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Short communication

Preparation of Eu^{2+}-doped AlN phosphors by plasma activated sintering

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Abstract

Eu^{2+}-doped AlN phosphors were prepared by plasma activated sintering at 1600–1850 °C for 5 min and using AlN, SiC, and Eu_2O_3 as starting materials. The effect of Si concentration on the phase purity and photoluminescence (PL) properties of the prepared phosphors was investigated. The doping of Si from SiC favored the formation of pure wurtzite-type AlN phase and doping of Eu^{2+} into the AlN lattice. The prepared AlN:Eu^{2+} phosphors exhibited a strong blue emission at 465 nm under the excitation at 330 nm when Si was doped. The highest PL intensity was achieved when the phosphors were sintered at 1800 °C.

Keywords: Aluminum nitride; Phosphors; Plasma activated sintering; Luminescence

1. Introduction

Rare-earth-doped nitride or oxynitride phosphors have been considered as promising candidates for phosphors in white light-emitting diodes (LEDs) and field emission displays (FEDs) due to their wide band gap, high efficiency, and excellent thermal and chemical stabilities [1]. Among them, Eu^{2+}-doped AlN has been intensively investigated because it can emit blue or green color with a broadband spectrum under UV or blue excitation [2–4]. Hirosaki et al. [2] and Inoue et al. [3] synthesized Eu^{2+}-doped AlN phosphors by firing the powder mixture of AlN, α-Si_3N_4, and Eu_2O_3 at 2050 °C for 4 h under 1.0 MPa N_2, and observed that the phosphors showed excellent luminescence properties and thermal stability. Very recently, Yin et al. [5] successfully prepared Eu^{2+}-doped AlN phosphors by a carbothermal reduction process at 1750 °C for 8 h in ambient N_2 atmosphere. Although AlN:Eu^{2+} phosphors exhibited great potential as a blue phosphor for white LEDs, the manufacturing costs are expensive because the process requires high firing temperature, high pressure atmosphere and long soaking time. Therefore, it is imperative to exploit an economical synthetic routes for preparing AlN:Eu^{2+} phosphors.

Plasma activated sintering (PAS), also known as spark plasma sintering (SPS), is a newly developed sintering technique by using special heat effects such as Joule heat, electromagnetic field and electrical discharge to realize the quick densification of ceramic powders in a very short time and at a relatively low temperature [6,7]. Despite PAS is a sintering technique, several studies [8–10] confirmed that it is also a feasible route to synthesize the inorganic phosphors. Sohn et al. [8] successfully fabricated $Sr_2SiO_{4-x}N_{2x/3}$:Eu^{2+} phosphors by using SPS technique for the first time in 2008. Do et al. [10] synthesized AlN:Eu^{2+} phophors by SPS using AlN, α-Si_3N_4, and Eu_2O_3 as starting materials, and the obtained phophors exhibited a strong blue emission at 480 nm under UV and electron excitation. However, the phosphors showed a small emission peak splitting at 460 nm, which could be caused by the variation of the local structure of Eu ion. Very recently, Dierre et al. [4] revealed that Si played a key role in the luminescence of Eu^{2+}-doped in AlN by enhancing the solubility of Eu^{2+} in the AlN lattice and reducing the volume of Eu-related secondary phase. It has also been proved that SiC was more effective in accommodating Eu in AlN than Si_3N_4 to achieve better luminescence properties. Therefore, in this study, AlN:Eu^{2+} phosphors were synthesized by PAS using AlN, SiC, and Eu_2O_3 as starting materials. The influence of the Si concentration and sintering temperature on the photoluminescence (PL) properties was also investigated.

