

Photoluminescence properties and synthesis of Eu^{2+} -activated Ca- α -SiAlON phosphor for white LED application

Y. H. Song, T. Masaki, K. Senthil and D. H. Yoon*

School of Advanced Materials and Science & Engineering, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

This study reports an approach for luminescent properties of Ca- α -SiAlON by solid state reaction method using two step firing. The optical properties on the overall composition of the host lattice have been investigated. The fluorescence excitation spectra of all of the nitrogen-rich phosphor powders showed two broad bands centered at about 300 nm and 400 - 475 nm. The first peak was assigned to the absorption of the host lattice and the second to the $4f^7 \rightarrow 4f^65d^1$ absorption of the Eu^{2+} ions, its senses improved $4f^7 \rightarrow 4f^65d$ excitation of Eu^{2+} ion. The emission intensity increased with increasing the Eu^{2+} concentration, but only up to a Eu^{2+} concentration ratio of 0.15. Moreover, the maximum emission peak is observed at $m = 2.0$ and $n = 1$.

Key words: Ca- α -SiAlON, White LEDs, Photoluminescence properties.

Introduction

At a present time, white light-emitting diodes (LEDs) have attracted significant attentions in that it has a lot of advantages like long life time, chemical stability, low energy consumption (less CO_2 gas) and high brightness compared with fluorescent lamps [1-3]. Methods to make the white LEDs are to combine InGaN blue chip with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) yellow to orange phosphor [4]. As I mentioned before, this white LEDs have commercialized in global market. Because cold white light is generated in that the WLEDs combined with YAG: Ce^{3+} has poor color rendering index (CRI) value by the deficiency, however, these can't be applied to indoor illumination source [5]. Therefore, it is necessary to develop highly efficient phosphor materials which can be replaced with oxide ones like YAG: Ce^{3+} . To work out the problems, the alternative ways for improving white light are to use a near-UV chip with RGB (red, green, and blue) phosphors or use blue chip with RG phosphors [6]. Especially, the nitride or oxynitride phosphor ranged from yellow to orange to orange colors excited under visible range around 450 nm have researched many compositions because these phosphors make it possible to compensate shortcomings of YAG: Ce^{3+} .

In particular, Xie et al. reported Eu^{2+} activated Ca- α -SiAlON phosphor on which the oxynitride based materialized warm-white LEDs by using one [7]. Also, the Ca- α -SiAlON host lattice has many advantages of their good thermal and chemical stabilities and excellent

resistance to friction and wear [8].

The general formula of α -SiAlON can be written by using $\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$. Even though Eu^{2+} ion alone can't stabilize the α -SiAlON structure because of large ionic size of Eu^{2+} ion, Ca cations occupy the interstitial sites in the α -SiAlON lattice and are coordinated by seven N, O anions [9]. According to this phenomenon, the rare earth ion is activated into α -SiAlON structure as rare earth ion like Eu^{2+} ion is substituted to Ca^{2+} ion.

In this paper, we focused on Eu^{2+} activated Ca- α -SiAlON ceramic compounds to generate the warm-white LEDs having lots of advantages compared to previous oxide or sulfide phosphors from the viewpoint of application in blue light region for white LEDs.

Experimental

Eu^{2+} doped Ca- α -SiAlON compounds were prepared as a function of m and n values as well as Eu^{2+} concentration from mixtures of α - Si_3N_4 (Aldrich, -325 mesh), Eu_2O_3 (High Purity Chemicals, 99.9%), CaCO_3 (High Purity Chemicals, 99.9%), and AlN (High Purity Chemicals, 99.9%). The raw materials were weighed out stoichiometrically. The mixtures of highly pure raw materials were mixed in an agate mortar and annealed at 800 °C for 24 hrs under 8 MPa using gas pressure sintering, and then fired at 1550 °C for 10 hrs under a reducing nitrogen atmosphere containing 5% H_2 by using a boron nitride crucible in a carbon crucible. The crystalline phase of phosphors prepared was investigated by X-ray powder diffraction (XRD, Cu K_α , 12 kW, Rigaku, Japan). The range of XRD pattern is from 20 ° to 80 °. To measure the luminescent properties of phosphors, the excitation and emission spectra were analyzed by the room temperature photoluminescence

*Corresponding author:
Tel : +82-31-290-7388
Fax: +82-31-290-7371
E-mail: dhyoon@skku.edu

spectrometer (PSI, Korea) equipped with a 500 W Xenon discharge lamp. The morphology of particle was measured by using Field Emission-Scanning Electron Microscope (FE-SEM, JEOL, JSM7500F, Japan) in detail.

Results and discussion

Fig. 1 shows XRD patterns of Eu^{2+} doped with Ca- α -SiAlON yellow to orange phosphors synthesized at 800 °C for 24 hrs under 8 MPa using gas pressure sintering at 1550 °C 10 hrs under 5% H_2 -95% N_2 atmosphere (two step firing). Patterns of sample are nearly matched with those of hexagonal structure. According to JCPDS Card (#41-3060), α - Si_3N_4 has hexagonal structure with P31c (159) space group, lattice parameter $a = 7.754 \text{ \AA}$ and $c = 5.621 \text{ \AA}$. The impurity phase and second phase is observed in compound which is synthesized at 800 °C for 24 hrs under 8 MPa. But, in case of synthesizing the compound at 1550 °C 10 hrs under 5% H_2 -95% N_2 atmosphere, the synthesized compound is exactly indexed.

