Synthesis and characterization of orange-yellow phosphor for inorganic EL device

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Abstract

Orange-yellow phosphor has been synthesized by solid-state method for inorganic EL devices. Zinc sulfide is used as host material for the phosphor and the phosphor consists of copper and manganese as activators. The dependence of the photoluminescence (PL) and electroluminescence(EL) properties on the copper and manganese concentrations has been investigated.

1. Introduction

Zinc sulfide is a famous phosphor material with various luminescence properties, such as photoluminescence (PL)[1], electroluminescence (EL) [2], and generally used in the fields of displays, sensors and lasers. With its long band-gap energy, we can have different radiation wavelengths by doping transition or rare earth metal ions. ZnS-based electroluminescence was first observed in 1936 at Curie's laboratory in Paris[3]. This EL phosphors have many commercial uses such as for LCD(liquid crystal display) backlight, copy machines, automotive dashboard displays, watch dials etc.

The emitting color of ZnS:Cu,Cl phosphor is blue or green depending on the activator concentration. ZnS based phosphors with Mn and Cu as activators is most widely studied materials for EL devices with yellowish orange emission centered at 584nm[4-6]. In fact, copper and manganese concentration is very important condition to obtain the phosphor that have commercially desirable brightness and color characteristics.

In this study, the dependence of the PL and EL properties on various copper and manganese concentration has been investigated.

2. Experimental

An orange-yellow phosphor is prepared in two sintering steps.

In the first sintering, zinc sulfide has been blended with appropriate amounts of a source of manganese, copper, zinc oxide, sulfur, and chloride. The chloride can be a mixture of alkali metal, an alkaline earth chlorides, preferably barium chloride, magnesium chloride, and sodium chloride. The copper has been taken from 100ppm to 700ppm relative to the weight of ZnS. Then the blended mixture has been sintered in air at 1150℃ for 4 hours. The sintered material is washed with acid, KCN and deionized water.

In the second sintering step, the material from the first sintering step has been blended with appropriate amounts of a copper source, manganese, and zinc oxide. The copper concentration has been varied from 0 wt.% to 3.5 wt.% and the manganese concentration has been varied from 0 wt.% to 10 wt.% relative to the weight of ZnS. The blended mixture sintered in air at 750℃ for 2 hours. This sintered material is fast cooled to room temperature in less then two hours and washed with acid, KCN and deionized water.

Thick film EL devices have been fabricated using the synthesized phosphor by screen-printing method. The layer structure of EL device was formed by printing in

the following sequence : ITO front electrode layer - ZnS:Mn,Cu,Cl phosphor layer - $BaTiO_3$ dielectric layer - silver back electrode layer.

The photoluminescence and electroluminescence properties have been investigated with CS-1000 spectrometer. Surface morphology, particle size and crystal structure have been studied using SEM and XRD respectively.

3. Results

Photoluminescence and electroluminescence spectra of the phosphors with various copper and manganese concentrations have been investigated. Figure 1 shows the dependence of PL and EL properties on various copper concentrations after 1st sintering step. It is observed from the spectra that PL intensity of Cu (500ppm) increased to about 28% than Cu (0ppm) and EL intensity of Cu (500ppm) increased to about 15% than Cu (100ppm). The sample without Cu has no EL emission. Therefore copper must be added in 1st sintering step to have electroluminescence properties. The average particle size of the phosphors is in the range of 20-25μm as observed from the SEM micrographs (Figure 2). Figure 3 shows the XRD patterns of the phosphor.

Figure 4 and Figure 5 show the dependence of PL and EL on various copper and manganese concentrations after 2nd sintering step. When the blended condition is Cu 2.5 wt.% and Mn 6.5 wt.% relative to the weight of ZnS, PL intensity increased to about 42% than 1st sintering material and EL intensity increased to about 30%. This sample has the main emission peak at 584nm, and color coordinate at x=0.5116, y=0.4461. Most of the samples consist of main emission peak at 583~586nm and have x color coordinate from about 0.5021 to 0.5122 and y color coordinate from 0.4592 to 0.4714. But the sample not having Mn in 2nd sintering step has the main peak at 461nm and has a color coordinate at x=0.1910, y=0.2639.

