Impact of Sintering Gas Pressure on Deep-red $EuSi_2O_2N_2$ Phosphors

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ABSTRACT

Deep red $EuSi_2O_2N_2$ phosphors were synthesized under various sintering gas pressures (1 atm, 2 atm, and 3 atm). They were in good agreement with the standard $EuSi_2O_2N_2$ ICSD card # 41-6046 (a monoclinic crystal system with space group of $P2_1/a$). Their photoluminescence intensities were significantly increased with increasing the gas pressures. They showed a broad band emission peaking at 680 nm due to $4f^65d^1$ - $4f^7$ of Eu^{2+} ion, which can be efficiently excited in the visible range up to 550 nm. The best one at 3 atm was applied for red LED based on blue chip, which showed the strong deep red emission.

Key Words : Red Emission, $EuSi_2O_2N_2$, Oxynitride, Sintering Gas Pressure, Photoluminescence, LED

1. Introduction

Europium-doped $MSi_2O_2N_2$ (M= Ca, Sr and Ba) compounds, including fully europium-concentrated $EuSi_2O_2N_2$ phosphor, have already been reported to emit tunable blue-green-yellow colors by [1-3]. Their emission colors were tuned from blue up to yellow by kinds of substituents. It is notable that the oxynitride compounds are easy to be synthesized from air-stable oxide and nitride as starting materials at a moderate temperature of about 1300 ℃ (by a general SiC heater) and under an oxygen-protected ambient (in a general alumina tube) unlike nitride phosphors synthesized with easily air-oxidized metal or metal-nitride materials under extremely high temperature and pressure conditions [4-7]. However, the red emission in all oxynitride series of $MSi_2O_2N_2$ (M= Ca, Sr and Ba) have not been reported up to date, even though the red emission has been observed in many nitride -based phosphors such as $Sr_2Si_5N_8$:Eu^{2+}, (Sr, Ca)AlSiN:Eu^{2+}, $LaSi_3N_5$:Eu^{2+}, and $SrSiN_2$:Eu^{2+} [8,9].

In this paper, we have, for the first time, presented the deep red emission in fully europium-concentrated $EuSi_2O_2N_2$ phosphors, which were reproducibly synthesized under different gas pressures of H_2-N_2 mixture through a conventional solid-state reaction method with the mixture of Eu_2O_3 and Si_3N_4 as starting materials. Here the following questions have been raised: why our $EuSi_2O_2N_2$ phosphor does emit the deep red color in spite of the others with the same composition and structure showed the yellow emission in chemical and physical aspects, and what kinds of processing make such big difference in photoluminescence [2-6]. The preliminary answer could be the slight variation in O-N ratio which is very difficult to be detected but can be controlled by ambient gas pressure. Thus, we have examined the effect of N_2 gas pressure on the red luminescence of $EuSi_2O_2N_2$ phosphor under different suitable gas pressures (1-3 atm), and compared the optical properties.

2. Experimental

2.1 Synthesis

The deep red emission $EuSi_2O_2N_2$ phosphors were synthesized at different gas pressures. The used raw materials

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for synthesis of $EuSi_2O_2N_2$ phosphors were Eu_2O_3 powders (99.99 %) and α-Si_3N_4 with keeping Eu/Si ratio at 0.5. The mixture was homogeneously wet-mixed by a hand mill for 30 min in acetone. After milling, the mixture was put into a horizontal tube furnace in an alumina crucible, and then vacuumed up to background pressure of 10^{-2} Torr until the temperature of 800 °C. Subsequently the mixture was sintered at 1300 °C for 4 hours under flowing 95% N_2-5% H_2 gas with pressure ranging from 1 to 3 atm. Finally, the red $EuSi_2O_2N_2$ powders were obtained, exhibiting a spherical shape with a deep red body color.

2.2 Analysis

The crystal structures were analyzed by X-ray powder diffraction (XRD, Rigaku-D/max 2550 PC diffractometer) with Cu-K_λ radiation (λ= 0.15405 nm). The XRD data were collected in the range of 10 – 80° in 2θ scan mode with a step size of 0.02° and a count time of 10 seconds per step. The surface morphologies were observed using a Scanning Electron Microscope (SEM JEOL Japan, Jsm-6700F operated at 15.0 KV). The photoluminescence emission (PL) spectra and excitation spectra (PLE) spectra measured by using the spectro-fluorometer PSI (Darsa Pro 5200 SYSTEM) where the sample was excited by a Xenon lamp (150 W).

