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# Eu-doped barium strontium silicate phosphor particles prepared from spray solution containing $NH_4Cl$ flux by spray pyrolysis

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**Abstract**

Eu-doped barium strontium silicate phosphor particles with high photoluminescence intensity under long wavelength ultraviolet were prepared from the spray solution containing $NH_4Cl$ flux by spray pyrolysis. It was found that the addition of $NH_4Cl$ to the spray solution makes it possible to greatly improve the photoluminescence intensity of $Ba_{1.488}Sr_{0.5}SiO_4$:$Eu_{0.012}$ phosphor particles under long wavelength ultraviolet of 410 nm. The highest photoluminescence intensity, which was achieved when the $NH_4Cl$ content was 5 wt.%, was about 150% of $Ba_{1.488}Sr_{0.5}SiO_4$:$Eu_{0.012}$ particles prepared from the spray solution without flux material at the post-treatment temperature of 1050 °C. The particle size of $Ba_{1.488}Sr_{0.5}SiO_4$:$Eu_{0.012}$ phosphor particles were enlarged by using the $NH_4Cl$ flux in the spray solution because of the large grain growth which was identified from the sharpening of the XRD peaks. Adding the $NH_4Cl$ flux into the spray solution was found to lower the optimal post-treatment temperature at which the $Ba_{1.488}Sr_{0.5}SiO_4$:$Eu_{0.012}$ phosphor particles are fully crystallized and have the maximum photoluminescence intensity. The phosphor particles prepared from spray solution containing 5 wt.% $NH_4Cl$ flux had the maximum photoluminescence intensity at post-treatment temperature of 1100 °C.


*Keywords:* Phosphor; Spray pyrolysis; LED; Flux

## 1. Introduction

The development of a new illuminator to replace conventional incandescent electric lamp or fluorescent lighting is one of great research topics. In special, the illuminators worked by light emitting diode (LED) has been received many researcher's attention because they have high brightness, long lifetime, small size and low power consumption. There are several processes for manufacturing LED emitting white light, which are achieved by pasting fluorescent materials above ultraviolet LED (UV LED), yellow phosphor material above blue LED and combining two or three different-color semiconductor chips. Among those processes, pasting fluorescent materials over UV LED chip is considered as the most efficient process because the process is simple and can produce full color. In order to apply LED for a light source instead of the conventional lamp, it is essential to develop LED chip that emits white light. In order to successfully apply phosphor-combined UV LED to the lighting, fluorescent materials must work under long-wavelength UV and have high emission efficiency [1].

Eu-doped oxide phosphor particles such as $(Ba,Sr)_2SiO_4$:Eu, $BaMgSiO_4$:Eu, $(Ca,Sr)_2MgSi_2O_7$:Eu, $SrAl_2O_4$:Eu, and $Ca_8Mg(SiO_4)_4Cl_2$:Eu are known as green emitting phosphor[2–6]. Among these green-emitting oxide phosphor materials, $(Ba,Sr)_2SiO_4$:Eu phosphor was known to suitable for UV LED phosphor because it has short decay time or high luminescence characteristics under long wavelength ultraviolet. $(Ba,Sr)_2SiO_4$:Eu phosphor particles were prepared by solid state reaction method in previous studies. Spray pyrolysis has been applied to the preparation of

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multicomponent oxide-phosphor particles and the phosphor particles prepared by spray pyrolysis process are almost satisfied the requirements for the applications to displays and lamps [7–11]. The phosphor particles prepared by spray pyrolysis have good characteristics such as spherical morphology, non-aggregation, fine size and narrow size distribution for application in displays.

In this work, high efficient $(Ba,Sr)_2SiO_4$:Eu phosphor particles were prepared by spray pyrolysis process. The effect of $NH_4Cl$ flux on the photoluminescence and morphology characteristics of $(Ba,Sr)_2SiO_4$:Eu phosphor particles prepared by spray pyrolysis was studied.

