Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 31 (2011) 151–157

www.elsevier.com/locate/jeurceramsoc

Combustion synthesis of $LaSi_3N_5$:Eu^{2+} phosphor powders

You Zhou[a,*], Yu-ichi Yoshizawa[a], Kiyoshi Hirao[a], Zoltán Lenčéš[b], Pavol Šajgalík[b]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, Japan*
[b] *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia*

Received 31 March 2010; received in revised form 26 July 2010; accepted 2 August 2010
Available online 15 September 2010

Abstract

$LaSi_3N_5$:Eu^{2+} phosphor powders were prepared by a highly efficient combustion synthesis method. It was found that the compositions of the raw powder mixtures had great influences on the phase compositions and particle morphologies of the synthesized powders. By selecting appropriate starting compositions and combustion parameters, single phase $LaSi_3N_5$:Eu^{2+} phosphors could be synthesized. When excited by a UV light, the $LaSi_3N_5$:Eu^{2+} phosphors emitted green light. The wavelength and intensity of the emission spectra were affected by the amount of Eu^{2+} dopant. With increasing amount of Eu^{2+} dopant, concentration quenching could occur and emission spectra shifted to longer wavelengths.

Keywords: B. Spectroscopy; C. Colour; C. Optical properties; D. Nitrides

1. Introduction

In recent years, some silicon-based nitride and oxynitride phosphors have emerged as a new family of luminescent materials and have drawn increasing attention.[1–15] These phosphors have excellent thermal and chemical stability which are attributed to their rigid structures built up of highly condensed [SiN4] tetrahedron-based networks. Moreover, they have long excitation/emission wavelengths and low thermal quenching which are ascribed to the high covalency of chemical bonding (nephelauxetic effect) and large crystal-field splitting due to the incorporation of nitrogen in the structure.[12] These attractive properties make the nitride and oxynitride phosphors more suitable for use as down-conversion luminescent materials in the fabrication of white light-emitting diodes (LEDs), compared with the conventional oxide and sulfide phosphors.

One interesting material in this family is an Eu-doped $LaSi_3N_5$ phosphor reported by Uheda et al. in 2000,[15] which showed a broad emission band with a maximum at 549 nm when excited by a UV light of 350 nm. In the structure of $LaSi_3N_5$, the large lanthanum atom is located in the center of two pentagonal holes which are composed of 5 [SiN4] tetrahedra joined by sharing corners.[16] Partial replacement of La^{3+} by Eu^{2+} resulted in the formation of a $LaSi_3N_5$:Eu^{2+} phosphor. In the study of Uheda et al.,[15] LaN was firstly synthesized by reacting La metal with NH_3 gas, then the synthesized LaN was mixed with Si_3N_4 and Eu_2O_3 and heated at 1900 °C for 2 h under a nitrogen pressure of 1.0 MPa. Due to their flammability and toxicity, complex procedures (e.g., avoiding exposure to air using glove box) must be adapted to handle the raw materials. The multistep procedure, difficult handling and long-term annealing at high-temperature and under high gas pressure make the manufacturing cost of $LaSi_3N_5$:Eu^{2+} phosphor very high. For its practical industrial application, a simple and efficient method of preparing $LaSi_3N_5$:Eu^{2+} phosphors needs to be explored.

Recently, we found that the host crystal $LaSi_3N_5$ could be synthesized by direct nitridation of a $LaSi + Si + Si_3N_4$ powder mixture, which was stable in air and easy to be handled.[17] Later, Cai et al. reported that a $LaSi_3N_5$:Ce^{3+} phosphor could be synthesized by nitridation of a powder mixture of $LaSi + CeSi + Si_3N_4$ at 1600 °C for 2 h.[18] On the other hand, recently we succeeded in synthesizing a β-SiAlON:Eu^{2+} phosphor by a highly efficient combustion synthesis method.[19] Combustion synthesis, also termed self-propagating high-temperature synthesis (SHS), is based on the high exothermic heat of formation of refractory materials.[20,21] When a compact of mixed powders of the constituent elements is ignited at one end, the highly exothermic reaction spontaneously propagates through the reactant mixture in a very short time, producing the refractory material. In the process heating is accomplished by

---

[*] Corresponding author. Tel.: +81 52 736 7161; fax: +81 52 736 7405.
E-mail address: you.zhou@aist.go.jp (Y. Zhou).

0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.08.004

the exothermic heat of the chemical reaction and does not require any external energy once initiated. Therefore, combustion synthesis is a time-saving and energy-efficient method. Considering the nitridation reactions of both LaSi and Si are exothermic,[17] it would be worth to investigate whether an Eu-doped $LaSi_3N_5$ phosphor could be synthesized by the combustion synthesis method.

