

Use of LiCl flux in the preparation of Y₂O₃:Eu phosphor particles by spray pyrolysis

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Abstract

The effect of LiCl flux on the luminescence characteristics, crystallinity and morphology of Y₂O₃:Eu phosphor particles was investigated. The maximum PL intensity of particles directly prepared at 1300 °C from solution with LiCl flux was 50% higher than that of particles prepared from solution without flux. The PL intensities of particles prepared at 700 and 900 °C from flux solution were 200 and 134% of those of particles prepared from solution without flux at the same preparation temperatures. Activation of Eu dopant was fully occurred even at 700 °C when LiCl flux was used while high temperature above 1100 °C was required without flux. LiCl flux played an important role of improving activation degree of Eu dopant into Y₂O₃ host and reducing defects of particles. © 2002 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Europium-doped yttrium oxide is an important phosphor in displays and lamps. Y₂O₃:Eu phosphor particles are mainly prepared by conventional solid state reaction and liquid solution methods.^{1–5} In both processes, halide flux is used as additive to increase luminescence characteristics of particles. The high luminescence characteristics of Y₂O₃:Eu particles cannot be obtained by increasing the degree of mixing of Y and Eu components in aqueous phase without flux.

Recently, spray pyrolysis is well applied to the preparation of oxide phosphor particles because spray pyrolysis has many advantages in terms of morphology.^{6–10} The phosphor particles prepared by the spray pyrolysis have complete spherical shape, submicron size, narrow size distribution and non-aggregation characteristics. These characteristics of phosphor particles cannot be obtained in conventional processes. Y₂O₃:Eu phosphor particles were also prepared by spray pyrolysis.^{9,10} Y₂O₃:Eu particles prepared by the spray pyrolysis had

high cathodoluminescence (CL) characteristics even though flux material was not used.¹⁰ In the spray pyrolysis, fine size, spherical shape and high dispersion of dopant inside host matrix of particles increased the CL intensities of Y₂O₃:Eu particles. The maximum CL intensity of Y₂O₃:Eu particles prepared by the spray pyrolysis was 30% higher than that of the commercial product. On the other hand, the Y₂O₃:Eu particles prepared by the spray pyrolysis had poor photoluminescence (PL) characteristics. The PL characteristics of Y₂O₃:Eu particles are more important in applications for plasma display panel (PDP) and fluorescent lamp than CL characteristics. This poor PL characteristics of Y₂O₃:Eu particles in the spray pyrolysis cannot be solved by optimizing doping concentration of Eu dopant, preparation and post-treatment temperatures, solution concentration, residence time of particles and types of process. So, in this paper, we have studied the influence of flux material on the photoluminescence characteristics of Y₂O₃:Eu phosphor particles in the spray pyrolysis.

In the conventional processes, in which the primary requirement of flux materials is the lower melting point than the firing temperature, chloride and carbonate materials are usually used as flux to the preparation of Y₂O₃:Eu phosphor particles. In addition, the solubility

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in solvent is another important factor of flux material in the spray pyrolysis. Therefore, many flux materials applied in conventional processes cannot be used in the spray pyrolysis. In this work, lithium chloride is applied as flux material for the preparation of $Y_2O_3:Eu$ phosphor particles by the spray pyrolysis. The effect of flux concentration and preparation temperature on the brightness, morphology and crystallinity of $Y_2O_3:Eu$ particles is investigated.

2. Experimental

The apparatus used in this work is ultrasonic spray generator with 1.7 MHz resonator. Spray solution is prepared by dissolving Y and Eu nitrates and lithium chloride into distilled water. Lithium chloride is selected as flux material because of its high solubility in water and low melting point of 613 °C.

The overall solution concentration is 0.3 M. The doping concentration of Eu is fixed at 6 at.% of Y component. The amount of LiCl additive is varied from 0 to 20 wt.% of Y_2O_3 product. The preparation temperature is changed from 700 to 1300 °C. The flow rate of air used as carrier gas is 2 l/min and the residence time of particles inside tubular furnace reactor is about 2 s.

