Morphology and Photoluminescence Characteristics of Halophosphate Phosphor Particles by Spray Pyrolysis and Flame Spray Pyrolysis

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Abstract
Flame spray pyrolysis was applied to improve the photoluminescence characteristics of blue-emitting $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles with high brightness for the application to LED phosphor. $Sr_5(PO_4)_3Cl:Eu^{2+}$ prepared from conventional spray pyrolysis had poor PL intensity than that of commercial products under long-wavelength ultraviolet(UV). $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by flame spray pyrolysis had PL intensity as same as that of commercial products under long-wavelength UV. Hollow morphology and porous structure of the particles prepared by the flame spray pyrolysis disappeared after posttreatment. Even though the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by the flame spray pyrolysis had irregular shape, the particles had dense structure and clear surface property.

1. Introduction
Recently, semiconductor light emitting diodes (LEDs) were studied and developed for few decades. LEDs have various applications such as lamps for digital number, letters and labels and outside display because they had merits such as full color display and energy conservation. However, LEDs had some problems like color purity, process complexity and embodiment of white light. To overcome these problems of LED chips, various methods such as growth of three-light (red, blue, green) thin film and paste of phosphor particles on the long wavelength ultraviolet excitation thin film were attempted. Among these methods, the pasting method of phosphor particles on the thin film of UV diode had advantage like color purity, semipermanent usage and color efficiency, etc.

Eu-doped alkaline-earth halophosphates as a blue emitting phosphor have a broad excitation band from vacuum ultraviolet (VUV) to long wavelength ultraviolet (UV). Also the halophosphates have many applications such as plasma display panels (PDPs), field emission displays (FEDs), three-way fluorescent lamps and light emitting diodes (LEDs) because of their excellent photoluminescence characteristics [1-8].

The conventional solid-state route and liquid-phase synthesis have been used to prepare the halophosphates. The particles prepared by these techniques have irregular morphology and wide size distribution because they need high temperature heat treatment for long time to make a good crystallinity and activate doping components in a host matrix. Now a day, spray pyrolysis has been studied for the preparation of oxide phosphor particles. The particles prepared by the spray pyrolysis have spherical shape, nonagglomerated morphology and narrow size distribution. However, the particles prepared by the spray pyrolysis had hollow morphology and porous structure, which are not good for the photoluminescence of phosphor particles. So, there have been many efforts to overcome these disadvantages. For example, the use of some additives such as flux and colloidal seed is effective to make spherical ceramic particles by the spray pyrolysis [9-10]. The use of a different heat source like flame also is one of important method to avoid the hollowness [11-14].

In this work, conventional spray pyrolysis by electric furnace and flame spray pyrolysis were introduced to prepare $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles. The phosphor particles prepared by the conventional spray pyrolysis have spherical shape. However, the particles had hollow morphology and porous structure. Also, photoluminescence intensity was not good as high as commercial products. To overcome these problems, flame spray pyrolysis was introduced to prepare $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles with a dense structure and high brightness. The photoluminescence (PL) intensity of the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by the flame spray pyrolysis was similar to that of commercial products under long-wavelength ultraviolet excitation light. Also, the particles prepared by flame spray pyrolysis had dense structure and clear surface characteristics.

2. Experimental
A conventional spray pyrolysis by electric furnace

and flame spray pyrolysis were used to prepare $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles. An ultrasonic generator with six vibrators with 1.7 MHz resonator was used as a apparatus in this work. In the conventional spray pyrolysis, the length and inside diameter of the quartz reactor were 1200 mm and 50 mm, respectively. The flow rate of air used as carrier gas was 45 l/min. The temperature of the reactor was fixed at 900℃. The flame spray pyrolysis consists of a droplet generator, flame nozzle, quartz reactor, bag filter, and vacuum pump. In the flame spray pyrolysis, propane and oxygen were used to generate high temperature flame. The flow rate of oxygen used as the flame nozzle gas and carrier gas was varied from 20 to 40 L/min.