2. Experimental

Our previous study showed that $LaSi_3N_5$ could be synthesized by a slow nitridation method according to the following general reaction:[17]

$$LaSi + (2-3m)Si + mSi_3N_4 + ((5/2)-2m)N_2 = LaSi_3N_5 \tag{1}$$

It was found that although $LaSi_3N_5$ could be obtained by nitridation of both a binary system $LaSi + Si_3N_4$ (i.e., $m = 2/3$ in Reaction (1)) and a ternary system $LaSi + Si + Si_3N_4$ (i.e., $m < 2/3$ in Reaction (1)) starting mixtures, adding Si in the starting materials would make the chemical reaction evolve larger amount of exothermic heat, and hence accelerate the nitridation reaction and help attain a single phase $LaSi_3N_5$ product.[17]

In the present study, the design of starting compositions was based on the above-mentioned reaction, and Eu_2O_3 was added into the starting mixtures to introduce an activator. Therefore, the combustion synthesis reaction can be expressed as:

$$(1-x)LaSi + (2-3m+x)Si + mSi_3N_4 + ((5/2)-2m)N_2 + (x/2)Eu_2O_3 \rightarrow La_{1-x}Eu_xSi_3N_5 \tag{2}$$

The ratio among the starting constituents for the host $LaSi_3N_5$ and the amount of doped activator were adjusted by changing the values of m and x in Reaction (2), respectively. The synthesized product would inevitably contain a small amount of oxygen, but for simplicity, the composition of the product was designated as $La_{1-x}Eu_xSi_3N_5$ and the oxygen therein was omitted.

High purity powders of LaSi (Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), Si (Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), α-Si_3N_4 (SN-E10, Ube Industries Co. Ltd., Yamaguchi, Japan), and Eu_2O_3 (Shin-Etsu Chemical Co. Ltd., Tokyo, Japan) were used as starting materials. The starting powders were weighed according to the compositions listed in Tables 1 and 2, which were designed to investigate the influences of the ratio among the starting constituents (Table 1) and the amount of activator (Table 2) on the properties of the synthesized products.

Table 1
Starting compositions for synthesizing a $La_{0.9}Eu_{0.1}Si_3N_5$ phosphor (in molar ratio).

Sample code	LaSi	Si	Si_3N_4	Eu_2O_3
Si-0	0.9	0	0.7	0.05
Si-1	0.9	0.45	0.55	0.05
Si-2	0.9	0.9	0.4	0.05
Si-3	0.9	1.2	0.3	0.05

Table 2
Starting compositions for synthesizing $La_{1-x}Eu_xSi_3N_5$ phosphors (in molar ratio).

Sample code	X in $La_{1-x}Eu_xSi_3N_5$	LaSi	Si_3N_4	Eu_2O_3
Eu001	0.01	0.99	0.670	0.005
Eu002	0.02	0.98	0.673	0.010
Eu005	0.05	0.95	0.683	0.025
Eu010	0.10	0.90	0.700	0.050

The powders were mixed in methanol using a planetary mill for 2 h in a Si_3N_4 jar with Si_3N_4 balls. After vacuum drying and sieving, the mixed powder was put into a cylindrical porous graphite crucible having an outer diameter of 35 mm, an inner diameter of 25 mm and a height of 50 mm. A pellet composed of titanium and carbon powders serving as an igniter was then placed on the top of the powder compact in the crucible. The crucible was placed into a combustion reaction chamber and after evacuation high purity N_2 gas (purity > 99.999%) was filled into the chamber till a pressure of 6.0 MPa. The combustion reaction was triggered by passing an electric current through a carbon ribbon which was set closely above the igniter pellet. Once it was ignited, the combustion reaction proceeded rapidly and the temperature rose drastically. The whole combustion synthesis process completed within a few minutes.

Phase identification for the synthesized powders was performed by X-ray diffraction analysis (XRD) (RINT2500, Rigaku, Tokyo, Japan) with Cukα radiation of 40 kV/100 mA. Morphologies of the powders were observed using a scanning electron microscope (SEM) (JSM-6340F, JEOL, Tokyo, Japan) equipped with a field emission gun. Photoluminescence spectra of the powders were measured using a fluorescent spectrophotometer (F-4500, Hitachi Ltd., Tokyo, Japan) with a 150 W xenon lamp as an excitation source.

3. Results and discussion

3.1. Influences of starting compositions

In the afore-mentioned Reaction (2), changing the m values from 0.7, 0.55, 0.4 to 0.3 while keeping the x value to be 0.1 gave the four starting compositions designated as Si-0, Si-1, Si-2 and Si-3 in Table 1. For the composition Si-0, no silicon powder was added; while the amount of added silicon powder increased in the sequence of Si-1 to Si-2 to Si-3. All these four starting compositions were designed to synthesize a phosphor having a nominal composition of $La_{0.9}Eu_{0.1}Si_3N_5$.