## 2. Experimental

An ultrasonic spray generator with six vibrators that has frequency of 1.7 MHz was used to produce large amount of droplets. The length and inside diameter of quarts reactor were 1200 and 50 mm, respectively. The temperature of the reactor was fixed at 900 °C. The flow rate of air used as carrier gas was controlled at 45 l/min and the residence time of the particles inside the reactor was 0.6 s. The precursor solutions were prepared from barium nitrate, strontium nitrate, europium oxide and tetraethyl orthosilicate (TEOS). The overall solution concentration was 0.3 M. The addition amount of $NH_4Cl$ used as flux material was changed from 1 to 11 wt.% of the $BaSrSiO_4$:Eu phosphor. The as-prepared particles were post-treated between 900 and 1400 °C for 3 h under 10% $H_2/N_2$ mixture gas. The morphology of phosphor particles was investigated by scanning electron microscopy (Philips XL 30S FEG). X-ray diffraction patterns of phosphor particles were obtained using X-ray diffractometer (Rigaku DMAX-33 X-ray) with Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å). Diffraction patterns were taken over the range of $20^\circ \leq 2\theta \leq 80^\circ$ with scan rate of $5^\circ$ $2\theta$/min. The X-ray diffractometer was operated at 40 kV and 40 mA. The photoluminescence spectra of $BaSrSiO_4$:Eu phosphor particles after the post-treatment were measured using a spectrofluorophotometer (Perkin-Elmer LS50-B) under the excitation of a 410 nm ultraviolet (UV) produced by an Xe flash lamp.

## 3. Results and discussions

Europium-doped $Ba_xSr_{2-x}SiO_4$ phosphor particles had various emission spectra according to the ratio ($x$) of barium to strontium component [2]. In the spray pyrolysis, the composition of host material and doping concentration of europium were optimized to obtain the highest photoluminescence intensity of the Eu-doped barium strontium silicate phosphor particles emitting the green light. In this work, the phosphor particles with the composition of $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ were prepared by spray pyrolysis from spray solutions with and without $NH_4Cl$ flux. $NH_4Cl$ was used as flux material for the preparation of silicate phosphor particles in conventional solid-state reaction method. $NH_4Cl$ flux improved the reaction rate and the luminescence characteristics of silicate phosphor particles at a given temperature [2,12].

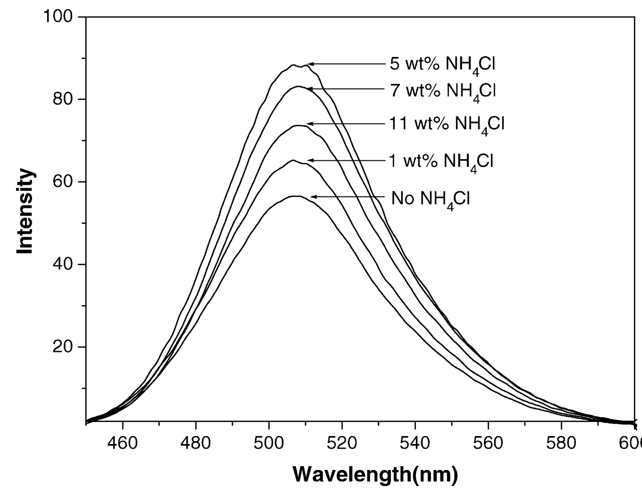


Fig. 1. PL emission spectra of $Ba_{1.488}Sr_{0.5}SiO_4:Eu^{2+}_{0.012}$ phosphor particles as a function of $NH_4Cl$ content.

$NH_4Cl$ flux was effective to control the luminous efficiency of $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles prepared by spray pyrolysis. The effect of the $NH_4Cl$ flux on the photoluminescence intensity of the $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles prepared by spray pyrolysis was shown in Fig. 1. The addition amount of $NH_4Cl$ flux was changed from 1 to 11 wt.% of the $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor. The as-prepared particles obtained by spray pyrolysis at 900 °C were post-treated at 1050 °C for 3 h under 10% $H_2/N_2$ mixture gas. The phosphor particles were excited by long wavelength ultraviolet light of 410 nm. The $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles had broad emission spectrum between 460 and 560 nm and had the maximum peak intensity at 508 nm. The $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles prepared from spray solution containing $NH_4Cl$ flux had higher photoluminescence intensity than those prepared from spray solution without flux material. As increasing the content of $NH_4Cl$ flux up to 5 wt.%, the photoluminescence intensity of the prepared $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles had improved photoluminescence intensity under 410 nm excitation. The maximum photoluminescence intensity of $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles was achieved from the spray solution containing 5 wt.% of $NH_4Cl$ flux and about 150% of the phosphor particles prepared from spray solution without flux material. The photoluminescence intensity of the phosphor particles was decreased when the addition amount of $NH_4Cl$ flux was above 5 wt.%.

The excitation spectra of the phosphor particles prepared from spray solutions with and without $NH_4Cl$ flux material were measured to show the potential of the $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor particles as UV LED phosphors. In Fig. 2, the excitation spectrum of the