To investigate the effect of LiCl flux on the brightness of $Y_2O_3:Eu$ particles, all the samples are directly prepared by the spray pyrolysis without post-treatment. The particles directly prepared by the spray pyrolysis have complete spherical shape and non-aggregation characteristics because of gas phase reaction without post-treatment regardless of flux addition.

The prepared particles are characterized with X-ray diffractometry (XRD), scanning electron microscopy (SEM). Photoluminescence characteristics of particles prepared from solutions with and without LiCl flux are also compared.

3. Results and discussions

Fig. 1 shows the PL characteristics of particles prepared at different doping amount of LiCl into $Y_2O_3:Eu$ particles. All the samples are directly prepared at 1300 °C by the spray pyrolysis. The PL intensities of particles are measured under 254 nm UV light. The particles directly prepared without post-treatment have high brightness because of submicron size, spherical shape, good dispersion of Eu dopant inside Y_2O_3 matrix, high purity and clean surface of particles. In the spray pyrolysis, milling process causing contamination and defects of particles is not necessary because the particles have fine size and non-aggregation characteristics. The PL intensity of particles is strongly affected by the doping amount of LiCl flux and has the maximum value at 20 wt.% LiCl of $Y_2O_3:Eu$ particles. The maximum PL intensity of particles prepared at 1300 °C from flux solution is 50% higher than that of particles prepared from solution without LiCl flux.

In Fig. 2, the effect of LiCl flux at different preparation temperatures on the PL intensities of particles is shown. The particles are prepared from solutions with 20 wt.% LiCl and without. The particles prepared from solutions containing LiCl flux have higher PL intensities than those of particles prepared from solutions without LiCl flux in all preparation temperatures. The PL

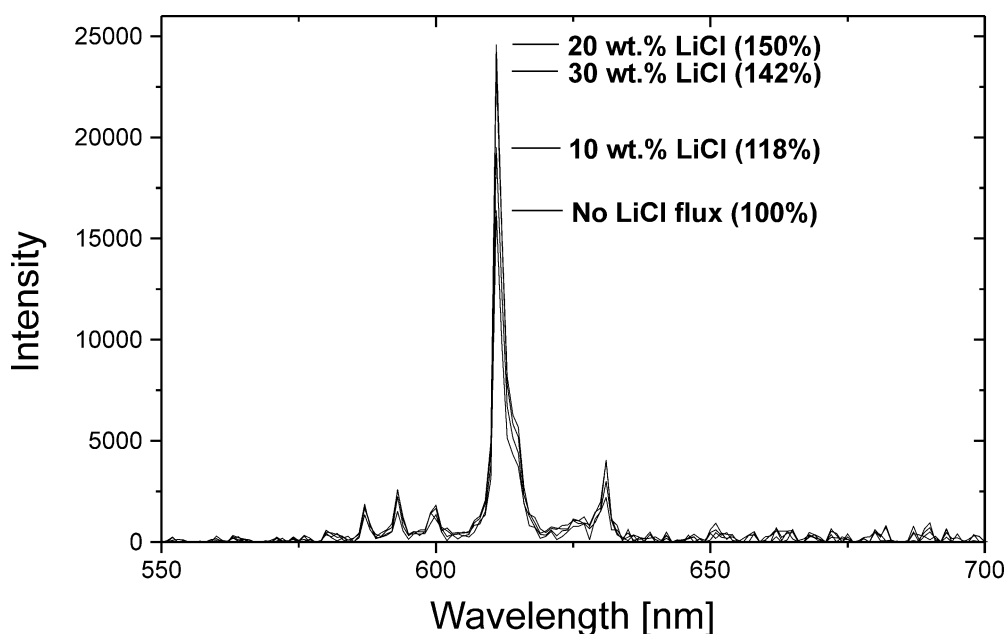


Fig. 1. PL spectra of particles prepared at different addition amounts of LiCl flux.

