

Synthesis of $C\alpha$ - α -SiAlON phosphor by one-step LPP-CRN method

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$C\alpha$ - α -SiAlON : Eu^{2+} phosphors used for white LEDs were synthesized by one-step LPP-CRN method. Crystalline cellulose was used as a carbon source for synthesizing $C\alpha$ - α -SiAlON : Eu^{2+} phosphors. This phosphor emits yellow to orange light. This phosphor showed a single broad band emission attributed to the $5d \rightarrow 4f$ transition of Eu^{2+} ions. The synthesized yellow- to orange-emitting phosphors obtained without using excess carbon were crystallized much effectively and showed higher emission intensity. This phosphor obtained using the LPP-CRN method is expected to lead to the synthesis of other oxynitride phosphors and to be applied to white LEDs.

Key words: $C\alpha$ - α -SiAlON : Eu^{2+} phosphor, White LEDs, LPP-CRN method.

Introduction

White light-emitting diodes (LEDs) have been attractive as a solid-state lighting source because of their potential application in indoor illumination, backlight, headlights of automobile, and so on. Phosphor-converted LEDs which can be used in many applications have many advantages such as long life time, lower energy consumption, good chemical stability, energy efficiency, and compactness [1].

Generally, simple LED-based white light sources can be generated by combining yellow-emitting $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ phosphor with InGaN blue emitting chips [2]. However, $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ -converted white light has a low color rendering index (CRI) value, in that $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ does not have a red component in the emission wavelength and a high correlated color temperature of over 5,000 K [3]. So, they cannot be applied as indoor illumination sources. To overcome these problems, a phosphor which can compensate for the disadvantages of $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ phosphor is required to generate warm white LEDs [4]. The Eu^{2+} -activated $C\alpha$ - α -SiAlON has received great attention for solid-state lighting sources as an alternative for white LEDs.

α -SiAlON is a solid solution with an M-Si-Al-O-N system that has a structure derived from α - Si_3N_4 (general formula: $\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$). M has a preference for elements such as Li, Mg, Ca, Y, Sr and rare-earth ions. Generally, rare-earth ions alone cannot occupy M-SiAlON structure due to large ionic size. If a rare-earth ion is codoped with calcium, the material can

emit light in various regions.

Generally, $C\alpha$ - α -SiAlON is synthesized with CaCO_3 , AlN, Si_3N_4 and SiO_2 by solid-state reaction method. To synthesize perfect $C\alpha$ - α -SiAlON, methods that require high temperature and pressure are needed, like gas pressure sintering (GPS) [5-8]. So, we tried to synthesize the phosphor at low temperature using carbothermal reduction nitridation (CRN) method with oxide materials and cellulose as a carbon source.

In this study, a single-phase $C\alpha$ - α -SiAlON : Eu^{2+} phosphor was synthesized by CRN method. The use of the CRN method leads to highly efficient photoluminescence properties. The crystal structure, luminescence properties, and particle size of orange-emitting $C\alpha$ - α -SiAlON: Eu^{2+} phosphor were analyzed using powder X-ray diffraction (XRD), photoluminescence spectrometry (PL), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX).

Experimental

$C\alpha$ - α -SiAlON phosphor was prepared by one-step LPP-CRN method. The raw materials were $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich, 99.0%), SiO_2 (sol, 20%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich, 98.0%), and $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma Aldrich, 99.9%). The mixtures of each dissolved raw material were magnetically stirred with de-ionized water at 60 °C for 3 hrs, and then the solution was impregnated into crystalline cellulose. The dried sample was fired at 600 °C for 4 hrs and then synthesized on an alumina boat at 1500 °C for 5 hrs in a tubular furnace under a reducing nitrogen atmosphere containing 5% H_2 gas.