4. Conclusions

ZnS-based phosphors with different amount of copper and manganese were successfully prepared and their photoluminescence and electroluminescence properties have been reported in this paper. It has been observed that the sample with 500ppm of Cu relative to the weight of ZnS after 1st sintering step has highest PL intensity and also Cu presence is required to have EL emission. The phosphor synthesized after blending with 2.5 wt.% of Cu and 6.5 wt.% of Mn in the 2nd sintering step has highest PL and EL properties with orange-yellow color coordinate at x=0.5116, y=0.4461

5. References

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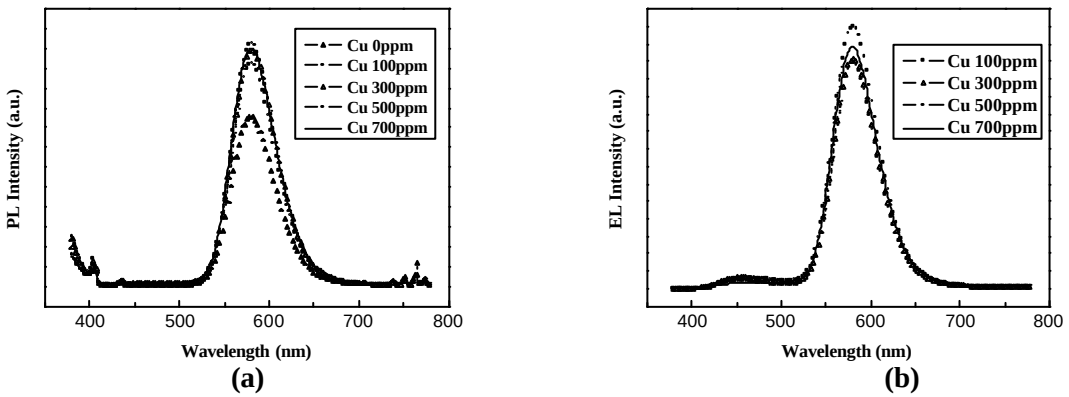
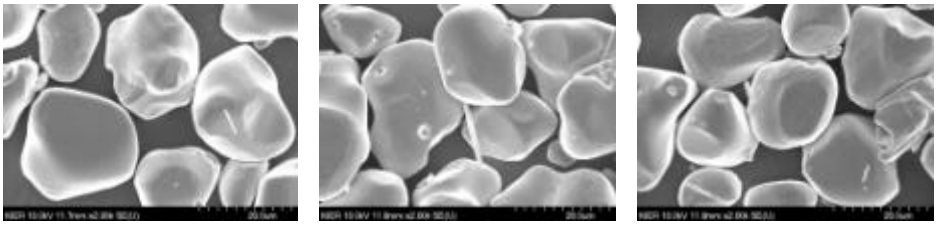
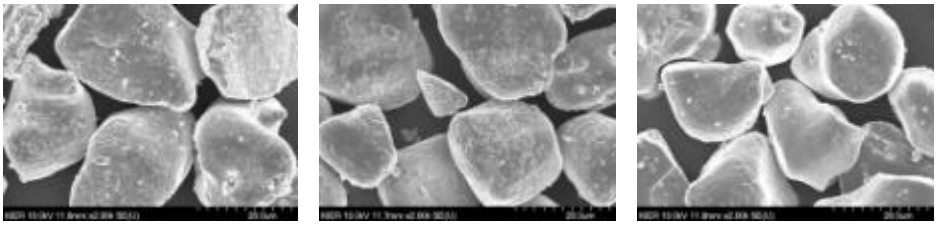


Figure 1. PL and EL emission spectra of ZnS phosphor with different amount of Cu ; (a) PL emission spectra (b) EL emission spectra at 100V, 400Hz



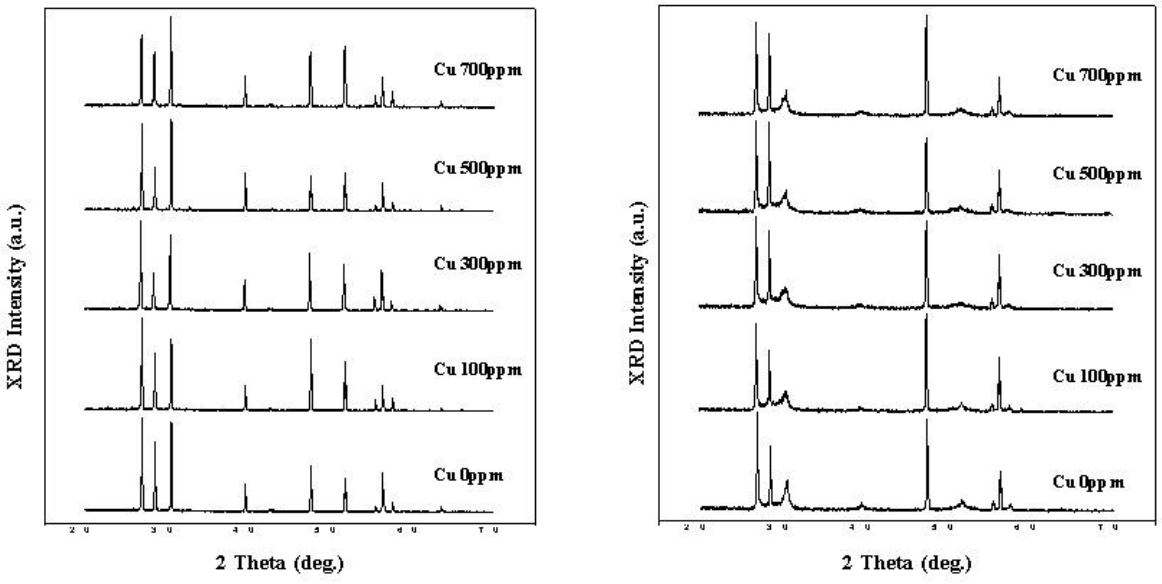
(1) (2) (3)