$Sr(NO_3)_2$, $SrCl_2{\cdot}6H_2O$, $NH_4H_2PO_4$ and Eu_2O_3 were dissolved in distilled water to prepare precursor solution. The total concentration of solution was 1M and the doping concentration of europium was fixed at 3.4 mol % of strontium and phosphorus components. The as-prepared phosphor particles by the conventional and flame spray pyrolysis were posttreated at 900 to 1100℃ for 3 h under a reduction atmosphere (5% H_2/N_2 mixture gas).

The crystal structure of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles was investigated by X-ray diffractometry (Rikaku DMAX-33 X-ray). The morphology of the particles was observed by scanning electron microscopy (PHILIPS XL 30S FEG). Photoluminescence characteristics of the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles were investigated under long-wavelength UV (ultraviolet) excitation evolved from Xe flash lamp.

3. Results and Discussions

Figure 1 shows the SEM photographs of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by conventional spray pyrolysis. The as-prepared and posttreated particles had similar morphology. The halophosphate as-prepared by the conventional spray pyrolysis had hollow morphology and porous structure, as shown in Fig. 1(a). When the droplets generated by ultrasonic nebulizer pass through quartz reactor, the droplets turn into the particles with hollow morphology and porous structure by rapid drying rate inside the hot wall reactor. The gas flux such as $SrCl_2{\cdot}6H_2O$ or NH_4Cl was used during the posttreatment in order to investigate its effect on the morphology of the $Sr_5(PO_4)_3Cl:Ei^{2+}$ phosphor particles prepared by spray pyrolysis. The morphology of the prepared $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles was greatly affected by the existence of gas flux such as $SrCl_2{\cdot}6H_2O$ or NH_4Cl, as shown in Fig. 1(b). As a result of having hollow morphology and porous structure, the phosphor particles prepared from the conventional spray pyrolysis had lower photoluminescence intensity when they were compared to commercial products under long-wavelength ultraviolet(UV) excitation.

Figure 2 shows the SEM photographs of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by the flame spray pyrolysis. After the droplets generated are carried into the high temperature diffusion flame by the oxygen carrier gas, they are decomposed and melted to form particles. Therefore, the as-prepared particles by the flame spray pyrolysis had more spherical shape and narrow size distribution than those as-prepared by conventional spray pyrolysis, as shown in Fig. 2(a). The particles as-prepared by the flame spray pyrolysis did not maintain dense structure because of rapid drying, decomposition rate and short residence time in the flame. However, during the high temperature post heat treatment for crystallization and activation of doping components in a host matrix, different morphology and luminescence characteristics occurred by adding gas phase flux such as $SrCl_2{\cdot}6H_2O$ or NH_4Cl. When the gas phase flux was not added during the posttreatment, the morphology of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles was hollow and the structure was porous. Also the photoluminescence intensity was lower than that of commercial products. To overcome these problems, gas phase flux such as $SrCl_2{\cdot}6H_2O$ or NH_4Cl were added during posttreatment in order to supplement chlorine source. As a result of adding gas phase flux, the phosphor particles having hollow morphology and porous structure disappeared. Furthermore, the halophosphate phosphor particles having dense structure and clear surface property were obtained. However, the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles obtained had agglomerate and irregular morphology, as shown in Fig. 2(b). It is due to the chlorine source used as gas phase flux during posttreatment. As a result of adding gas phase flux, the PL intensity of the particles became similar to that of commercial products under long-wavelength UV excitation light, as shown in Fig. 3.

The $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by the conventional spray pyrolysis and flame spray pyrolysis had same X-ray diffractometry (XRD) patterns. However, the particles prepared by the flame spray pyrolysis had bigger crystallite size than that of the particles prepared by the conventional spray pyrolysis. It is because the as-prepared particles by the flame spray pyrolysis had more stable phase than those as-prepared by the conventional spray pyrolysis, and gas phase flux affect the morphology of the particles. Consequently, the photoluminescence characteristics in the halophosphate prepared by the conventional and flame spray pyrolysis were affected by dense structure and crystallite size.

