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Luminescence properties of $La_2Si_6O_3N_8:Eu^{2+}$ phosphors prepared by spark plasma sintering

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ABSTRACT

Bluish green-emitting $La_2Si_6O_3N_8:Eu^{2+}$ phosphors were synthesized by a spark plasma sintering (SPS) method, and the effects of sintering temperature, Eu doping concentration, post-annealing, and acid washing on the photoluminescence (PL) properties were investigated. A single phase $La_2Si_6O_3N_8:Eu^{2+}$ was successfully achieved at 1700 °C by SPS. As-synthesized $La_2Si_6O_3N_8:Eu^{2+}$ phosphors exhibited a single band emission centered at 483–496 nm under the excitation of 370 nm. The post-annealing and acid-washing significantly improved the emission intensity by increasing the crystallinity, reducing the carbon content, and changing the morphology of particles. Unexpectedly, $La_2Si_6O_3N_8:Eu^{2+}$ phosphors showed a strong thermal quenching.

1. Introduction

White light emitting diodes (LEDs) have been extensively investigated as an alternative for the conventional light sources due to their excellent properties such as high brightness, low energy consumption, long lifetime, and reliability [1]. The conventional method to fabricate white LEDs is to combine a yellow-emitting $YAG:Ce^{3+}$ phosphor with a blue LED chip. However, these white LEDs have a poor color rendering index and a high color temperature due to a deficiency of the red color [2,3]. To improve the color rendering properties, a three-band white LED has been suggested by combining a blue LED with high efficient red and green phosphors [4,5]. Another approach to improve the color properties is to use red, green, and blue-emitting phosphors with a near UV (NUV) radiation [6].

For that purpose, Ce^{3+}-activated blue-emitting oxynitride phosphors have been developed [7–9], and one of the representative host materials is the La–Si–O–N system, which includes $La_5Si_3O_{12}N$, $La_4Si_2O_7N_2$, $LaSiO_2N$, and $La_3Si_8O_4N_{11}$ (or $La_2Si_6O_3N_8$) phases. The emission properties strongly depended on the Si/La and N/O ratios, but a blue emission was observed in all lanthanide silicon oxynitrides under UV irradiation. Among them, $La_3Si_8O_4N_{11}:Ce^{3+}$ showed the highest efficiency and thermal stability. The La N(ew)-phase was initially believed to be $La_2Si_6O_3N_8$ ($La_2O_3{\cdot}2Si_3N_4$), but NMR studies have shown that the composition is close to $La_3Si_8O_4N_{11}$ [10,11]. Both phases have the same monoclinic crystal structure, but $La_2Si_6O_3N_8$ has a doubled *c*-axis. Thus, it is expected that both phases produce similar photoluminescence and thermal stability. Recently, Ce-doped lanthanum silicon oxynitride phosphors were prepared by a solid-state reaction, but a single phase $La_2Si_6O_3N_8$ could not be realized [12]. In addition, the (oxy)nitride phosphors are commonly activated by Eu^{2+} [1,13–19], but Eu^{2+} has not been employed as an activator in La–Si–O–N system, to the best of our knowledge.

In this work, Eu^{2+}-doped $La_2Si_6O_3N_8$ phosphor was synthesized by spark plasma sintering (SPS). SPS is proved to be an efficient method to synthesize (oxy)nitride phosphors at a relatively lower temperature and shorter time than the conventional solid state reaction method [13,20–22]. The effects of sintering temperature, Eu doping concentration, post-annealing, and acid-washing on luminescence properties of $La_2Si_6O_3N_8:Eu^{2+}$ phosphors were examined. Also, the temperature dependence of photoluminescence was measured in the range from 25 to 200 °C.