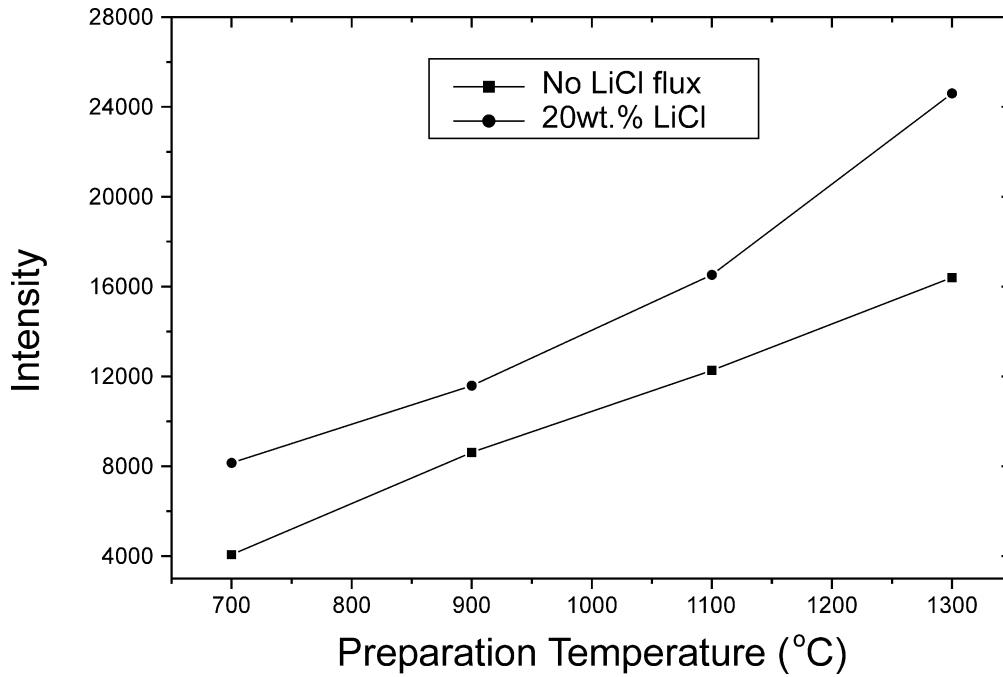


Fig. 2. PL intensities of particles at different preparation temperatures.

intensities of particles prepared at 700 and 900 °C from flux solution are 200 and 134% of those of particles prepared from solution without flux at the same preparation temperatures. The addition of 20 wt.% LiCl flux is equivalent to increasing the preparation temperature by 200 °C. The PL intensities of particles prepared from solution of LiCl flux at 700 and 900 °C have similar values to those of particles prepared from solution without flux at 900 and 1100 °C, respectively.

From the XRD spectra and SEM photographs of particles prepared from solutions with and without flux, the role of LiCl flux in the spray pyrolysis is proposed. Fig. 3 shows the XRD spectra of particles prepared at 900 and 1300 °C from solutions with and without LiCl flux. The particles have the similar crystallinity at the same preparation temperatures regardless of LiCl flux material. The LiCl flux has no effect on the growth of Y_2O_3 crystallite because of short residence time of particles as

