Blue-Emitting Eu-Doped $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl}$ Phosphor Particles Prepared by Spray Pyrolysis from the Spray Solution Containing Ammonium Chloride

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Blue-emitting strontium magnesium halophosphate phosphor particles were prepared by spray pyrolysis from the spray solutions with ammonium chloride. The ammonium chloride was used as the source of chlorine and the flux material. The prepared $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles had regular morphologies and fine sizes. The mean sizes of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were each 1.2 and 1.9 μm when the ratios of strontium to chlorine components were 1 : 0.5 and 1 : 1. The ratios of strontium to chlorine components in the as-prepared and post-treated particles were each 1 : 0.26 and 1 : 0.21. The $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles that were prepared from the spray solution with the ratio of strontium to chlorine components of 1 : 1.5 had the maximum photoluminescence intensity, which was 176% of that of the commercial $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ phosphor particles under excitation wavelength of 400 nm.

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1. Introduction

The Eu-doped strontium magnesium halophosphate ($(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$) phosphors are used as blue-emitting phosphors applicable for plasma display panels (PDPs), field emission displays (FEDs), tricolor lamps and light emitting diodes (LEDs) because of their broad excitation band from vacuum ultraviolet (VUV) to long-wavelength ultraviolet (UV) and high photoluminescence characteristics. The $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ is known as the efficient blue-emitting phosphors. However, there exist a poor blue emission and the low luminous efficiency in the long-wavelength UV LED system due to the suddenly decreasing of excitation intensity of the $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ around 400 nm.¹⁾

Conventionally, the halophosphate phosphor particles are prepared by a solid state reaction method.^{2)–6)} In the solid state reaction method, high temperature and long heating time are required for activation of doping components into the matrix of host materials. Recently, spray pyrolysis method has been well applied to the preparation of multicomponent oxide phosphor materials.^{7)–13)} Spray pyrolysis has been also utilized in order to improve the photoluminescence intensity of the blue-emitting halophosphate phosphor particles for the LED applications.^{7),8)} In the preparation of halophosphate phosphor particles, the types of materials used as chlorine source affect the characteristics of the phosphor particles, such as morphology, phase purity, and photoluminescence intensities. In the previous paper, strontium chloride was mainly used as the source of chlorine.^{7),8)} However, the use of strontium chloride as the source of chlorine had limited performance in controlling the characteristics of the halophosphate phosphor particles in the spray pyrolysis.

In conventional solid state reaction and liquid solution methods, flux is used to improve wetting of reactants and to form well-crystallized particles. The flux also plays an important role in the control of mean size, size distribution, and shape of phosphor particles. Fluxes are usually compounds of alkali- or alkaline earth metals having low melting points. In the spray pyrolysis, flux materials were used to improve the brightness of spherical shape phosphor particles with micron size.^{14)–16)}

In this work, the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were prepared by spray pyrolysis from the spray solutions that contained an excess amount of ammonium chloride. The ammonium chloride was used as the source of chlorine and the flux material. Ammonium chloride did not act as the source of metal contaminants. The effects of the ammonium chloride added to the spray solution on the morphology, crystallinity, and photoluminescence intensities of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were investigated.

2. Experiments

The composition of $(\text{Sr}_{0.9}\text{Mg}_{0.1})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were prepared by ultrasonic spray pyrolysis. A 1.7 MHz ultrasonic spray generator having six vibrators is used to generate large production of droplets, which are carried to the reactor. The precursor solution was atomized and carried into the quartz tube of an electrical furnace. The length and inside diameter of the tube were 1200 mm and 50 mm, respectively. The flow rate of air used as carrier gas was 40 L/min and the reactor temperature was fixed at 900°C. And the residence time of the particles inside the reactor was 0.6 s. Strontium nitrate, magnesium nitrate, ammonium dihydrogen phosphate and europium nitrate were used as the source of Sr, Mg, P, and Eu, respectively. And the ammonium chloride was used as the source of chlorine and the flux material. The total concentration of the metal components was 0.5 M. To obtain the stoichiometric amount of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles, the concentrations of ammonium chloride dissolved to the spray solution were changed. The as-prepared particles obtained by spray pyrolysis were post-treated at the temperature of 1000°C under a reducing atmosphere (5% H_2/N_2 mixture gas) for the activation of Eu.