The phase identification of the obtained samples was carried out by X-ray diffraction (XRD, Rigaku, Japan) using a $\text{Cu K}\alpha$ target in the 2θ range of 20-80 °. The

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photoluminescence spectra were recorded using a spectrometer (SCINCO, FS-2, Korea) with a xenon lamp excitation source (150 W). The microstructure, morphology, and specific surface area of the phosphor particles were examined by scanning electron microscopy (FESEM, JSM6700F, JEOL)

Results & Discussion

Fig. 1 shows XRD patterns of the product powders calcined at 1500 °C for 5 h under a reducing nitrogen atmosphere containing 5% H₂ gas. The XRD patterns of the as-prepared samples were well indexed to the reference card (JCPDS card No. 41-3060). But, the samples using a 10% excess carbon source indicated impurity phases, including an AlN phase. The crystal structure of the as-prepared samples belongs to a trigonal system with a space group of P31c (159) [9, 10]. The patterns exhibit that the sample without an excess carbon source and with 5% carbon have a single-phase crystal structure of α -Si₃N₄ (JCPDS card No. 41-3060).

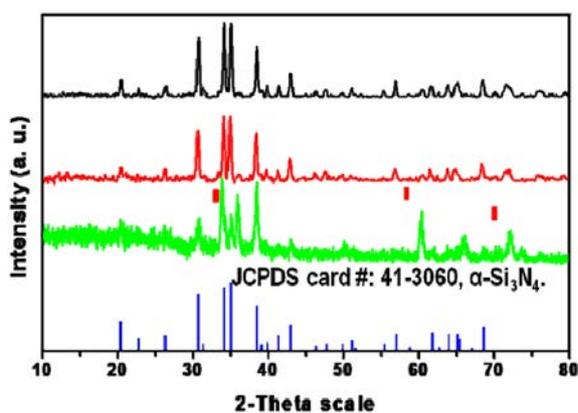


Fig. 1. X-ray patterns of $C\alpha$ - α -SiAlON : Eu²⁺ phosphors synthesized at 1500 °C for 5 hrs to examine reaction of residual carbon in LPP-CRN method.

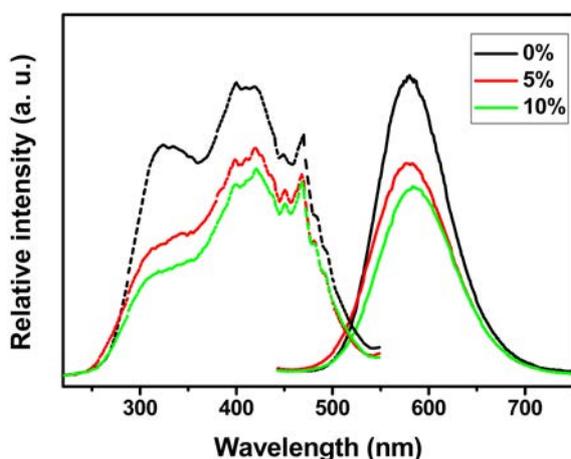
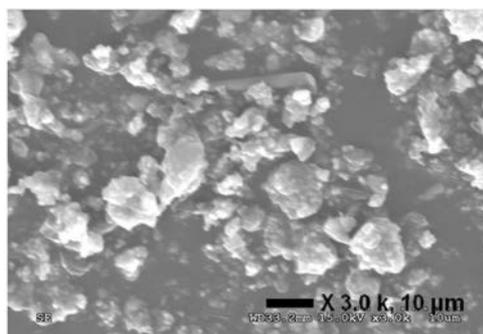
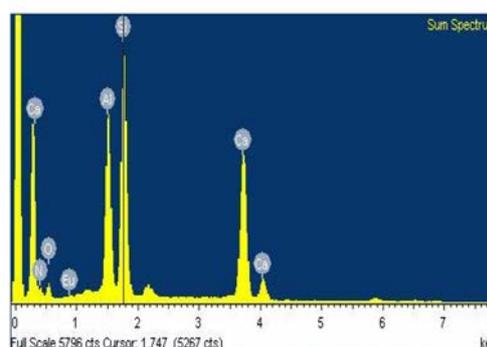


Fig. 2. Photoluminescence properties of $C\alpha$ - α -SiAlON : Eu²⁺ phosphors dependent on additional carbon in synthesis process by LPP-CRN method.