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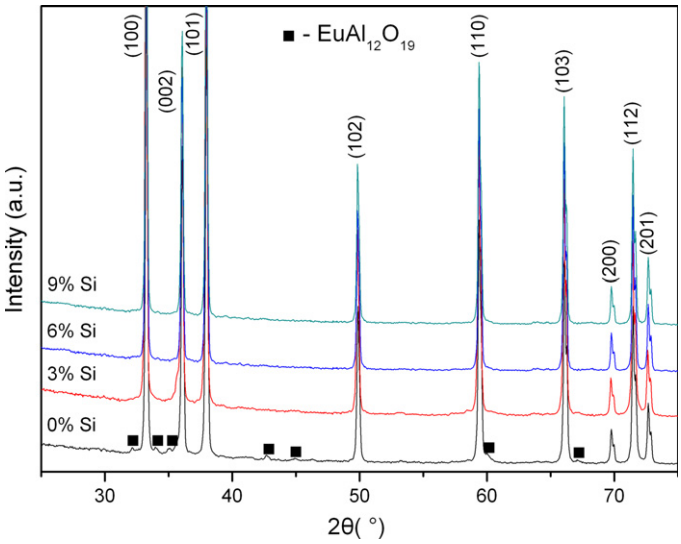

Fig. 1. XRD patterns of the synthesized AlN:Eu^{2+} phosphors with different Si concentrations at a fixed sintering temperature of 1800 °C. The peaks marked with ■ represent $EuAl_{12}O_{19}$.

2. Experimental procedure

AlN powder (Type H, Tokuyama K.K., Tokyo, Japan), β-SiC (Ultra-fine, Kaier Nano. Co. Ltd., Hefei, China) and Eu_2O_3 (Yuelong Nonferrous Metals Ltd., Shanghai, China) were used as the starting powders. The concentration of Si was adjusted from 0 to 9 at.% and all the samples were doped with 0.48 at.% Eu with respect to AlN. The powders were weighed according to the designed compositions, and then mixed in a mortar by hand.

One gram of the mixed powders was loaded into a 10 mm inner diameter graphite die and then sintered by PAS (Ed-PASIII, Elenix Ltd., Japan) at the temperature ranging from 1600 to 1850 °C (heating speed: 100 °C/min) for 5 min under a uniaxial pressure of 30 MPa in vacuum ($<10^{-2}$ Pa). The temperature was measured using an optical pyrometer focused on a little hole at the surface of the die. In order to reduce the carbon contamination, h-BN pellets were inserted between the graphite punch and the powders, and the h-BN slurry was also pasted on the inner surface of the die. After sintering, the h-BN parts were removed by grinding and polishing. Then, the samples were softly ground to powders for the following measurements.

Phase purity of the synthesized powders was examined by X-ray diffraction (XRD, JDX-3530, JEOL, Japan) with Cu Kα radiation at a scanning rate of 0.5°/min. Morphologies of the powders were observed using a scanning electron microscopy (SEM, VEGAII XMU, Tescan, Czech). PL spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer (Hitachi, Japan) at room temperature with a Xe lamp as the excitation source.

3. Results and discussion

Fig. 1 shows the XRD patterns of AlN:Eu^{2+} phosphors with different Si concentrations at a fixed sintering temperature of 1800 °C. The sample without SiC doping shows almost pure AlN phase (JCPDS No. 25-1133, space group: P63mc) along with a trace of impurity phase of $EuAl_{12}O_{19}$. This indicates that the Eu atoms are not dissolved in the AlN lattice totally. For the samples doped with SiC, the impurity phases disappear and the single AlN wurtzite phase is obtained, indicating that the SiC doping favors the entire dissolution of Eu^{2+} into the AlN lattice. The possible mechanism for the entire dissolution should be that some defects are formed in AlN with SiC doping which strongly promotes the incorporation of Eu [4]. In addition, with the increase of Si concentration from 3 to 9 at.%, the diffraction peaks of AlN shift to higher degrees monotonously, indicative of the continuous dissolution of a smaller Si^{4+} ion ($r = 0.26$ Å) into the host lattice to replace the Al^{3+} ion ($r = 0.39$ Å). The continuous dissolution of SiC into AlN can be described as the following reaction [11]:

$$(1-x)\mathrm{AlN} + x\mathrm{SiC} \rightarrow \mathrm{Al}_{(1-x)}\mathrm{Si}_x\mathrm{C}_x\mathrm{N}_{(1-x)} \quad (1)$$

which can react in a wide range.