3. Result and discussion

The recorded XRD patterns of our products were quite similar to that reported in the literature [2-4]. Fig. 1 showed XRD patterns of $EuSi_2O_2N_2$ phosphors annealed at 1300 °C with different pressures (1 atm, 2 atm and 3 atm). The XRD patterns of all three samples agree with that of the standard

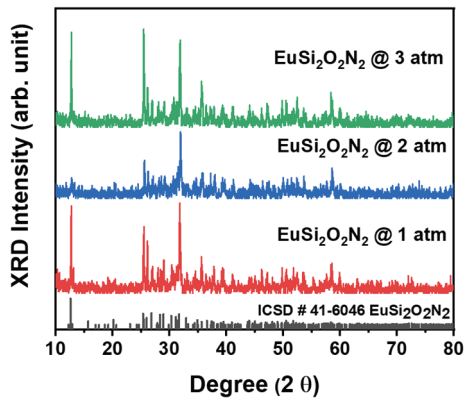

Fig. 1. XRD patterns of red $EuSi_2O_2N_2$ phosphors sintered at 1300 ℃ conditions under different pressures (1-3 atm), compared to the standard data for EuSi2O2N2 (ICSD NO. 41-6046).

patterns of $EuSi_2O_2N_2$ (ICSD Card No. 41-6046), which means that they were well crystallized in a monoclinic crystal system with space group = $P2_1/a$ and crystal lattice parameters of a = 13.151 Å, b = 17.311 Å, c = 7.956 Å [2,3]. No peaks corresponding to other impurities such as SiO_2 or Si_3N_4 were observed, which means that two end members of Eu_2O_3 and Si_3N_4 were completely combined to form $EuSi_2O_2N_2$ structure. Our red $EuSi_2O_2N_2$ phosphor sintered at 3 atm pressure showed the highest XRD intensity, indicating the highest crystalline quality so as to cause the improvement in PL intensity.

Fig. 2 shows the SEM images of $EuSi_2O_2N_2$ phosphor powders. The sizes of sample (1 atm) and sample (2 atm) were ranging from 500 nm to 2 μm. With increasing preparing pressure to 3 atm, the particles got smaller, which is attributed to the prevention of thermal diffusion and

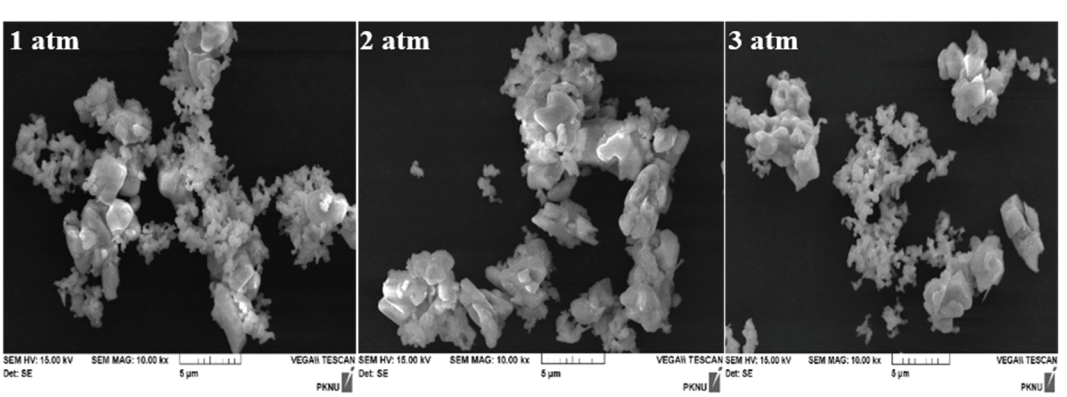

Fig. 2. SEM Images of red $EuSi_2O_2N_2$ phosphors sintered at 1300 °C under different pressures (1-3 atm).

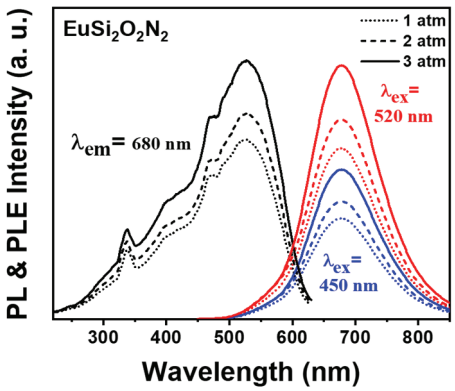

Fig. 3. Excitation (left) and emission (right) spectra of red $EuSi_2O_2N_2$ phosphors sintered at 1300 ℃ under different pressure (1-3 atm), where the excitation sources (450 nm and 520 nm) were applied.

aggregation due to strong surface compression caused by the highest gas pressure process.