Fig. 1 shows the appearance of the four combusted compacts. At first glance, the four cylindrical compacts all showed a core–shell structure, which was thought to be caused by a temperature gradient within the powder compact during combusting. Because the porous carbon crucible was not surrounded with an insulator, combustion heat generated at the outer part of the powder compact could easily get lost. As a result, the temperature of the outer part (the shell) of the compact was lower than that of the inner part (the core) and the combustion became incomplete at the surface layer. Owing to the different combustion products

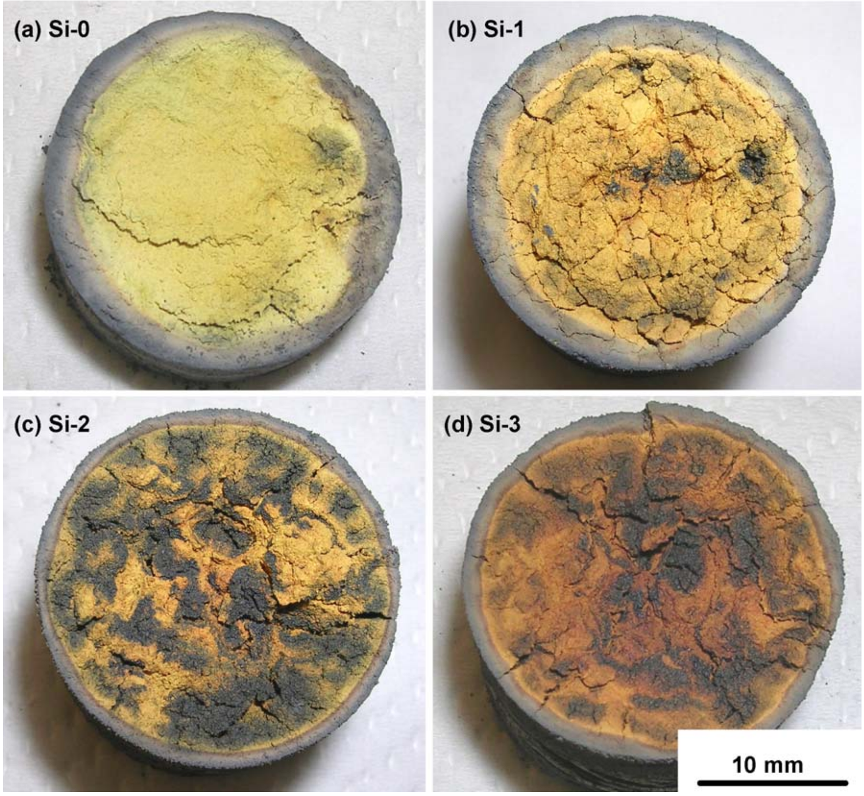

Fig. 1. Appearances of the combusted powder compacts containing various amounts of silicon in the starting compositions: (a) sample Si-0, (b) sample Si-1, (c) sample Si-2, and (d) sample Si-3.

the combusted powder compact had a core–shell structure. For the four compacts, the thicknesses of the shells were 2–3 mm. Hereafter, if not specifically mentioned, all samples for analysis were taken from the inner part of the combusted compacts.

Sample Si-0 displayed a greenish yellow colour. (For interpretation of the references to colour in this text, the reader is referred to the web version of the article.) With the addition of silicon into the starting compositions, some black portions appeared in the combusted compacts; and from samples Si-1 to Si-2 to Si-3, the area of black portions increased when more silicon was added. Certainly, these black phases are very detrimental to photoluminescent properties by causing unwanted absorption. To understand the cause of the formation of the black portions, phase identification analyses were conducted. As shown in Fig. 2, the XRD pattern of sample Si-0 coincided well with that of a single phase $LaSi_3N_5$. The diffraction peaks assigned to $LaSi_3N_5$ were a combination of the peaks listed in JCPDS Powder Diffraction File No. 42-1144 and the peaks calculated by Lenčéš et al.[17] However, in the XRD patterns of samples Si-1, Si-2 and Si-3, besides the peaks of $LaSi_3N_5$, peaks of Si and LaSi appeared. As shown in Figs. 2(b) and (c), the peaks of Si and LaSi in sample Si-2 were stronger than those in sample Si-1. In other words, addition of silicon powder into the starting compositions resulted in the residual Si and LaSi in the combusted sample; and the more silicon addition in the starting materials, the larger amount of residual Si and LaSi in the combusted products. The black portions in the combusted samples shown in Fig. 1 were then attributed to the existence of the residual Si and LaSi.

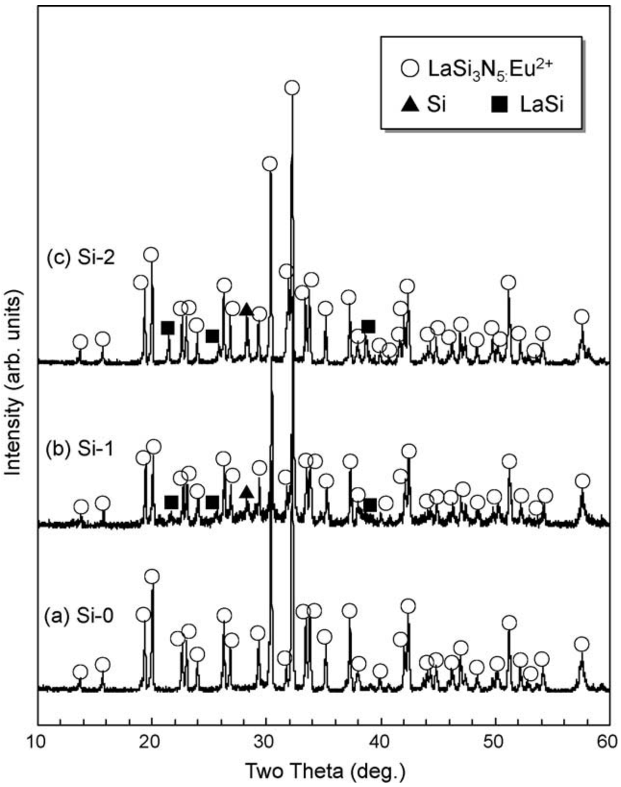

Fig. 2. XRD patterns of the combusted samples containing various amounts of silicon in the starting compositions: (a) sample Si-0, (b) sample Si-1, and (c) sample Si-2.