The morphological characteristics of the particles were analyzed by using scanning electron microscopy (SEM, JEOL, JSM 6060). The crystal structures of the prepared phosphor particles were analyzed by using X-ray diffractometry (XRD, RIGAKU, DMAX-33). The crystallite size of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles was calculated from the line broadening of the (211) peak using Scherrer's equation. The compositions of the phosphor particles were analyzed by using energy dispersive X-ray (EDX). Optical properties of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were meas-

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Fig. 1. SEM photographs of the as-prepared particles obtained from the spray solution with ammonium chloride.

ured by spectrofluorophotometry (Perkin Elmer LS50B) under the excitation by long-wavelength UV light produced by a Xe flash lamp. The aluminum powder holder plated with black color was used. The radius and height of the powder holder are each 3 and 2 mm.

3. Result and discussion

The effects of changing the concentration of an ammonium chloride added to the spray solution as chlorine source on the characteristics of the prepared phosphor particles were studied. **Figs. 1** and **2** show the morphologies of the as-prepared and post-treated $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles obtained from the spray solutions with different concentrations of ammonium chloride. The ratio of strontium to the chlorine components that were dissolved in the spray solutions was changed from 1 : 0.5 to 1 : 2. Figure 1 shows the SEM photographs of the as-prepared particles that were obtained by spray pyrolysis. All as-prepared particles had a spherical shape, hollow structure and micron size irrespective of the amount of ammonium chloride added to the spray solution. One particle was formed from one droplet by gas phase reaction. However, the morphologies and the mean size of the post-treated particles were affected by the amount of ammonium chloride added to the spray solution as shown in Fig. 2. The blue-emitting halophosphate phosphor particles were not directly prepared by spray pyrolysis because of short residence time of the particles inside the hot wall reactor as 0.6 s. The as-prepared particles obtained by spray pyrolysis were post-treated at temperature of 1000°C for 3 h. The spherical shape of the as-prepared particles disappeared after post-treatment

irrespective of the amount of ammonium chloride added to the spray solution. The mean sizes of the post-treated $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles increased with increasing the ammonium chloride added to the spray solutions. The $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles prepared from the spray solutions with low amounts of ammonium chloride added to the spray solution had regular morphologies and fine sizes. The mean sizes of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were each 1.2 and 1.9 μm when the ratios of strontium to chlorine components were 1 : 0.5 and 1 : 1. The phosphor particles prepared from the spray solutions containing high ratios of strontium to chlorine components had large sizes, as shown Figs. 2(c) and (d). Ammonium chloride added to the spray solution acts as the flux material in the preparation of phosphor particles by spray pyrolysis. The high amount of ammonium chloride acted as the flux material increased the mean size of the phosphor particles during the post-treatment.

The effects of types of chlorine source on the morphologies of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles were shown in **Fig. 3**. Figure 3 shows the SEM photographs of the as-prepared and post-treated $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ particles obtained from the spray solution without ammonium chloride. Strontium chloride was used as the sources of strontium and chlorine components. The source of strontium is 20% of the strontium nitrate and 80% of the strontium chloride and the source of chlorine is all the strontium chloride. As a result, the ratio of strontium to chlorine components was a 1 : 1.6, in which the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles had the maximum photoluminescence

Fig. 2. SEM photographs of the post-treated particles obtained from the spray solution with ammonium chloride.

intensity under long-wavelength ultraviolet. The types of chlorine source added to the spray solution did not affect the morphology of the as-prepared particles. The as-prepared particles obtained from the spray solution without ammonium chloride had also spherical shape, micron size and hollow structure. However, the post-treated $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles obtained from the spray solution with strontium chloride as the source of chlorine had larger size and more aggregated morphologies than those obtained from the spray solution with ammonium chloride as the source of chlorine.

The compositions of the phosphor particles were analyzed by EDX. Figure 4 shows the EDX spectra of the as-prepared and post-treated $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ particles prepared from the spray solutions, in which the ratio of strontium to chlorine components was 1 : 1.5. In the EDX spectra, the element composition ratios of the oxygen, magnesium, phosphorous, chlorine, strontium and europium components were analyzed. The composition ratios of the oxygen, magnesium, phosphorous, and strontium components of the as-prepared and post-treated particles were similar in comparison with the composition ratios of the spray solution. The ratios of strontium to chlorine components in the as-prepared and post-treated particles were each 1 : 0.26 and 1 : 0.21. The stoichiometric ratio of strontium to chlorine components in the $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles was 1 : 0.22. Therefore, the ratio of strontium to chlorine components in the as-prepared particles was higher than the stoichiometric ratio of strontium to chlorine components of the $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles. The content of the chlorine compo-

nent of the phosphor particles was decreased after post-treatment. The composition ratio of strontium to chlorine components of the post-treated particles was similar to that of the stoichiometric ratio of strontium to chlorine components of the $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles. The evaporation of the excess chlorine component of the phosphor particles occurred at high post-treatment temperature.