Fig. 3 shows PLE spectra at left side and PL spectra at right side of three samples sintered at different pressure (1 atm, 2 atm, and 3 atm). It is noted that the PL intensity increases as the sintering gas pressure increases. This PL enhancement is consistent with the crystallinity of the phosphor as conformed by the sharpness of XRD pattern: the higher PL intensities, the sharper XRD patterns.

The phosphors exhibited a broad red emission with a maximum at 680 nm upon blue (λ_{ex} = 450 nm) and visible excitation lights (λ_{ex} = 520 nm), which can be ascribed to the allowed 4f → 5d transitions of Eu^{2+}. In general, a broad charge-transfer excitation band of Eu^{3+} lies at wavelengths < 300 nm, and the emission of Eu^{3+} shows sharp lines, due to optical transitions between levels of the $4f^n$ configuration [8,9]. Therefore, a broad emission band without sharp-line emission indicates that europium ion exists in the divalent state in $EuSi_2O_2N_2$ lattice structure [3,4]. The half widths of the emission bands are almost similar with about 132 nm within a machine error (1 nm) with ranging from 1 atm to 3 atm in pressure. Upon varying the excitation wavelengths (450 nm and 520 nm) there is no significant change in the emission spectra except the emission intensity. It indicates that this red phosphor can be excitable and thus combined with various excitation sources such as blue and green LEDs.

Two red LED were fabricated by combining the 450 nm chip with the red $EuSi_2O_2N_2$ phosphor sintered at 3 atm. Fig. 4 shows the emission spectra of two kinds of red LEDs (10 wt.% (a) and 50 wt.% (b) with respect to epoxy resin), where

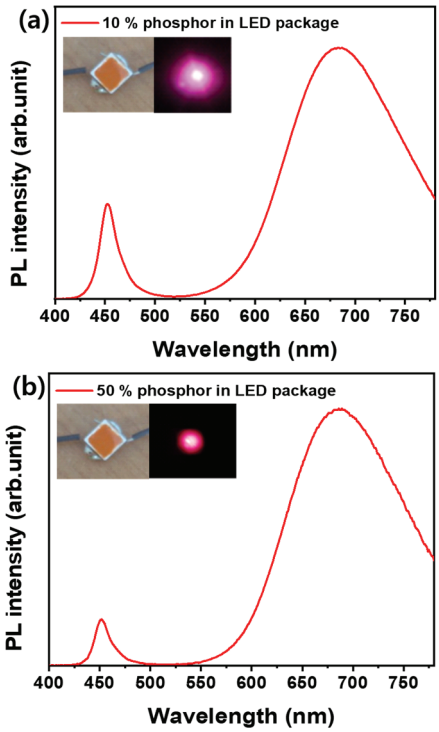

Fig. 4. Emission spectra of red LEDs packaged with the red $EuSi_2O_2N_2$ phosphor on blue LED chip, where 10 wt.% (a) and 50 wt.% (b) of phosphors with respect to epoxy resin were added.

they were operated under voltage of 2.60 V and current 350 mA. The color coordinates were varied together with the amounts of the red $EuSi_2O_2N_2$ phosphor; (0.487, 0.241) in Fig.4 (a) and (0.566, 0.274) in Fig. 4(b). The inset images show the red LED on and off the blue LED. For example, the deep red LED, so-called, blood color, can make some fleshes more vivid and fresh in butcher shop, and thus customers can express a rising desire for such products [10]. In addition, our red LED spectrum is suitable for photosynthesis, and for bio imaging agent due to high transparency on living cell [11,12].

4. Conclusion

Deep red $EuSi_2O_2N_2$ phosphors were synthesized under various sintering gas pressures (1 atm, 2 atm, and 3 atm) through a conventional solid state reaction method at 1300 ºC. They all have a monoclinic crystal system with a space group of $P2_1/a$. Their particles were fine with less than 2 μm in size They showed a broad band emission peaking at 680

nm with a half width of 132 nm due to $4f^65d^1$ - $4f^7$ of Eu^{2+} ion. They had the efficient excitation band ranged up to 550 nm. Their photo-luminescence intensities were significantly increased with increasing the gas pressures. The best one at 3 atm was applied for red LED based on blue chip, which showed the strong deep red emission. It can be applicable for special lighting applications such as butcher shop and photosynthesis and phototherapy treatment.

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