Journal of the Korean Ceramic Society
Vol. 49, No. 4, pp. 325~327, 2012.
http://dx.doi.org/10.4191/kcers.2012.49.4.325

Luminescent Properties of Europium-Doped Lanthanum Silicon Nitride Phosphor

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(Received May 22, 2012; Revised June 28, 2012; Accepted July 2, 2012)

ABSTRACT

Europium-doped $LaSi_3N_5$ phosphor was synthesized from $LaSi/Si/Si_3N_4/Eu_2O_3$ mixture by nitridation at 1390°C and additional annealing at 1650°C for 4 h. The phosphor shows emissions in the green light region with a maximum at 560 nm. With increasing europium content in the general formula $La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z}$ from z = 0.01 to 0.06 there was a maximum emission for z = 0.04 followed by concentration quenching for the highest europium content (z = 0.06).

Key words : Lanthanum silicon nitride, Nitridation, Luminescence, Phosphor, Europium

1. Introduction

Ternary silicon nitrides/oxynitrides have attracted a high attention due to their ability to serve as a host lattices for phosphors. These phosphors emit visible light under NUV or blue-light irradiation and generally have superior thermal and chemical stability to their sulfide and oxide counterparts and can be used as conversion luminescent materials for white LEDs, displays, etc.

Lanthanum silicon nitride ($LaSi_3N_5$) attracted an attention as engineering ceramic material and phosphor.[1,2] Upon doping of $LaSi_3N_5$ with Eu^{3+} or Ce^{3+}, a luminescent compound is formed.[3-7] Uheda et al.[3] prepared a solid solution $La_{0.9}Eu_{0.1}Si_3N_{5-x}O_x$ ($x = 0.1$) by sintering the $LaN\text{-}Si_3N_4\text{-}Eu_2O_3$ starting mixture at 1900°C for 2 h and this phosphor showed a broad excitation and emission band with maxima at ~350 and 549 nm, respectively. Another phosphor with high Eu content ($LaEuSi_2N_3O_2$), however, exhibits an emission band shifted to the red spectral region centered at ~650 nm. Suehiro et al. used a multicomponent system of La_2O_3 - CeO_2 - SiO_2 for the preparation of the ternary $LaSi_3N_5$ phosphor doped with Ce^{3+} using the gas-reduction-nitridation method.[8] The system allocates a broad emission band in a blue region. Addition of aluminum into $LaSi_3N_5{:}Ce^{3+}$ phosphor slightly red-shifted both the excitation and emission bands and enhanced the eligibility of this phosphor for application in white LEDs.[9] Ten Kate et al. prepared Yb^{3+} doped $LaSi_3N_5$ phosphors suitable for application as spectral conversion materials for infrared LEDs or solar cells.[10]

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In this work we report on the preparation of Eu-doped $LaSi_3N_5$ phosphor from LaSi/Si/ Eu_2O_3 starting mixture by direct nitridation method. The exothermic reaction was controlled by the addition of Si_3N_4 to the system. The influence of post-nitridation annealing on the PL properties of $LaSi_3N_5{:}Eu^{2+}$ phosphor is also discussed.

2. Experimental Procedure

The starting powder composition for the synthesis of $LaSi_3N_5$ was determined using the following equation:

$$y\,LaSi + (3\text{-}3x\text{-}y)\,Si + x\,Si_3N_4 + (5/2\text{-}2x)\,N_2 = LaSi_3N_5 \quad (1)$$

Compositions $x = 0.55$ and $y = 1$ were chosen on the base of our previous study.[2] Europium was used as a doping element for the preparation of phosphors and was added in the form of Eu_2O_3. The europium content was adjusted according to the general equation:

$$(1\text{-}z)\,LaSi_3N_5 + z/2\,Eu_2O_3 + z\,Si_3N_4 = La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z} \quad (2)$$

The value of z was in the range of 0.1-0.6 with a step of 0.1. High purity powders of LaSi (Kojundo Chemicals Laboratory Co. Ltd., Japan), Si (grade 2C, SicoMill, Vesta Ceramics AB, Sweden), α-Si_3N_4 (SN-E10, Ube Industries Ltd., Japan), and Eu_2O_3 (99,99%, Treibacher Industries AG, Austria) were used as starting materials. About 3 g of each powder mixture was homogenized in agate mortar. From the powders pellets of a diameter 12 mm were pressed with a pressure of 100 MPa. Tablets were placed into a BN crucible and nitrided in a graphite resistance furnace at 1390°C for 4 h. Afterwards the samples were annealed in a gas pressure furnace at 1650°C for 2-4 h under 2 MPa nitrogen pressure.

