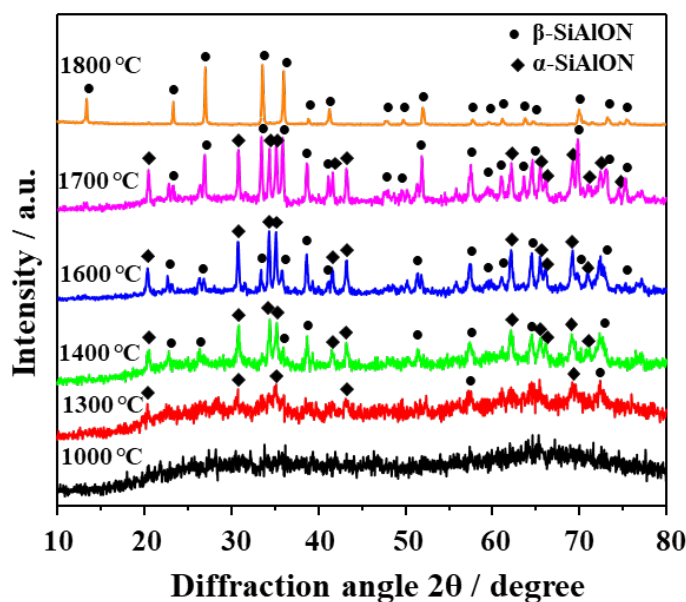


FIGURE S1 Phases evolution of the NA63E1 sample [20] during the heat treatment up to 1800 °C