4. Conclusions

$Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles were prepared by conventional spray pyrolysis and flame spray pyrolysis. The effect of synthesis methods on the crystallinity, morphology and photoluminescence intensities of the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles were investigated. The phosphor particles prepared by the conventional spray pyrolysis had spherical shape. However, the structure of the particles was porous and PL intensity was not good even though high temperature post heat treatment at 1000 °C for 3h. To overcome these problems, a diffusion flame was used and gas phase flux such as $SrCl_2{\cdot}6H_2O$ or NH_4Cl was added for post heat treatment. As a result of changing synthetic route and adding gas phase flux, the $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by the flame spray pyrolysis had dense structure, clear surface property, big crystallite size and high luminescence characteristics under long wavelength ultraviolet (UV) excitation.

5. References

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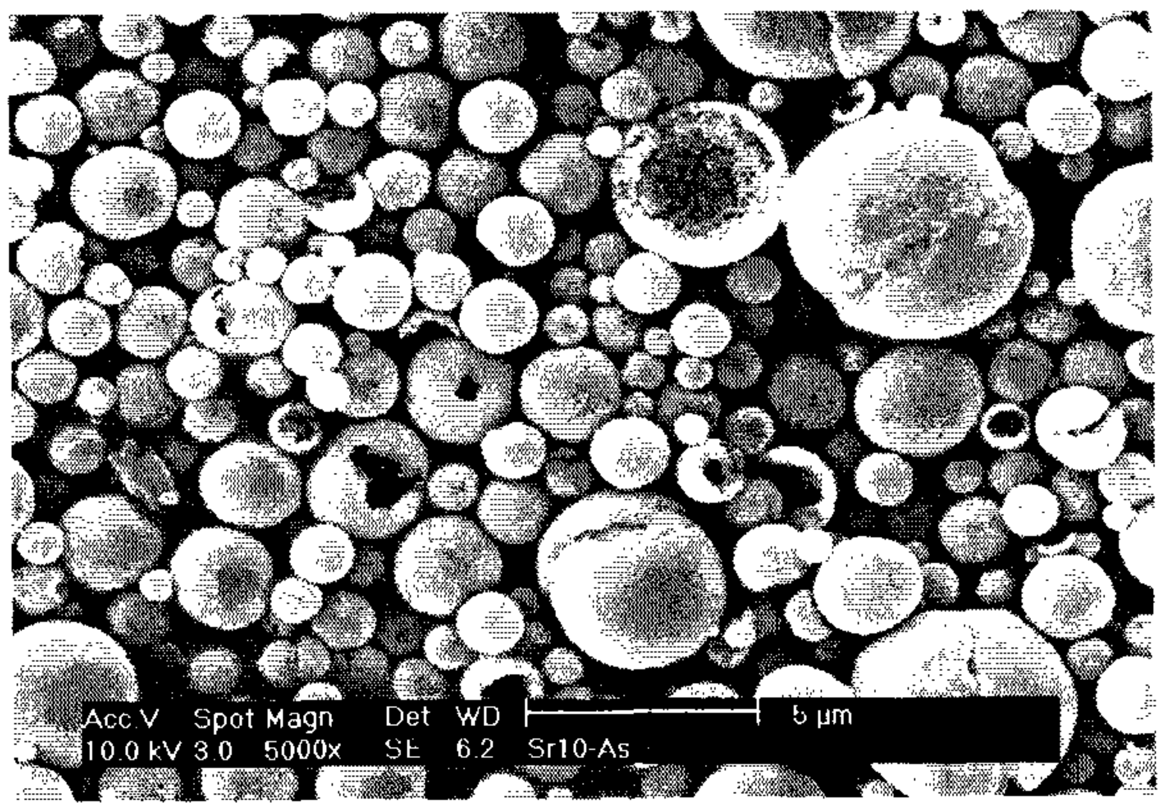
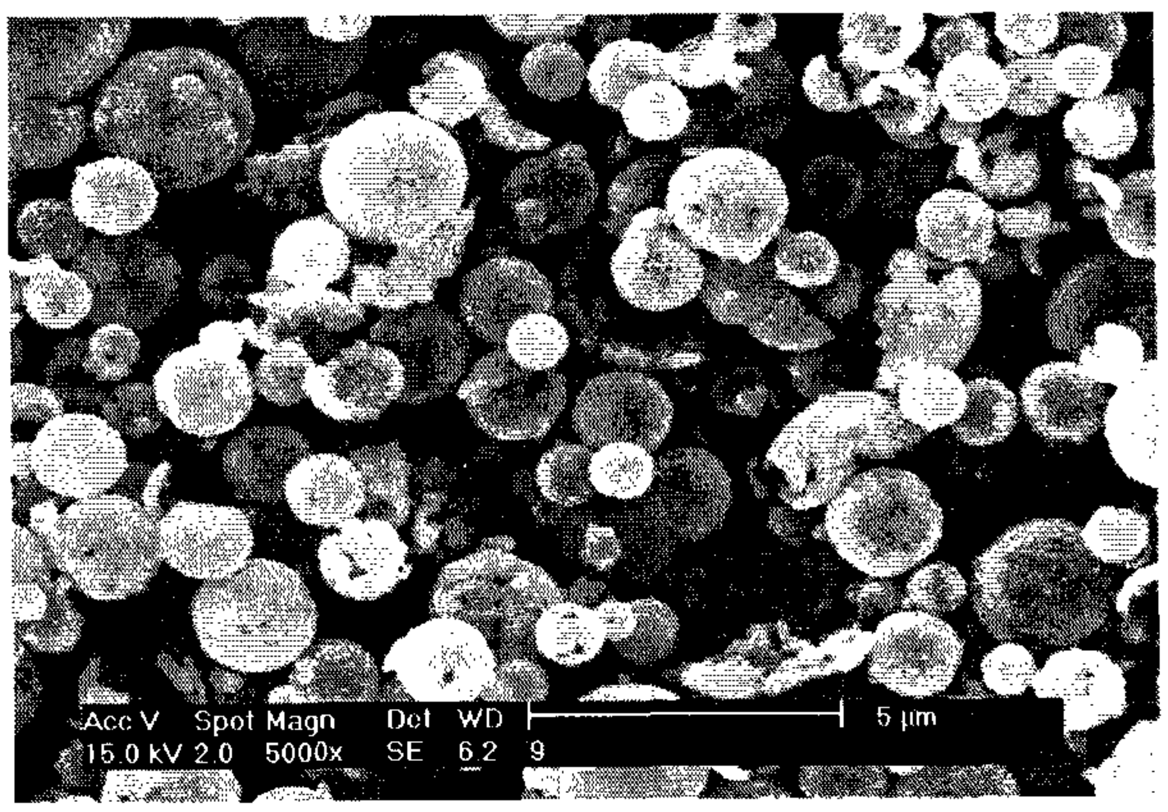
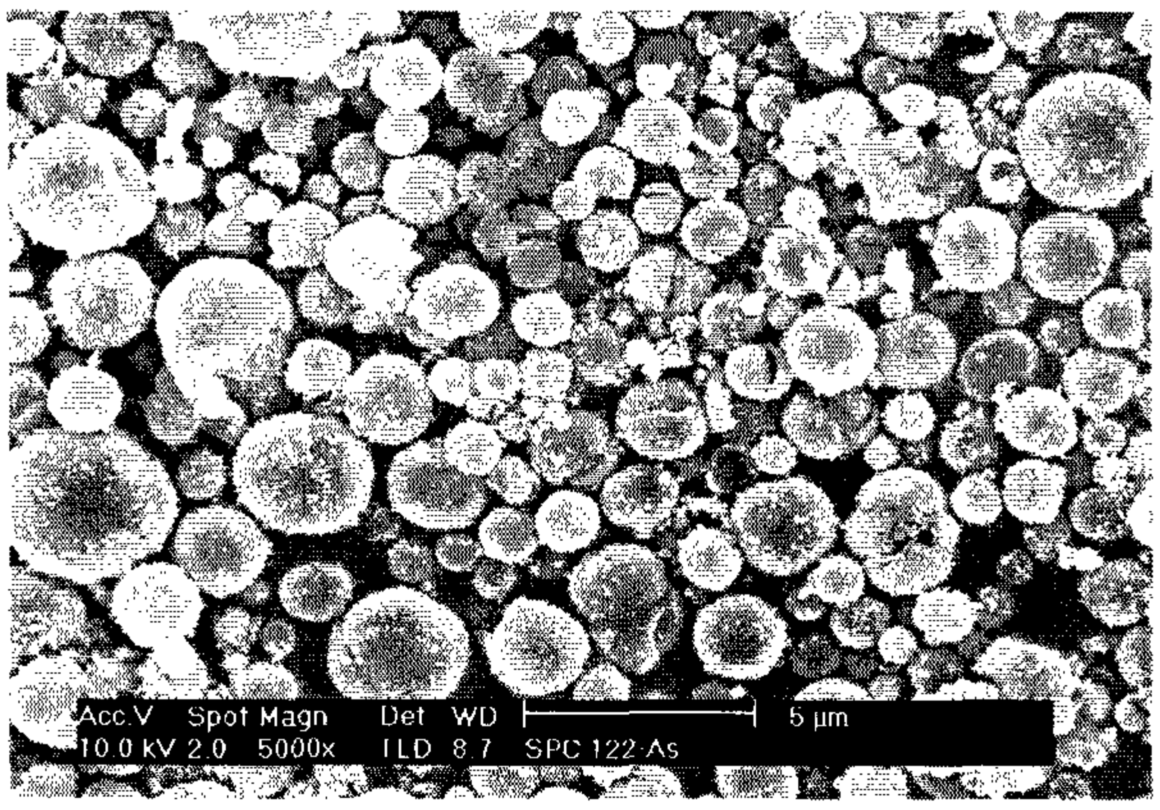