Figure 2. (a) The shape of the phosphor after 1st sintering ; (1) Cu 0ppm, (2) Cu 500ppm, (3) Cu 700ppm



(1) (2) (3)

Figure 2. (b) The shape of the phosphor after 2nd sintering ; (1) Cu 0ppm, (2) Cu 500ppm, (3) Cu 700ppm



(a) (b)

Figure 3. The XRD patterns of ZnS:Mn,Cu phosphor ;
(a) after 1st sintering step, (b) after 2nd sintering step

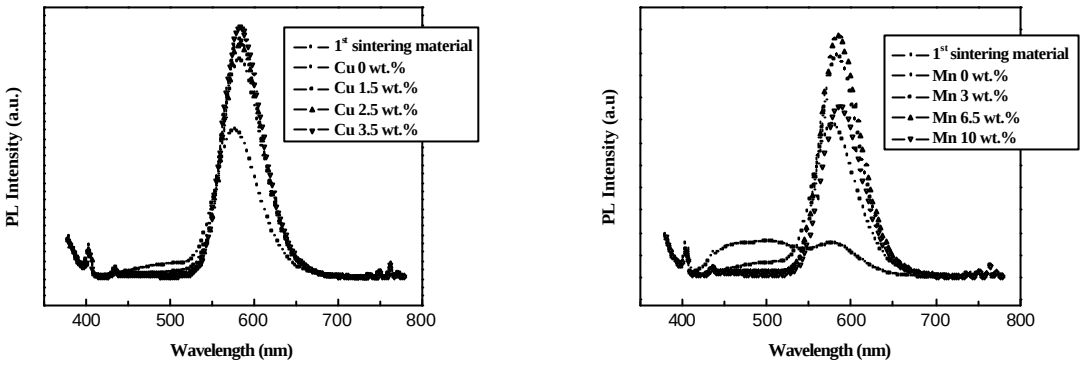


Figure 4. PL emission spectra with different amounts of Cu and Mn after 2nd sintering step ; (a) different amount of Cu (Mn = 6.5 wt.%), (b) different amount of Mn (Cu = 2.5 wt.%)

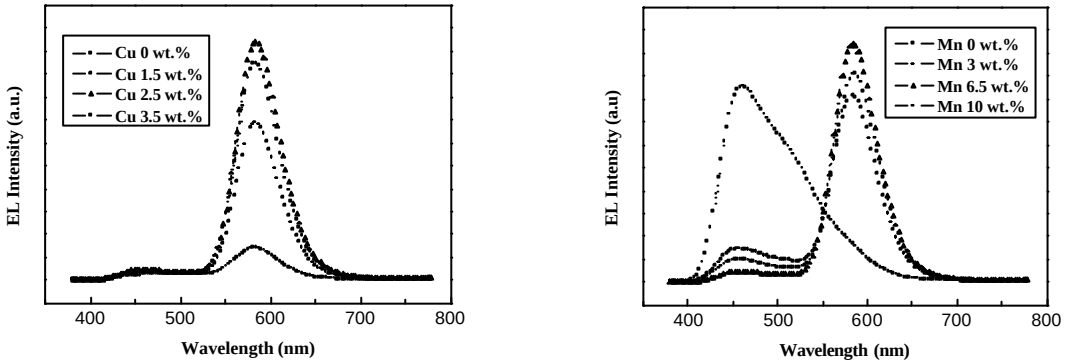


Figure 5. EL emission spectra with different amounts of Cu and Mn at 100V, 400Hz ; (a) different amount of Cu (Mn = 6.5 wt.%), (b) different amount of Mn (Cu = 2.5 wt.%)