2. Experimental

$La_{2-x}Si_6O_3N_8:Eu_x^{2+}$ ($x = 0.01–0.1$) phosphors were prepared by SPS using La_2O_3 (Aldrich, Milwaukee, WI), Si_3N_4 (E-10, Ube America Inc., New York, NY), and Eu_2O_3 (Aldrich, Milwaukee, WI) as the starting materials. The stoichiometric mixture was thoroughly hand-mixed in alumina mortar for 30 min. For SPS, 1 g of the powder mixture was placed into a 10 mm diameter graphite die and BN slurry was pasted on the graphite punch to reduce the carbon contamination. Sintering was conducted in vacuum (200–300 mTorr) under a uniaxial pressure of 30 MPa with a heating rate of

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100 °C/min. The sintering temperature was varied from 1500 to 1700 °C for 5 min. After sintering, the BN coatings were removed from the pellets by grinding, and the remaining specimens were softly ground into powder. The obtained powder was post-annealed at 1650 °C for 3 h in a reducing atmosphere of 5% H_2/N_2 gas and acid-washed in 5 M HCl for 20 min.

The phases of the obtained phosphors were determined by X-ray diffraction (XRD, D8-Advance, Bruker Miller Co.) using Cu Kα radiation (λ = 1.5406 Å). The morphology of the phosphors was observed by a field emission scanning electron microscope (FESEM, JSM-7401F, JEOL). The chemical composition of the phosphors was analyzed by element analyzer (Flash EA 1112. Thermo Electron Co., USA). The La and Si contents in the acid-washed solution were determined using ICP-AES (Optima 4300DV, PerkinElmer, USA). The PL spectra were measured at room temperature using a fluorescence spectrometer (Darsa-5000, PSI Co., Ltd.). The temperature dependence of emission properties was investigated in the range of 25–200 °C with an interval of 25 °C under the excitation of 370 nm (PS-PLEU-X1420, PSI, Korea).

3. Results and discussion

The XRD patterns for $La_{2-x}Eu_xSi_6O_3N_8$ (x = 0.03) phosphors sintered at various temperatures are shown in Fig. 1. At 1500 °C, $La_5Si_3O_{12}N$ intermediate phase and unreacted starting materials (La_2O_3 and Si_3N_4) were detected along with the desired $La_2Si_6O_3N_8$ phase (Fig. 1(A)). With increasing the sintering temperature, the intermediate phase and starting materials gradually transformed into $La_2Si_6O_3N_8$, and a single phase $La_2Si_6O_3N_8$ was realized at 1700 °C (Fig. 1(C)). The preparation of pure $La_2Si_6O_3N_8$ was not successful at 1700 °C in solid-state reaction and the co-existence of $La_5Si_3O_{12}N$ and some amorphous glass could not be avoided [12]. Thus, SPS was very effective to synthesize a single phase Eu-doped $La_2Si_6O_3N_8$.

The emission spectra of $La_{2-x}Eu_xSi_6O_3N_8$ (x = 0.03) phosphors are shown in Fig. 2 as a function of sintering temperature. The excitation spectrum (inset of Fig. 2) showed a broad band, and the highest peak intensity was observed at ~374 nm. Three excitation peaks at 255, 331, and 367 nm have been reported for Ce-doped $La_2Si_6O_3N_8$ (2%) phosphor [12]. The emission intensity increased with increasing the sintering temperature, and above 1600 °C, the emission spectra exhibited a broadband centered at 483 nm under the excitation of λ_{ex} = 370 nm, which is attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} [23–25]. The emission spectrum of 2% Ce-doped $La_2Si_6O_3N_8$ showed a broadband at 411 nm with a shoulder at 444 nm under the excitation of λ_{ex} = 260 nm [12],

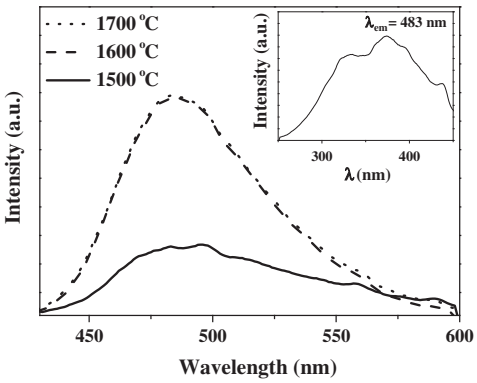

Fig. 2. Emission spectra of $La_{2-x}Eu_xSi_6O_3N_8$ (x = 0.03) phosphors as a function of sintering temperature (the inset is the excitation spectrum of $La_{2-x}Eu_xSi_6O_3N_8$ phosphor synthesized at 1700 °C).

and 6 mol% Ce^{3+}-doped $La_3Si_8O_4N_{11}$ exhibited an emission spectrum consisting of a broadband situated at 424 nm with a shoulder at 458 nm when it was excited at 365 nm [7]. Thus, the emission peak was shifted to a lower energy when Ce^{3+} was replaced with Eu^{2+}.