(a) as-prepared particles

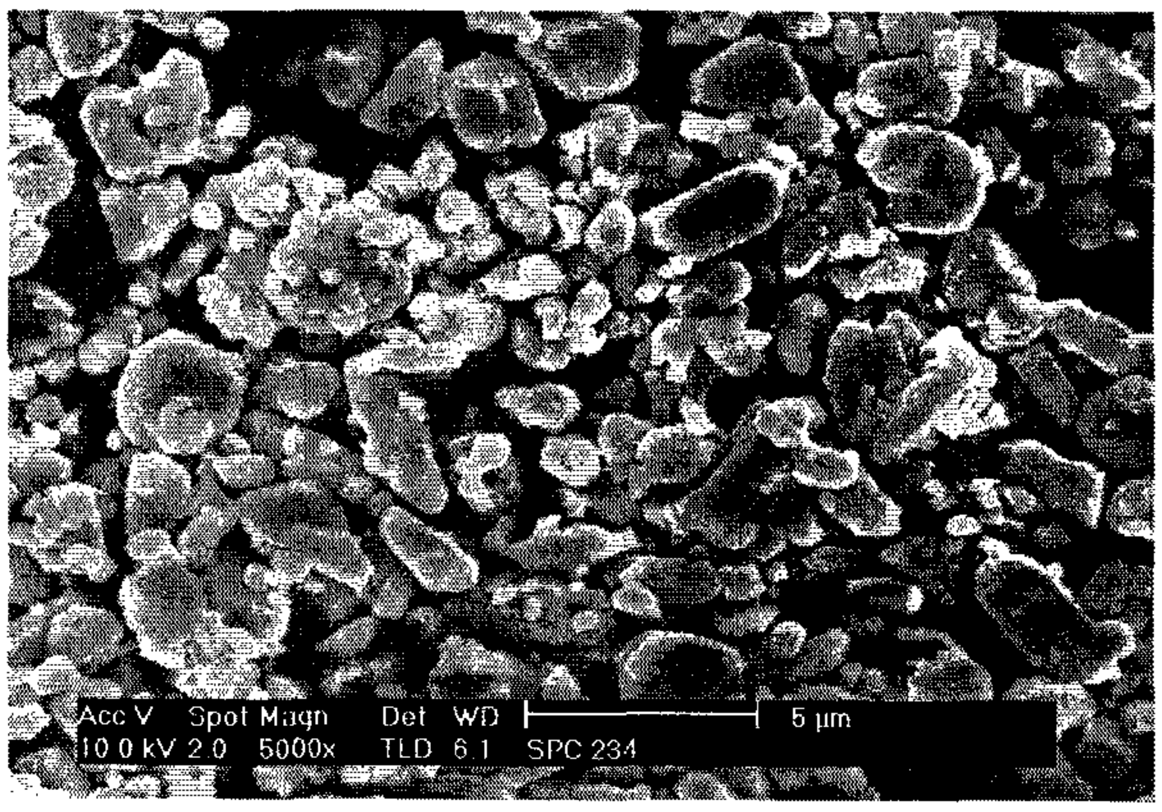


(b) posttreated particles

Figure 1. SEM photograph of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by conventional spray pyrolysis.



(a) as-prepared particles



(b) posttreated particles