Fig. 2 represents the excitation and emission spectra ($m, n = 1$) as a function of maintenance time 5, 10 and 15, respectively. All samples are synthesized using two step firing at 1550 °C under reducing atmosphere. As shown in Fig. 2(a), the excitation spectra indicates a typical broad band because of $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} ions [10]. In the emission spectra of Fig. 2(b), emission spectra assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions is observed to a typical emission spectra of Ca- α -SiAlON yellow to orange phosphors [11]. The excitation and emission spectra of phosphor that is synthesized for 10 hrs indicate the highest ones. In this data, it is confirmed that the optimized maintenance time of Ca- α -SiAlON synthesized is 10 hrs.

Fig. 3 indicate the scanning electron microscope images of the Eu^{2+} doped with Ca- α -SiAlON yellow to orange phosphors synthesized using two step as a function of maintenance time and Eu^{2+} concentration was fixed as 0.15 mol. With increasing the maintenance time, the particle size is increased. The morphology of the synthesized Ca- α -SiAlON yellow to orange phosphors had an irregular shape with a particle size of 0.5-3 μm . In

addition, the synthesized compounds showed some aggregation, which decreased the PL intensity.

Fig. 4 indicate excitation and emission spectra ($m, n = 1$) of the prepared nitrogen-rich $\text{Ca}_{0.9}\text{Si}_9\text{Al}_3(\text{O},\text{N})_{16}$ phosphor powders with varying Eu^{2+} doping concentrations at room temperature using the two step firing. In the excitation spectra of Fig. 3(a), a typical broad band is observed in all phosphors attributed to $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} ions. The excitation peak intensity increased with increasing the Eu^{2+} doping concentration. However, the Eu^{2+} concentration was $> 0.2 \text{ mol}$, it is

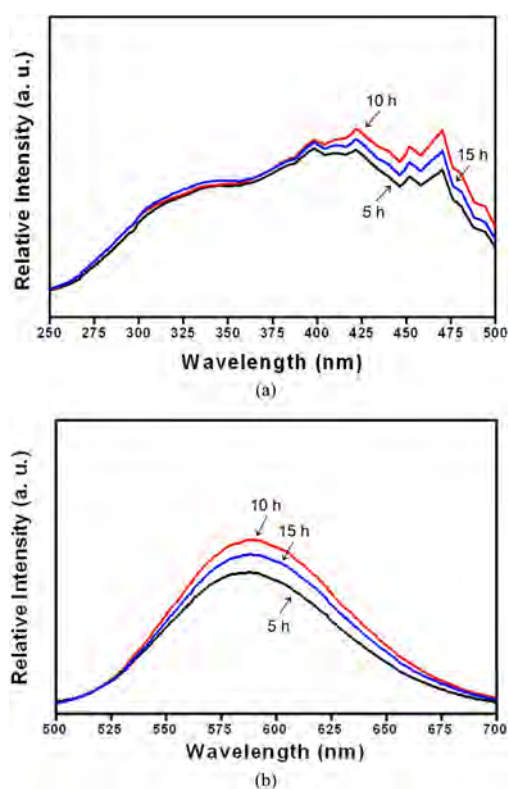


Fig. 2. PL spectrum of (a) excitation and (b) emission (monitored at 460 nm) spectra of the samples prepared by two step firing as function of maintenance time.

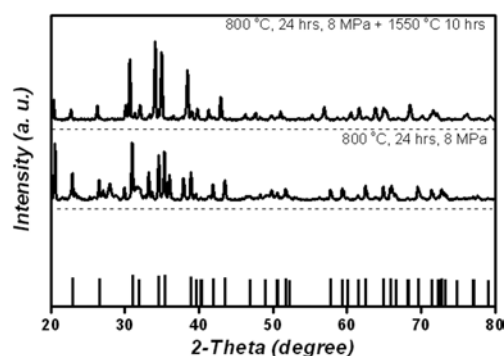


Fig. 1. XRD patterns of Eu^{2+} -activated Ca- α -SiAlON samples using different firing condition.

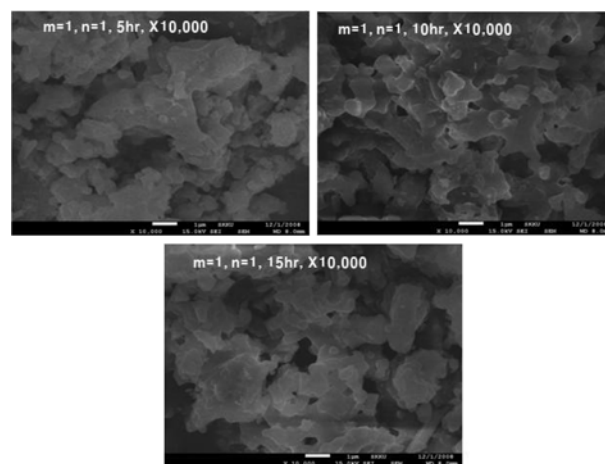


Fig. 3. SEM image of the prepared Eu^{2+} -activated Ca- α -SiAlON as function of maintenance time.