The effects of Eu doping concentration on the relative emission intensity and wavelength in $La_2Si_6O_3N_8$:Eu^{2+} phosphors are shown in Fig. 3. All the phosphors were sintered at 1700 °C, and a single phase $La_2Si_6O_3N_8$ formation was confirmed by XRD (not shown here). Up to x = 0.1, there was no noticeable shift in the diffraction peaks, and no secondary or Eu-containing phase was detected indicating that Eu^{2+} solubility in $La_2Si_6O_3N_8$ is higher than x = 0.1. The emission spectra were obtained at room temperature under the excitation of 370 nm. The emission intensity slightly increased at low Eu doping concentration, but it rapidly decreased after x = 0.035. Thus, the highest PL intensity was observed at x = 0.035. The sharp intensity decrease after x = 0.035 can be attributed to the concentration quenching, which is the non-radiative energy transfer between active ions or between active ion and host in high doping levels. There was an overlap between the excitation and emission spectra at 430–470 nm (Fig. 2), which implies that the interaction exists in the phosphor and is the probable reason of energy migration [1]. The emission wavelength was continuously shifted to a longer wavelength from 480 to 496 nm with increasing Eu doping concentration. The blue shift of emission peak is expected based on the crystal field effect when the larger sized Eu^{2+} ion substitutes the smaller La^{3+} host ion. The red shift can be attributed to the change of the Eu^{2+} site distribution and energy transfer between the different sites similar to that observed in

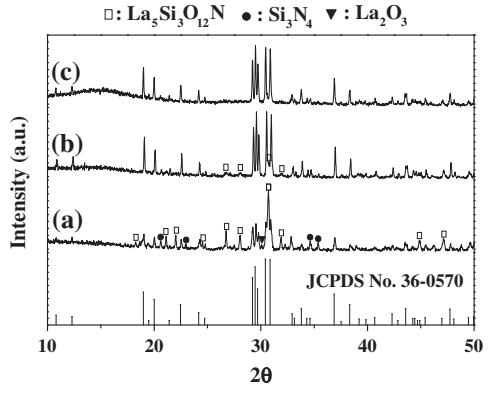

Fig. 1. X-ray diffraction patterns of $La_{2-x}Eu_xSi_6O_3N_8$ (x = 0.03) phosphors as a function of sintering temperature: (a) 1500, (b) 1600, and (c) 1700 °C. The reference diffraction pattern of $La_2Si_6O_3N_8$ (JCPDS No. 36-0570) is included.

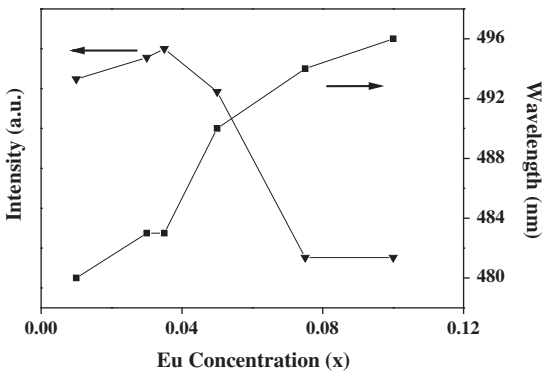

Fig. 3. Relative PL intensity and wavelength of $La_{2-x}Eu_xSi_6O_3N_8$ phosphors as a function of Eu^{2+} doping concentration (sintering temperature = 1700 °C, λ_{ex} = 370 nm).