Fig. 2 shows the SEM images of AlN starting powder and AlN:Eu^{2+} phosphors sintered at 1800 °C with varying Si concentrations. The AlN starting powder shows spherical shape with the average size of ~0.5 μm (Fig. 2(a)). After the PAS, the particle size of the obtained AlN phosphors grows to 1–2 μm for the sample doped with 6 at.% Si (Fig. 2(b)) and 1–3 μm for the sample doped with 9 at.% Si (Fig. 2(c)), respectively. In addition, the former phosphors exhibits well-faceted equiaxial shape with more uniform particle size distribution and the latter one shows severe agglomeration and abnormal grain growth. The agglomeration and abnormal grain growth should be caused by the higher SiC concentration which strongly promotes the AlN grain-growth according to the solid solution reaction of Eq. (1).

The PL excitation ($\lambda_{em.} = 465$ nm) and PL emission ($\lambda_{ex.} = 330$ nm) spectra of AlN:Eu^{2+} with varying Si concentrations

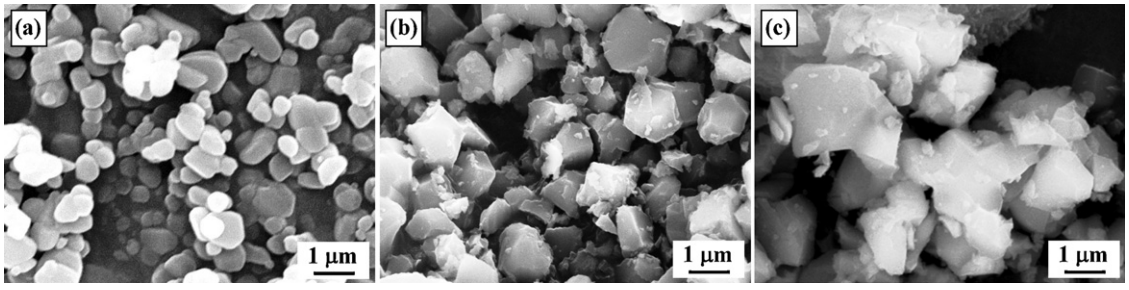

Fig. 2. SEM images of (a) AlN starting powder and AlN:Eu^{2+} phosphors fabricated by PAS at 1800 °C with varying Si concentrations: (b) 6 at.%, (c) 9 at.%.

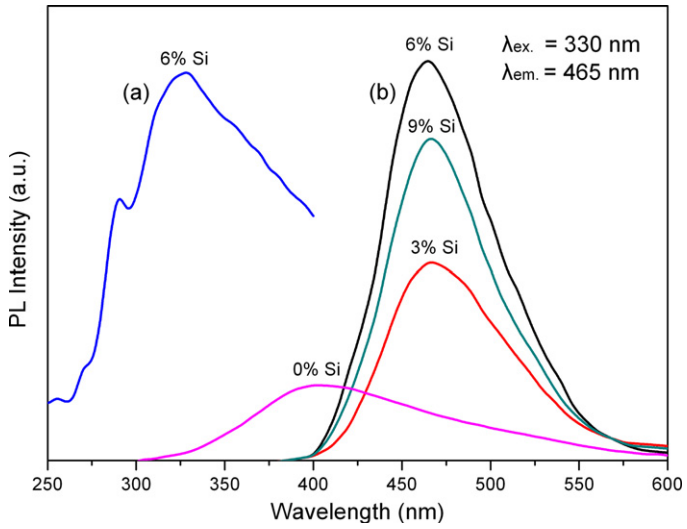

Fig. 3. PL excitation (a) and PL emission (b) spectra of AlN:Eu^{2+} with varying Si concentrations.