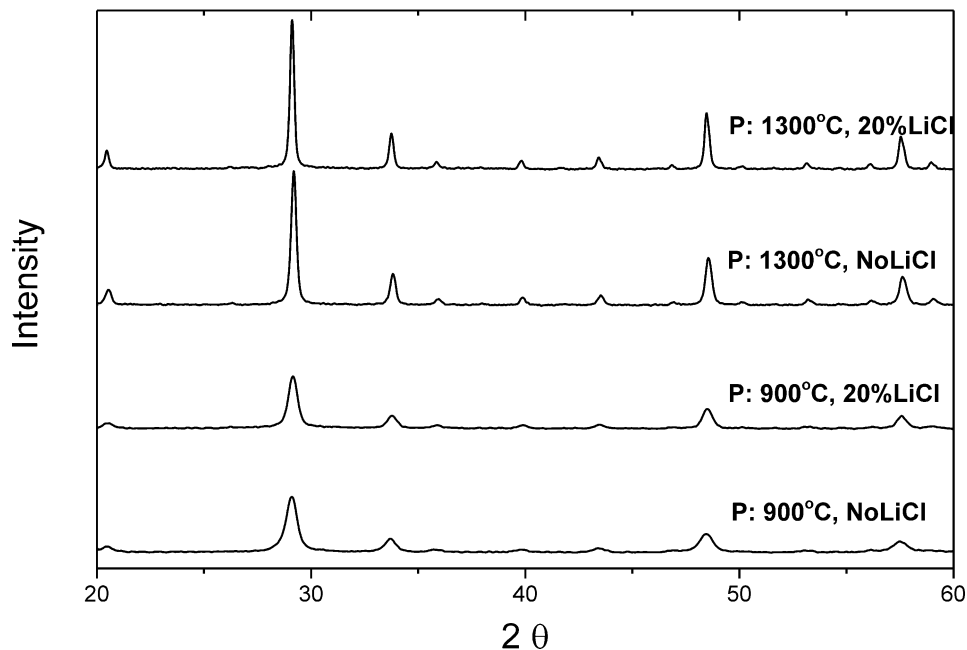


Fig. 3. XRD spectra of particles prepared from solutions with and without LiCl flux.

2 s in the spray pyrolysis. So, the increase of brightness of particles prepared from flux solution is not resulted from the improvement of crystallinity of particles.

Fig. 4 shows the SEM photographs of particles prepared at 1300 °C at the different doping amount of LiCl flux. The particles prepared from solutions with and without flux have similar mean size and size distribution. The mean size of particles measured from the SEM photograph (Fig. 4b) is 0.7 μm. The particles prepared from solution without flux have spherical shape and non-aggregation characteristics and the particles prepared from solution with 10 wt.% LiCl have the same morphology as those prepared from solution without flux. On the other hand, the particles prepared from solution of 20 wt.% LiCl flux have some irregular shape and aggregation between particles even if post-treatment at high temperature is not performed. This aggregation between particles is due to LiCl present at the surface of Y₂O₃:Eu particles. Aggregation phenomenon of particles disappeared after elimination of flux inside particles using dilute nitric acid solution.

The results of XRD spectra and SEM photographs of Y₂O₃:Eu particles indicate that the improvement of brightness of particles prepared from flux solution is not resulted from the improvement of crystallinity and morphology characteristics at the same preparation temperatures. In the spray pyrolysis with short residence time of particles inside hot reactor region, dispersion and activation degrees of dopant inside Y₂O₃ host played a key role of brightness of Y₂O₃:Eu particles. To see the relative activation degree of Eu dopant of particles prepared from solution with and without LiCl flux, the chromaticity of particles is investigated. The chromaticity of particles prepared from solutions without LiCl flux moved into dark red region when the preparation temperature increased from 700 ($x=0.6387$, $y=0.3569$) to 1300 °C ($x=0.6517$, $y=0.3465$). On the other hand, the chromaticity of particles prepared from solution with LiCl flux changed insignificantly with preparation temperatures. The chromaticity of particles prepared at 700 °C changed from $x=0.6501$ and $y=0.3473$ to $x=0.6537$ and $y=0.3451$ when the preparation temperature was 1300 °C. These results of chromaticities of particles indicate that LiCl flux played an important role of improving the activation degree of Eu dopant into Y₂O₃ host.

From the above results of PL, XRD, SEM and chromaticities of particles, we concluded that the increase of PL intensity of particles prepared from solution with LiCl flux with increasing the preparation temperature is due to the crystallinity of particles. Because the activation of Eu dopant was fully occurred even at 700 °C when LiCl flux was used, the high crystallinity of particles at 1300 °C increased the PL intensity. On the other hand, the crystallinity and activation degree affected the PL intensities of particles prepared from solutions without flux. Even