The crystal structures of the post-treated $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles prepared by spray pyrolysis from the spray solutions with different concentrations of ammonium chloride were investigated. As shown in Fig. 5, we presented the X-ray diffraction peaks of the $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ (JCPDS, 16-0666) particles. By comparison between file 16-0666 of $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ and the sample of $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$, the position and intensity is nearly same. All samples possessed an hexagonal crystal structure for $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor. Using Scherrer's equation, the mean crystallite sizes of the phosphor particles were measured. The mean crystallite sizes of the phosphor particles were changed from 48 to 51 nm according to the ratios of strontium to chlorine components added to the spray solutions.

The excitation spectra of the post-treated $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles prepared by spray pyrolysis from the spray solutions with different concentrations of ammonium chloride are shown in Fig. 6. The photoluminescence spectra of the prepared phosphor particles were compared with those of the commercial $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ phosphor particles prepared by solid-state reaction method. The effect of the types of chlorine source on the photoluminescence spectra of the $(\text{Sr, Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles was also

(a) As-prepared

(b) Post-treated

Fig. 3. SEM photographs of the particles prepared from the spray solution with strontium chloride.

Fig. 5. XRD spectra of the particles obtained from the spray solution with ammonium chloride.

Fig. 6. Excitation spectra of the phosphor particles.

(a) As-prepared

(b) Post-treated

Fig. 4. EDX spectra of the particles obtained from the spray solution with ammonium chloride.

investigated. The excitation spectra of the phosphor particles were measured by monitoring the emission of 446 nm. The $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ and $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ phosphor particles had broad excitation wavelengths that ranged from 260 to 420 nm. The peak intensities of the excitation spectrum of the commercial $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor particles decreased rapidly in the wavelength range between 360 and 420 nm. Therefore, the prepared $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ phosphor particles had high peak intensities around the wavelength of 400 nm in comparison with that of the commercial $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor particles. The $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ phosphor particles obtained from the spray solutions with ammonium chloride as the source of chlorine with the ratios of strontium to chlorine components of 1 : 1.5 and 1 : 1 had higher peak intensities than those obtained from the spray solution with strontium chloride as the source of chlorine in the all wavelength. The mean sizes and stoichiometries of the prepared phosphor particles affected the photoluminescence intensities of the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ phosphor particles. Therefore, the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ phosphor particles prepared from the spray solution with a excess of chlorine could be well applied as a blue phosphor for phosphor-combined UV-LED instead of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor particles.

Figure 7 shows the emission spectra of the prepared

Fig. 7. Emission spectra of the phosphor particles.

$(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ and the commercial $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ phosphor particles. The prepared phosphor particles were excited by a long-wavelength UV light of 400 nm. The prepared $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor shows a blue emission peak with a maximum peak intensity at 446 nm. The prepared $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles had higher photoluminescence intensities than the commercial $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ phosphor particles. The $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles that were prepared from the spray solution with the ratio of strontium to chlorine components of 1 : 1.5 had the maximum photoluminescence intensity, which was 176% of that of the commercial $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$ phosphor particles. The photoluminescence intensity of the phosphor particles that were prepared from the spray solution with ammonium chloride as chlorine source was 116% of that of the phosphor particles prepared from the spray solution with strontium chloride as chlorine source.

4. Conclusion

The high brightness $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles emitting blue light under long wavelength ultraviolet were prepared by spray pyrolysis. The effects of the amount of the ammonium chloride added to the spray solutions on the morphologies, mean sizes, and photoluminescence charac-

teristics of the prepared phosphor particles were studied. Ammonium chloride used as the chlorine source and the flux material played a key role in the preparation of $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles in the spray pyrolysis. The optimum ratio of strontium to chlorine components in the spray solution to produce the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles with high brightness, fine size and regular morphology was 1 : 1.5. The prepared phosphor particles had high photoluminescence intensities under long wavelength ultraviolet. Therefore, the $(\text{Sr}, \text{Mg})_5(\text{PO}_4)_3\text{Cl} : \text{Eu}^{2+}$ phosphor particles prepared from the spray solutions with ammonium chloride could be well applied as a blue phosphor for phosphor-combined UV-LED.

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