Figure 2. SEM photograph of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles prepared by flame spray pyrolysis.

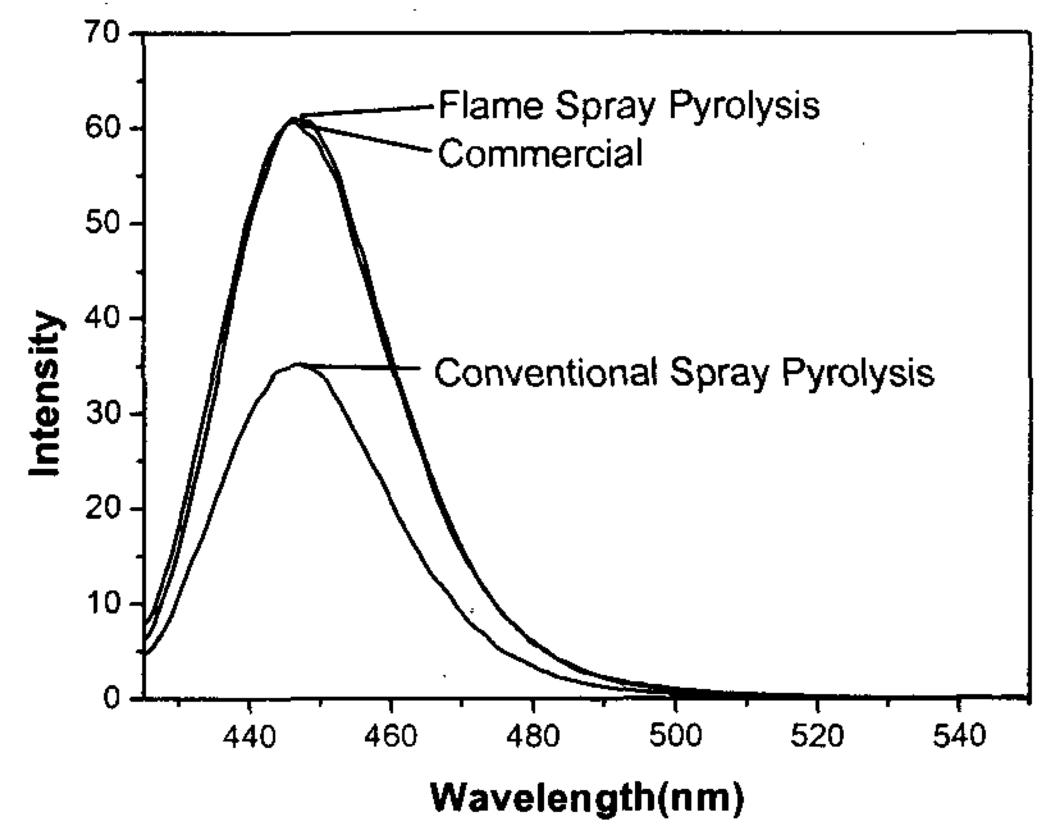


Figure 3. Photoluminescence characteristics of $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor particles.