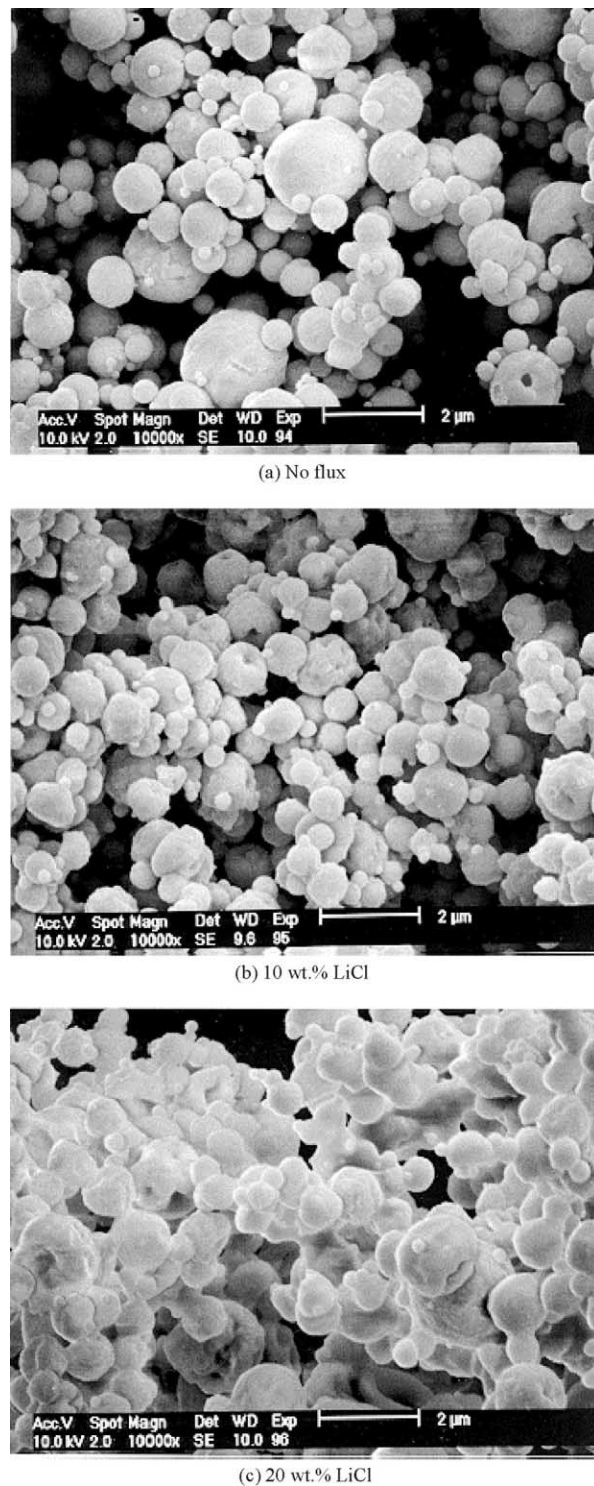


Fig. 4. SEM photographs of particles at different addition amounts of LiCl. (a) No flux, (b) 10 wt.% LiCl, (c) 20 wt.% LiCl.

at the similar activation degree of Eu dopant at the preparation temperature of 1300 °C, the higher PL intensity of particles prepared from solution with LiCl flux than that of particles prepared from solution without flux is due to the change of surface characteristics of

particles. The particles prepared from solution with flux have lower surface defects than those prepared from solution without flux. This result was supported by the fact that the flux effect was more effectively occurred in $\text{Gd}_2\text{O}_3:\text{Eu}$ than $\text{Y}_2\text{O}_3:\text{Eu}$ system. In the spray pyrolysis, the $\text{Gd}_2\text{O}_3:\text{Eu}$ phosphor particles had more porous and hollow structure than $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor particles.^{7, 9}

4. Conclusions

Flux material is applied to the preparation of $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor particles in the spray pyrolysis. Flux material is also effective to the preparation of oxide phosphor particles in the spray pyrolysis. Flux material play a key role of the preparation of $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor particles in conventional solid state reaction and aqueous solution methods. In conventional preparation methods, flux material increases the crystallite and the mean sizes of particles. However, LiCl flux played an important role of activation of Eu dopant to the preparation of $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor particles by the spray pyrolysis. The $\text{Y}_2\text{O}_3:\text{Eu}$ particles prepared from solution with LiCl flux are fully activated even at 700 °C. On the other hand, the high temperature above 1100 °C is required to activate Eu dopant into Y_2O_3 host without flux. The other function of LiCl flux in the spray pyrolysis was the decrease of defects of particles. Therefore, the preparation temperature can be decreased to obtain the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor particles with optimum brightness introducing flux materials in the spray pyrolysis.

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