Phase composition was identified by X-ray diffraction analysis (D8-Discover, Bruker, Madison, WI, CuKα radiation). Photoluminescence spectra of the powders were investigated by a fluorescence spectrometer (Fluorolog 3-11, ISA/ Jobin Yvon-SPEX, Longjumeau, France).

3. Results and Discussion

All the powders had a yellow color after annealing at 1650°C. The brightest color had the powder containing 1 mol% Eu. The particle size of synthesized $LaSi_3N_5$:Eu phosphor was in the range 1-3 μm. The phase compositions of Eu-doped $LaSi_3N_5$ samples are shown in Fig. 1. All the major diffractions belong to $LaSi_3N_5$ according to the data in the PDF 42-1144 card and also the calculated XRD profile.[2] However, the $LaSi_3N_5$ diffraction peaks are shifted little to the smaller 2Θ angles (Fig. 2) which can indicate the formation of $LaSi_3N_5$-based solid solution. Very weak diffractions on the level of background intensity were observed and indicate the presence of $LaEuSiO_3N$.

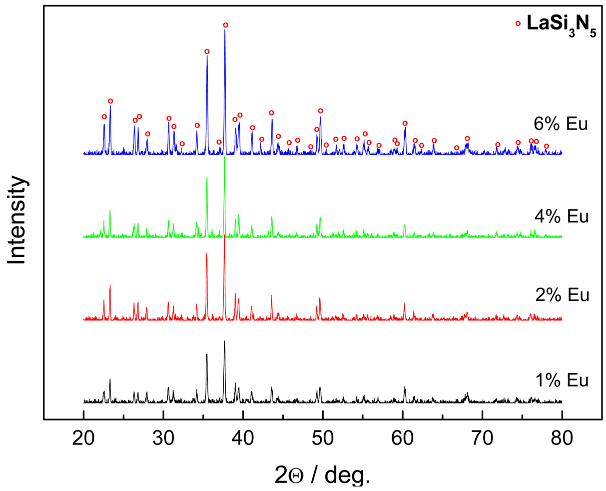

Fig. 1. XRD patterns of $LaSi_3N_5$ samples doped with Eu.

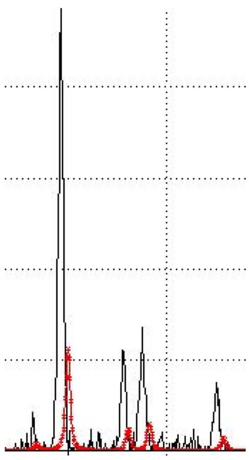

Fig. 2. Left shift of the diffractions of $LaSi_3N_5$ samples doped with 4% Eu in comparison to PDF 42-1144 card (2Θ rage 37°-42°).

The emission spectra of $LaSi_3N_5$ sample with 4 mol% Eu content after annealing at 1650°C for 2 h are shown in Fig. 3. The excitation wavelength was 360 nm, 370 nm and 380 nm. The emission spectra were not smooth, which suggests the presence of some defects and/or Eu^{3+}. For the purpose to finish the reduction of Eu^{3+} to Eu^{2+} in $LaSi_3N_5$ samples and the formation of $La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z}$ type solid solution the annealing time was prolonged at 1650°C in nitrogen atmosphere (2 MPa). As it was shown by de Graaf et al.,[11] Eu^{3+} can be reduced in nitrogen atmosphere according the following equation:

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

Fig. 4 shows the excitation and emission spectra of Eu-doped $LaSi_3N_5$ samples annealed for 4 h. The excitation spectra of the $La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z}$ samples (Fig. 4(a)) measured at λ_{em} = 560 nm covered a range from 310 to 500 nm with a maximum centered at approximately 410 nm for samples with Eu content z = 0.01 and 0.02, respectively. This peak can be assigned to $4f^7 \rightarrow 4f^65d^1$ absorption of the Eu^{2+} cations.[12]

The emission spectra of Eu-doped $LaSi_3N_5$ samples (Fig. 4(b)) show that the longer annealing time (4 h) had a beneficial effect on luminescent properties of these materials. The emission spectra exhibited a broadband with a maximum wavelength centered in the region 560 - 580 nm after excitation at 350 nm. Zhou et al. studied a similar system prepared by combustion synthesis method.[13] They observed an emission peak at 553 nm. This emission was described to the $5d4f^6 \rightarrow 4f^7$ transition of Eu^{2+}. The position of the peak maximum in our case was shifted to higher wavelengths, which could be caused by the different condition of synthesis, i.e. lower temperature and N_2 pressure.