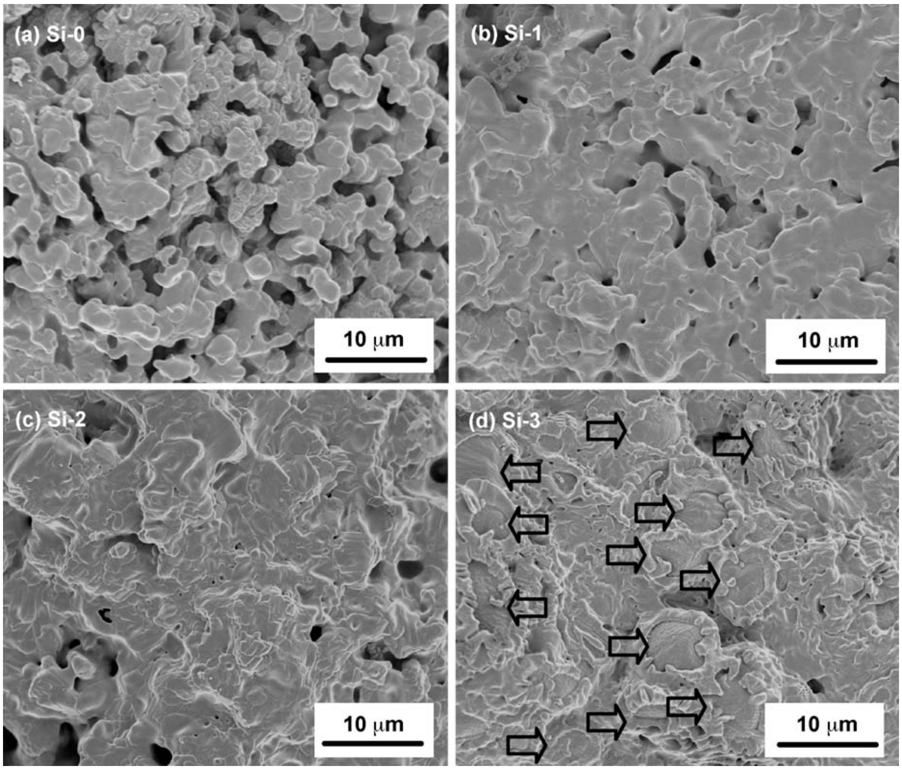

Fig. 3. Scanning electron micrographs of the combusted samples containing various amounts of silicon in the starting compositions: (a) sample Si-0, (b) sample Si-1, (c) sample Si-2, and (d) sample Si-3.

In our previous work of synthesizing $LaSi_3N_5$ by a slow heating method, addition of silicon into a binary mixture of $LaSi + Si_3N_4$ could help the formation of a single phase $LaSi_3N_5$, but it was not the case in the present combustion synthesis. In the combustion synthesis, nitridation of LaSi and Si under a N_2 gas pressure of 6.0 MPa released a large amount of exothermic heat within very short time, thereby causing the melting of other silicon particles ($T_m(\mathrm{Si}) = 1414\,^{\circ}\mathrm{C}$) prior to the arrival of the flame front. Once silicon particles got melted, the liquid would then fill in some pores of the unreacted powder compact. As a result, some pathways for transportation of nitrogen gas were blocked, and hence the nitridation reactions of Si and LaSi were kinetically hindered and some of them remained as residues in the final product.

The particle morphologies of the synthesized samples were observed by SEM and are shown in Fig. 3. Sample Si-0 revealed a very porous structure. Although the particles were connected with each other through necking, they could be easily crushed to obtain separate particles. Most particles showed rounded surfaces and sizes of a few micrometers. All these characteristics were advantageous when considering their application as phosphor powders for fabrication of white LEDs. When silicon was added into the starting compositions, the synthesized samples became less porous. From samples Si-1 to Si-2 to Si-3, with more addition of silicon, their structures became denser. The samples revealed sintered structures in which individual particles could hardly be distinguished. In sample Si-3, as indicated by the arrows in Fig. 3(d), many spherical particles were observed. It would be reasonable to regard that these spherical particles were formed from the molten droplets of silicon during the high-temperature combustion, which were mentioned in the previous paragraph.