(a)



(b)

Fig. 3. FEM-SEM of the prepared $C\alpha$ - α -SiAlON : Eu²⁺ phosphors prepared using LPP-CRN method.

Fig. 2 presents the PLE and PL spectra of the $C\alpha$ - α -SiAlON : Eu²⁺ phosphors obtained without using an excess carbon source, and with 5% and 10% excess carbon at 1500 °C for 5 hrs under a reducing nitrogen atmosphere containing 5% H₂ gas. The excitation and emission spectra without an excess carbon source showed the highest intensity. But, the excitation and emission intensity is decreased with increasing excess carbon source. The carbon source in the $C\alpha$ - α -SiAlON : Eu²⁺ phosphors plays a role in decreasing the luminescence intensity. The excitation spectra of the prepared sample indicated a typically broad excitation band at 322, 400, and 470 nm. These two excitation bands correspond to the 4f⁷-4f⁶5d transition absorption of Eu²⁺ under 450-nm excitation. This excitation peak corresponds to the general $C\alpha$ - α -SiAlON : Eu²⁺ phosphors. The emission spectra show a single broad emission band. The emission of Eu²⁺ displays a single broad emission band in the range of 500-700 nm, which results in yellow to orange emission. The broad emission band is attributed to the allowed 4f⁶5d-4f⁷ transition of Eu²⁺ ions. Because the sample can also be excited appropriately to the wavelength of the blue-light and near-UV regions, the yellow- to orange-emitting $C\alpha$ - α -SiAlON : Eu²⁺ phosphors are promising materials to be applied with InGaN blue light-emitting diodes [11-14].

Fig. 3 shows the emission spectra as a function of

Eu^{2+} contents from 0.05 to 0.11 mol. The typically broad emission band is observed in all the as-prepared samples. It is attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions. The emission intensity is increased with Eu^{2+} contents, and the $\text{Eu}^{2+}_{0.09}$ activated $\text{Ca}\alpha\text{-}\alpha\text{-SiAlON}$ phosphor indicated the highest emission intensity. However, when the Eu^{2+} content is 0.11 mol, the emission intensity is suddenly decreased. This phenomenon can be explained as a concentration quenching mechanism. The concentration quenching is mainly caused by the energy transfer among the activators including Eu^{2+} ions. The probability of energy transfer is increased.

With increasing Eu^{2+} contents, the emission band is shifted to the red region. From the Eu^{2+} ions at the higher levels of 5d to those at the lower levels of 5d, increases with Eu^{2+} contents. This makes it possible for the high Eu^{2+} contents to lower the emission energy level to allow for the energy transfer from the low 5d excited state to the 4f ground state [15]. Therefore, red shifting of the emission peak can be observed in Fig. 2.

Fig. 3 indicates the scanning electron microscope (a) and EDX spectrum (b) images of the $\text{Ca}\alpha\text{-}\alpha\text{-SiAlON}$ product synthesized using the LPP-CRN method. The particles of the as-prepared sample have irregular shape and sizes in the range of about 8-15 μm . In addition, a small amount of aggregation is indicated. The Ca, Si, Al, O, N and Eu atomic profiles were identified. We confirmed that the $\text{Ca}\alpha\text{-}\alpha\text{-SiAlON}:\text{Eu}^{2+}$ phosphors were successfully synthesized using the LPP-CRN method.

Conclusions

In summary, yellow-emitting $\text{Ca}\alpha\text{-}\alpha\text{-SiAlON}:\text{Eu}^{2+}$ phosphors were synthesized using a one-step LPP-CRN method. The synthesized phosphor also shows a good stoichiometric composition. But, the excess carbon sources of 5 and 10% were added non-stoichiometrically. The $\text{Ca}\alpha\text{-}\alpha\text{-SiAlON}:\text{Eu}^{2+}$ yellow phosphor typically has a single broad emission band when excited by light in the UV to blue region of the spectrum. The emission intensities of the synthesized phosphor with the

addition of excess carbon sources of 5 and 10% had poorer photoluminescence properties than the phosphor without additional carbon source.

Acknowledgments

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