The investigation of the influence of Eu-content on the photoluminescence properties of $LaSi_3N_5$-based phosphors

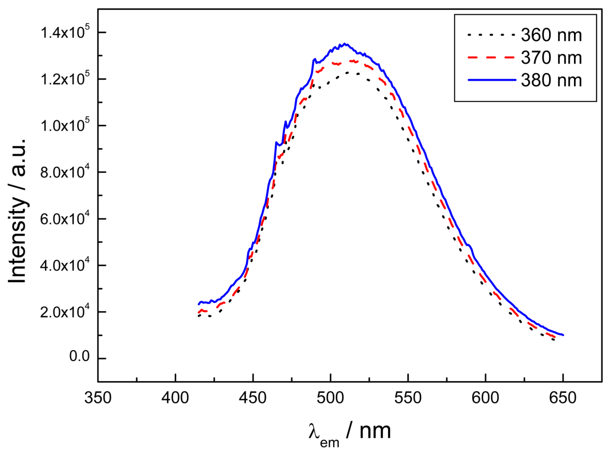

Fig. 3. Emission spectra of $La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z}$ samples (z = 0.04) after annealing at 1650°C for 2 h (λ_{exc} = 360 nm, 370 nm and 380 nm).

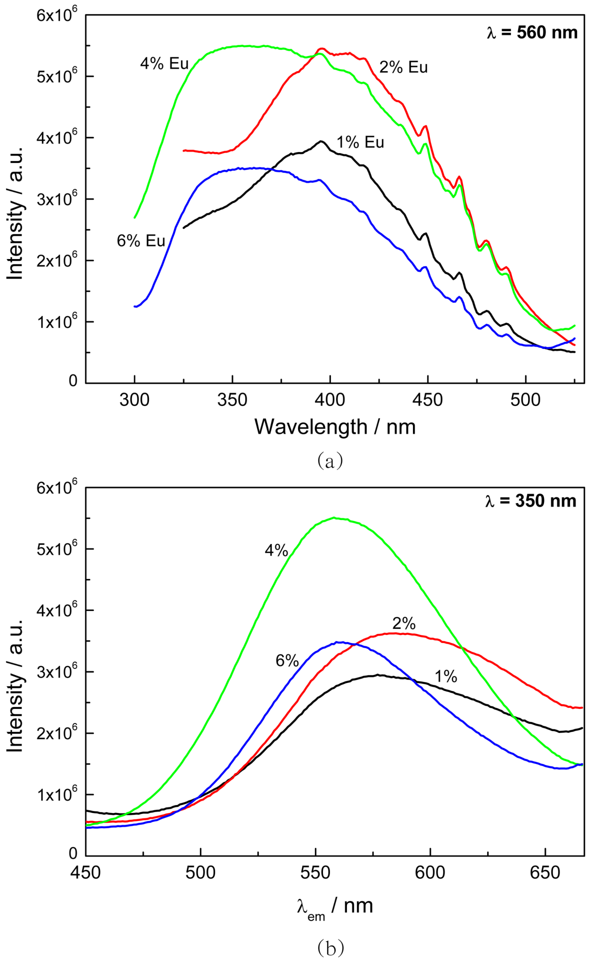

Fig. 4. Excitation (a) and emission spectra (b) of $La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z}$ samples with different molar concentrations of Eu after annealing at 1650°C for 4 h.

indicates that the PL intensity increases up to 4 mol% Eu and then decreases for z = 0.06 due to the concentration quenching (Fig. 4(b)).

4. Conclusion

Europium-doped $LaSi_3N_5$ phosphor was synthesized from $LaSi/Si/Si_3N_4/Eu_2O_3$ mixture by nitridation at 1390°C and additional annealing at 1650°C for 4 h. The phosphor shows emissions in the green light region with a maximum at 560 nm. With increasing europium content in the general formula $La_{1-z}Eu_zSi_3N_{5-z}O_{1.5z}$ from z = 0.01 to 0.06 there was a maximum emission for z = 0.04 followed by concentration quenching for the highest europium content (z = 0.06).

Acknowledgments

This work was supported by the Slovak Grant Agency VEGA 2/0178/10, LPP-0394-09 and 7th FP Marie Curie Initial Training Network "FUNEA" (264873). This contribution is the result of the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions - Stage II supported by the Research & Development Operational Programme funded by the ERDF.

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