The photoluminescence spectra of sample Si-0 are shown in Fig. 4. The photoluminescence spectra of the other three samples are not shown here, because they contained too many black colour impurities which greatly lowered the intensity of the spectra. As shown in Fig. 4, the excitation spectrum covered a wide range of 250–500 nm and showed a broadband centered at 335 nm. When excited by a UV light of 335 nm, the emission

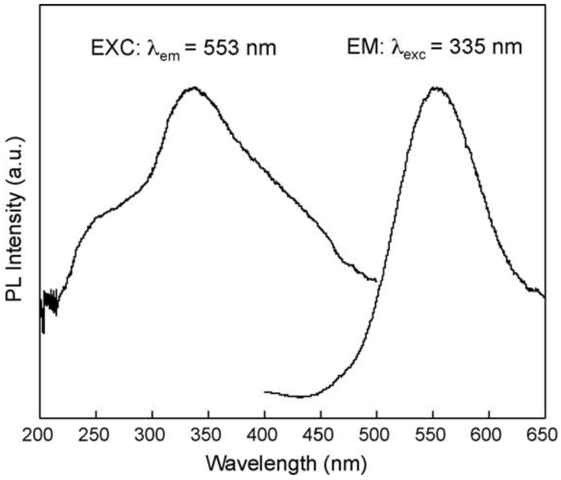

Fig. 4. Excitation and emission spectra of sample Si-0 prepared by combustion synthesis.

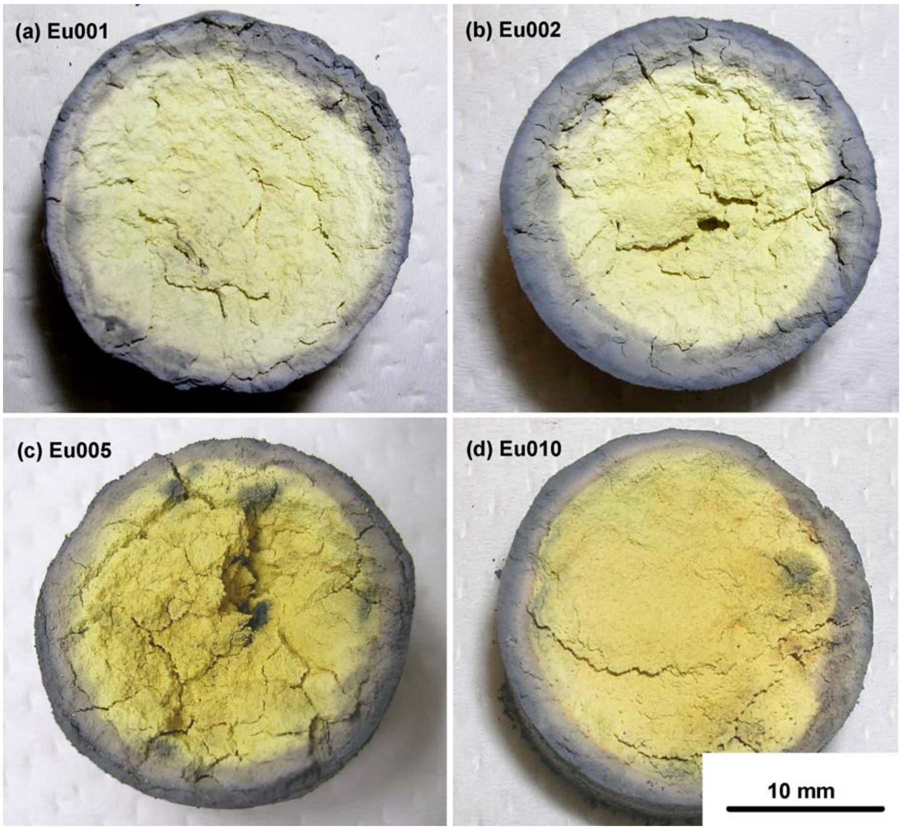

Fig. 5. Appearances of the combusted powder compacts containing various amounts of Eu_2O_3 in the starting compositions: (a) sample Eu001, (b) sample Eu002, (c) sample Eu005, and (d) sample Eu010.