are shown in Fig. 3. The PL excitation spectrum shows a peak at 330 nm with a shoulder at 290 nm (Fig. 3(a)). For the sample without Si-doping, the PL emission spectrum (Fig. 3(b)) shows a broad emission band centered at 400 nm, which can be ascribed to the radiative recombination processes involving oxygen related impurity and Al vacancies [12,13]. However, after Si-doping, the emission spectra show a blue emission band peaking at 465 nm, which is attributed to $4f^6 5d–4f^7$ transitions of Eu^{2+} [2]. No red emission is observed indicating that the Eu ions exist as Eu^{2+}. Moreover, the emission intensity increases with the increase of Si concentration until a maximum intensity is reached when doping with 6 at.% Si, and then the intensity decreases. The decrease should be ascribed to the severe agglomeration and abnormal grain growth of AlN particles (as shown in Fig. 2(c)) [14].

Fig. 4 shows the effect of sintering temperature on the emission spectra of the 6 at.% Si-doped AlN:Eu^{2+} phosphors under excitation at 330 nm. All the phosphors obtained at temperatures from 1600 to 1850 °C exhibit a blue emission band with a maximum at 465 nm and no peak splitting is observed. Meanwhile, the emission intensity increases with the increase of sintering temperature, but it decreases when the temperature is above 1800 °C. The increasing of PL intensity is caused by the increase of the solubility of Eu ion in AlN [3]. However, the pellet sintered at 1850 °C shows gray color, indicating carbon penetrated into the pellet, similar as Do et al. reported [10]. Therefore, the decrease of emission intensity can be ascribed to the carbon contamination. Furthermore, the pellet sintered at 1850 °C is very hard and difficult to grind to powder. Hence, a heavy force needs to be used to pulverize, which may destroy the crystal structure of the phosphors and decrease the emission intensity.

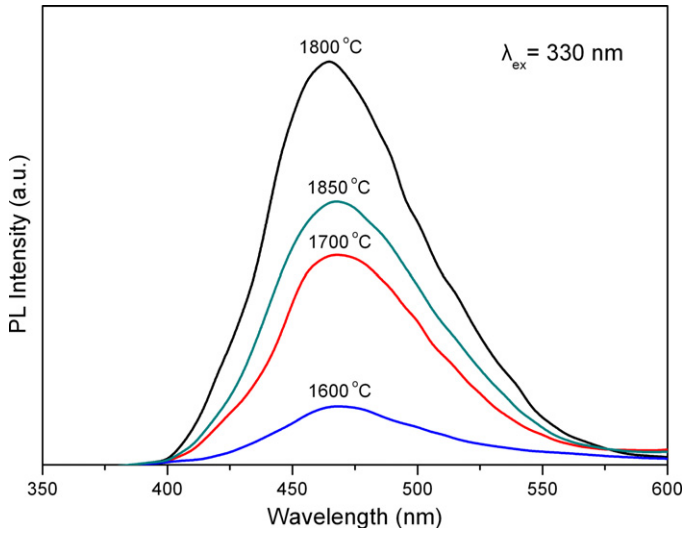

Fig. 4. PL emission spectra of 6 at.% Si-doped AlN:Eu^{2+} synthesized at different sintering temperatures under $\lambda_{ex.}$ = 330 nm excitation.

4. Conclusions

In summary, blue Eu^{2+} and Si codoped AlN phosphors were successfully prepared by PAS. The codoping of Si favored the formation of pure wurtzite-type AlN phase and full doping of Eu^{2+} into the AlN lattice. The prepared phosphors showed a blue emission band centered at 465 nm under the excitation at 330 nm. PAS therefore has the potential to reduce the time, cost, and required energy for the high quality production of Eu^{2+}-doped nitride or oxynitride phosphors.

Acknowledgements

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