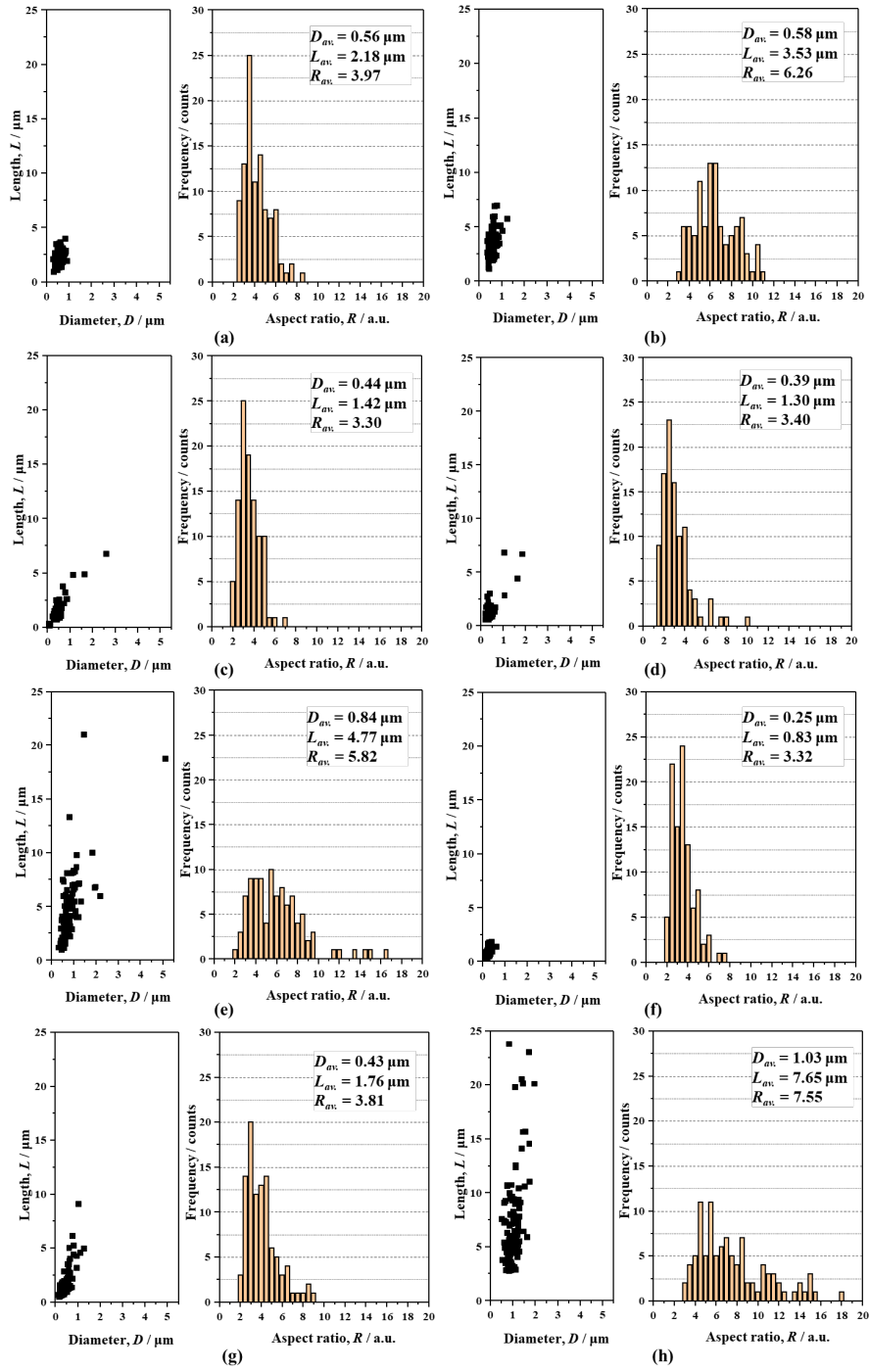


FIGURE S2 Grain size distribution and average grain diameter, length and aspect ratio evaluated for the selected samples of (a) 1800°C-NA90E1 [19] (b) 1800°C-NA90E5 [19], (c) 1800°C-NA63E1 [20], (d) 1800°C-NHA63E1 [20], (e) 1800°C-NHA66E1 and reference samples of (f) PMM63-1h, (g) PMM63-8h and (h) PMM-8h

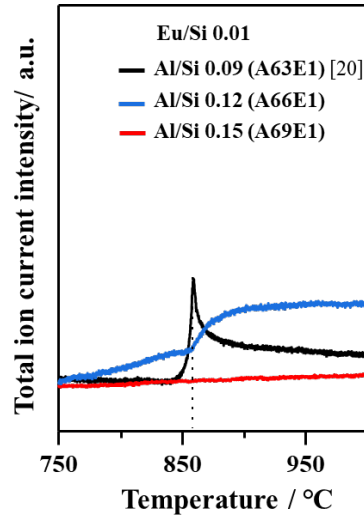


FIGURE S3 TICC curves from 750 to 1000 °C of **A63E1** [20], **A66E1**, and **A69E1** samples measured under He flow.

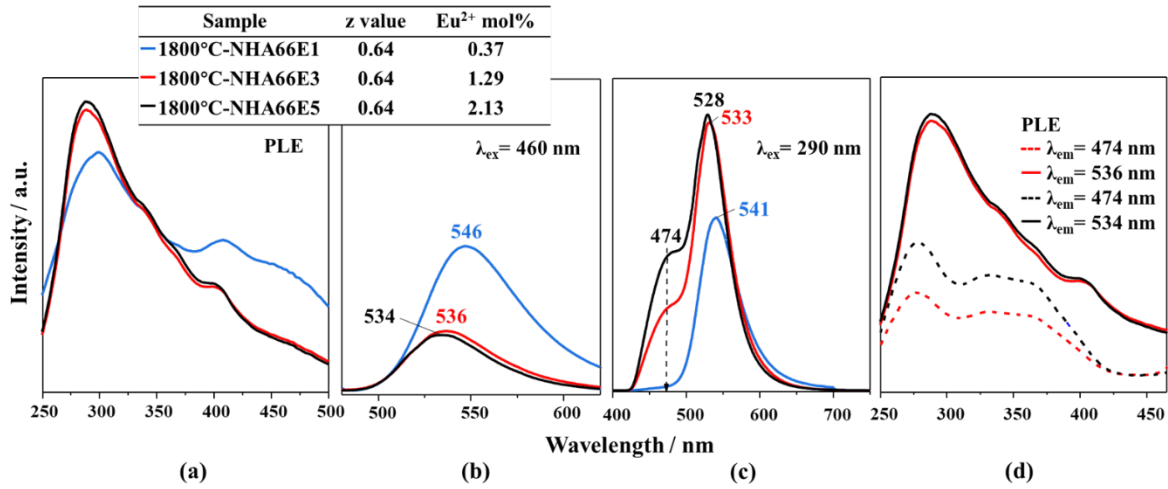


FIGURE S4 (a), (d) excitation and (b), (c) emission spectra of **1800°C-NHA66E1**, **1800°C-NHA66E3**, and **1800°C-NHA66E5** samples