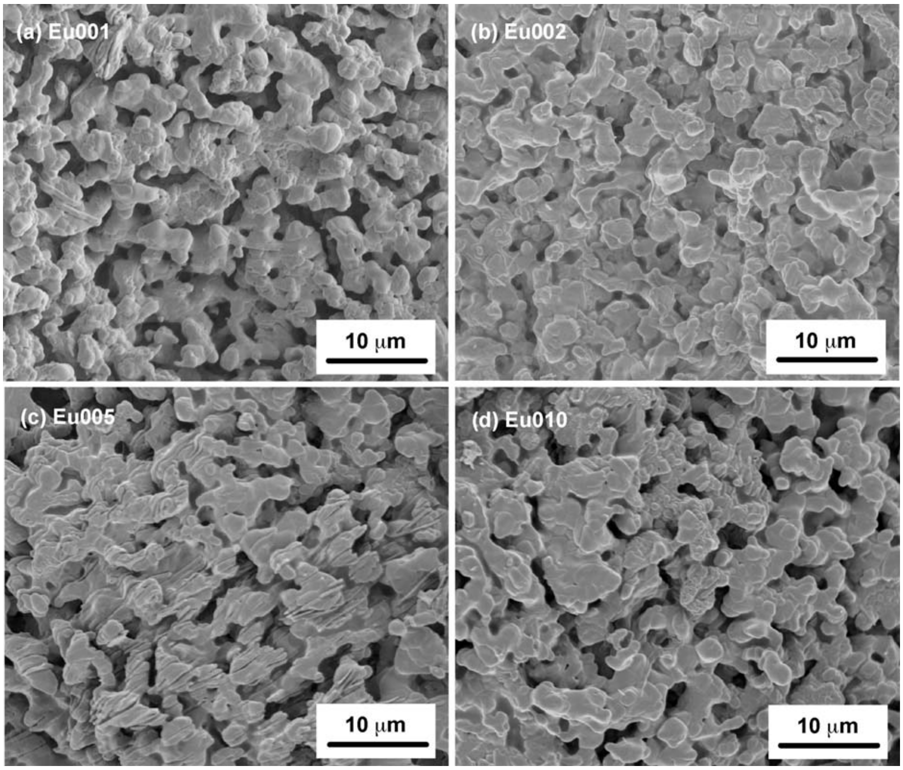

Fig. 6. Scanning electron micrographs of the combusted samples containing various amounts of Eu_2O_3 in the starting compositions: (a) sample Eu001, (b) sample Eu002, (c) sample Eu005, and (d) sample Eu010.

spectrum exhibited a single broadband with a maximum at 553 nm. The broadband emission should be ascribed to the $5d4f^6 \rightarrow 4f^7$ transitions of Eu^{2+}. Previous studies have revealed that Eu^{2+} can give broadband emission while Eu^{3+} yields line emission at well-defined wavelengths.[2–5,15] Therefore, the broadband emission of the synthesized phosphor powder indicates that the Eu^{3+} ions in the Eu_2O_3 starting powder were reduced to Eu^{2+} ions during the combustion reaction. In a nitride environment, the reduction of Eu^{3+} might take place according to the following general reaction[4]:

$$6Eu^{3+} + 2N^{3-} \rightarrow 6Eu^{2+} + N_2 \qquad (3)$$

The above-mentioned results showed that a $LaSi_3N_5$:Eu^{2+} phosphor could be prepared by a rapid combustion synthesis method within a few minutes. It was also revealed that adding silicon into the starting compositions would make it difficult to obtain a single phase $LaSi_3N_5$-based phosphor. Therefore, in the continuing experiments described in the following section, silicon was not added in the starting materials.

3.2. *Influences of concentration of Eu^{2+} dopant*

The above-mentioned experimental results were all targeted to synthesize a phosphor having a nominal composition of $La_{0.9}Eu_{0.1}Si_3N_5$, which was originally reported by Uheda et al.[15] In the composition, 10 at.% of La^{3+} was replaced by Eu^{2+}. In other words, the activator concentration was 10 at.%, which was rather high, and possibly too high, for a rare-earth-activated phosphor. Therefore, experiments of doping smaller amount of Eu^{2+} were then conducted. Table 2 lists the starting compositions of this series of experiments, in which the concentrations of Eu^{2+} dopant were 1 at.%, 2 at.%, 5 at.% and 10 at.% for the samples designated as Eu001, Eu002, Eu005 and Eu010, respectively.

Fig. 5 shows the appearances of the synthesized samples doped with various amounts of Eu^{2+}. The sample doped with 1 at.% of Eu^{2+} showed a light green colour. (For interpretation of the references to colour in this text, the reader is referred to the web version of the article.) With increasing amount of Eu^{2+} dopant, the colour of the samples gradually turned to be more yellowish. X-ray diffraction analyses revealed that all the four synthesized samples were a $LaSi_3N_5$-based single phase, and their XRD patterns were almost the same as that of the sample Si-0 shown in Fig. 2(a). SEM observations revealed that the particle sizes and morphologies of the four combusted samples were similar. As shown in Fig. 6, the compacts were highly porous and easy to be crushed to obtain separate particles. Almost all particles had rounded morphologies with sizes of a few micrometers. All these features are beneficial for the application of these powders as phosphor in white LEDs.