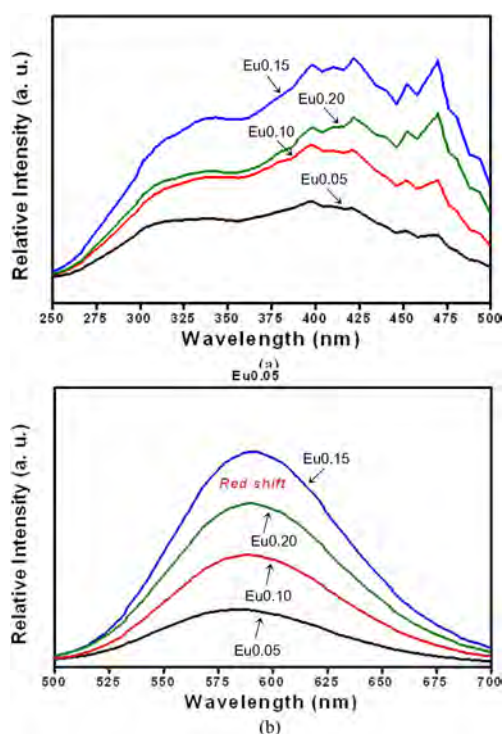


Fig. 4. PL spectrum of (a) excitation and (b) emission (monitored at 460 nm) spectra as a function of effect of Eu^{2+} concentration.

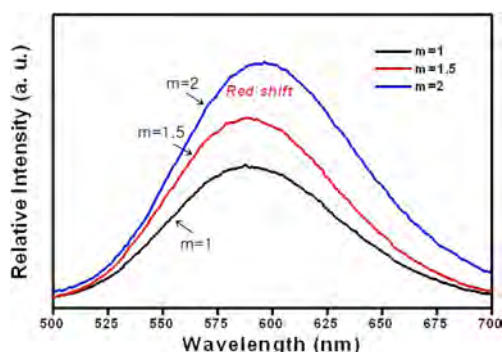


Fig. 5. Emission spectra (monitored at 460 nm) of Eu^{2+} -activated $\text{Ca-}\alpha\text{-SiAlON}$ as a function of m value ($m = 1.0, 1.5, 2.0$).

decreased. This is explained as concentration quenching, which is mainly caused by the energy transfer between Eu^{2+} ions [12]. The emission spectra of the prepared Eu^{2+} doped with $\text{Ca-}\alpha\text{-SiAlON}$ yellow to orange phosphors as shown in Fig. 3(b), all exhibited a typical broad emission band in the 500 - 700 nm region assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions and the highest emission intensity always is shown at 592 nm. As shown in Fig. 2, photoluminescence properties of Eu^{2+} doped with $\text{Ca-}\alpha\text{-SiAlON}$ yellow to orange phosphors is confirmed as the photoluminescence properties of $\text{Ca-}\alpha\text{-SiAlON}$ compounds depend on the Eu^{2+} doping concentration.

Fig. 5 shows the photoluminescence properties of the synthesized phosphor as a function of m values ($m = 1, 1.5, 2$) when Eu^{2+} ion is 0.15 mol. The n value is fixed

at 0.5. The strongest luminescence is achieved at $m = 2$ as the concentration of Eu^{2+} is fixed at 0.15 mol. The explanation for the compositional dependence of $\text{Ca-}\alpha\text{-SiAlON}$ is still unclear; the above result, however, implies that the luminescence properties of Eu^{2+} -activated $\text{Ca-}\alpha\text{-SiAlON}$ can be tailored by controlling the overall composition of the host lattice. Furthermore, a red shift of emission peak is observed with increasing the m value from 1 to 2. The red shift can be explained by the following reasons. The improvement of m means that the cell volume expands, which leads to less rigidity of the host lattice. Therefore, the stoke shift occurs larger with increasing the m value, which leads to the red shift of emission peak.

Conclusion

Orange-emitting Eu^{2+} -activated $\text{Ca-}\alpha\text{-SiAlON}$ with good PL properties successfully synthesized by solid state reaction method using two step firing. The fluorescence excitation spectra of all of the nitrogen-rich $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$ phosphor powders showed two broad bands centered at about 300 nm and 400 - 475 nm.

The emission intensity increased with increasing the Eu^{2+} concentration, but only up to a Eu^{2+} concentration ratio of 0.15. Moreover, the maximum emission peak of synthesized phosphor for 10 hrs is observed at $m = 2.0$ and $n = 1$.

This suggests that synthesized phosphor can be used as alternative high efficiency emitting phosphors in white LED applications.

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