The photoluminescence spectra of the four samples are shown in Fig. 7. Although the spectra showed similar shapes, their excitation and emission intensities were quite different. The sample doped with 2 at.% of Eu^{2+} had higher emission intensity than the sample doped with 1 at.% of Eu^{2+}. But further increase of Eu^{2+} content resulted in lower emission intensities. Such a decrease in emission intensity beyond a critical concentration of dopant can be explained by concentration quenching, which is mainly caused by energy transfer among the activator ions.[22] Another feature observed in the spectra was that with increasing Eu^{2+} concentration the emission bands shifted towards the long wavelength side (i.e., redshift). The emission peaks of the samples doped with 1 at.%, 2 at.%, 5 at.% and 10 at.% were located at 539 nm, 544 nm, 548 nm and 553 nm, respectively. The phenomenon of redshift of emission band at higher concentration of activator dopant has frequently been reported in various kinds of Eu-doped phosphors, e.g., $BaSi_5N_8$:Eu^{2+} phosphor,[2] $BaYSi_4N_7$:Eu^{2+} phosphor,[9] α-SiAlON:Eu^{2+} phosphor,[6] $Sr_2Si_5N_8$:Eu^{2+} phosphor,[7] $CaAlSiN_3$:Eu^{2+} phosphor[11] and β-SiAlON:Eu^{2+} phosphor.[23] The reason for the occurrence of redshift is still not clear. One possible explanation is that the probability of energy transfer from the Eu^{2+} ions at higher levels of 5*d* to those at lower levels of 5*d* increased with increasing Eu^{2+} concentration, thereby lowering the emission energy for transfer from the low 5*d* excited state to the 4*f* ground state and then emitting light of longer wavelength.[6]

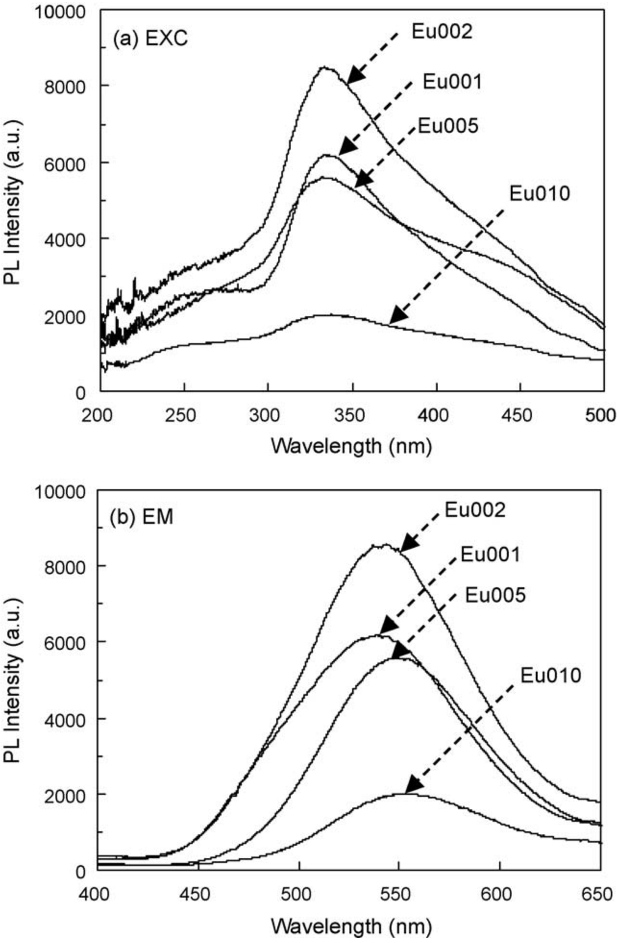

Fig. 7. (a) Photoluminescence excitation and (b) emission spectra of the synthesized $LaSi_3N_5$:Eu^{2+} phosphors doped with various amounts of Eu_2O_3 in the starting compositions. The emission spectra were measured under 335 nm excitation, and the excitation spectra were monitored at 539 nm, 544 nm, 548 nm and 553 nm for samples Eu001, Eu002, Eu005 and Eu010, respectively.

4. Conclusions

$LaSi_3N_5:Eu^{2+}$ phosphor powders were successfully prepared by a very rapid combustion synthesis method, which required no external heating and could be completed within a few minutes instead of hours. Starting from a binary system mixture of $LaSi + Si_3N_4$ doped with Eu_2O_3, single phase $LaSi_3N_5$-based phosphors could be obtained; while starting from a ternary system mixture of $LaSi + Si + Si_3N_4$ doped with Eu_2O_3 would result in residual Si and LaSi in the combusted products which had a black colour and were detrimental to the photoluminescent properties. When excited by a UV light, the synthesized $LaSi_3N_5:Eu^{2+}$ phosphors emitted green light. When the concentration of Eu^{2+} dopant changing in the range from 1 at.% to 10 at.%, the emission intensity reached the highest at a dopant concentration of 2 at.%, and doping more Eu^{2+} led to concentration quenching. With increasing amount of Eu^{2+} dopant, the emission spectra shifted to the long wavelength side.

Acknowledgements

This work has been financially supported by Japan Society for the Promotion of Science (JSPS) and partly by the Slovak Grant Agency VEGA-2/0178/10.

References

1. van Krevel JWH, Hintzen HT, Metselaar R, Meijerink A. Long wavelength Ce^{3+} emission in Y–Si–O–N materials. *J Alloys Compd* 1998;**268**:272–7.
2. Höppe HA, Lutz H, Morys P, Schnick W, Seilmeier A. Luminescence in Eu^{2+}-doped $Ba_2Si_5N_8$: fluorescence, thermoluminescence, and upconversion. *J Phys Chem Solids* 2000;**61**:2001–6.
3. van Krevel JWH, van Rutten JWT, Mandal H, Hintzen HT, Metselaar R. Luminescence properties of terbium-, cerium-, or europium-doped α-SiAlON materials. *J Solid State Chem* 2002;**165**:19–24.
4. de Graaf D, Hintzen HT, Hampshire S, de With G. Long wavelength Eu^{2+} emission in Eu-doped Y–Si–Al–O–N glasses. *J Eur Ceram Soc* 2003;**23**:1093–7.
5. Hintzen HT, van Krevel JWH, de Graaf D, Metselaar R, Menke Y, Hampshire S. Evidence for the presence of Eu^{2+} in (Y,Eu)–Si–Al–O–N glass by luminescence spectroscopy. *J Mater Sci* 2004;**39**:2237–8.
6. Xie RJ, Hirosaki N, Mitomo M, Yamamoto Y, Suehiro T, Sakuma K. Optical properties of Eu^{2+} in α-SiAlON. *J Phys Chem B* 2004;**108**:12027–31.
7. Xie RJ, Hirosaki N, Suehiro T, Xu FF, Mitomo M. A simple, efficient synthetic route to $Sr_2Si_5N_8:Eu^{2+}$-based red phosphors for white light-emitting diodes. *Chem Mater* 2006;**18**:5578–83.
8. Hirosaki N, Xie RJ, Kimoto K, Sekiguchi T, Yamamoto Y, Suehiro T, et al. Characterization and properties of green-emitting β-SiAlON:Eu^{2+} powder phosphors for white light-emitting diodes. *Appl Phys Lett* 2005;**86**:211905.
9. Li YQ, de With G, Hintzen HT. Synthesis, structure, and luminescence properties of Eu^{2+} and Ce^{3+} activated $BaYSi_4N_7$. *J Alloys Compd* 2004;**385**:1–11.
10. Li YQ, Delsing ACA, de With G, Hintzen HT. Luminescence properties of Eu^{2+}-activated alkaline–earth silicon–oxynitride $MSi_2O_{2-\delta}N_{2+2/3\delta}$ (M = Ca, Sr, Ba): a promising class of novel LED conversion phosphors. *Chem Mater* 2005;**17**(12):3242–8.
11. Piao XQ, Machida K, Horikawa T, Hanzawa H, Shimomura Y, Kijima N. Preparation of $CaAlSiN_3:Eu^{2+}$ phosphors by the self-propagating high-temperature synthesis and their luminescent properties. *Chem Mater* 2007;**19**:4592–9.
12. Xie RJ, Hirosaki N. Silicon-based oxynitride and nitride phosphors for white LEDs—a review. *Sci Technol Adv Mater* 2007;**8**:588–600.
13. Watanabe H, Imai M, Kijima N. Nitridation of AEAlSi for production of $AEAlSiN_3:Eu^{2+}$ nitride phosphors (AE = Ca, Sr). *J Am Ceram Soc* 2009;**92**(3):641–8.
14. Höppe HA. Recent developments in the field of inorganic phosphors. *Angew Chem Int Ed* 2009;**48**:3572–82.
15. Uheda K, Takizawa H, Endo T, Yamane H, Shimada M, Wang CM, et al. Synthesis and luminescent property of Eu^{3+}-doped $LaSi_3N_5$ phosphor. *J Lumin* 2000;**87–89**:967–9.
16. Inoue Z, Mitomo M, Ii N. A crystallographic study of a new compound of lanthanum silicon nitride, $LaSi_3N_5$. *J Mater Sci* 1980;**15**:2915–20.
17. Lenčéš Z, Benco L, Madejová J, Zhou Y, Kipsová L, Hirao K. Reaction synthesis and characterisation of lanthanum silicon nitride. *J Eur Ceram Soc* 2008;**28**:1917–22.
18. Cai LY, Wei XD, Li H, Liu QL. Synthesis, structure and luminescence of $LaSi_3N_5:Ce^{3+}$ phosphor. *J Lumin* 2009;**129**:165–8.
19. Zhou Y, Yoshizawa Y, Hirao K, Lenčéš Z, Šajgalík P. Preparation of Eu-doped β-SiAlON phosphors by combustion synthesis. *J Am Ceram Soc* 2008;**91**(9):3082–5.
20. Munir ZA. Synthesis of high temperature materials by self-propagating combustion methods. *Am Ceram Soc Bull* 1988;**67**(2):342–9.
21. Hirao K, Miyamoto Y, Koizumi M. Synthesis of silicon nitride by a combustion reaction under high nitrogen pressure. *J Am Ceram Soc* 1986;**69**(4):C60–61.
22. Ferguson J, Matsui H. Mechanism of concentration quenching of the fluorescence from $^1T_{2g}$ of Ni^{2+} in $KZnF_3$. *J Phys Soc Jpn* 1977;**42**(5):1640–6.
23. Xie RJ, Hirosaki N, Li HL, Li YQ, Mitomo M. Synthesis and photoluminescence properties of β-SiAlON:Eu^{2+} ($Si_{6-z}Al_zO_zN_{8-z}:Eu^{2+}$): a promising green oxynitride phosphor for white light-emitting diodes. *J Electrochem Soc* 2007;**154**(10):J314–9.