

Development of yellow and blue phosphor and their emission properties

Soo-Gil Park[†], Seong-Ryoul Cho, Won-Ken Son*,
Kee-Joe Lim** and Ju-Seong-Lee***

*Department of Industrial Chemical Engineering, Chungbuk National University Cheongju 361-763,
Chungbuk, Korea*

**Department of Polymer Engineering, Chungnam National University Youseong 305-764, Daejeon, Korea*

***Department of Electric Engineering, Chungbuk National University Cheongju 361-763, Chungbuk, Korea*

****Department of Industrial Chemical Engineering, Hanyang University Seoul, 133-791, Korea*

Abstract

Electroluminescence (EL) comes from the light emission obtained by the electrical excitation energy passing through a phosphor layer under an applied high electrical field (10^6 V/cm). The preparation of white and blue phosphors and characterizations of light emitting alternating current powder electroluminescent devices (ACPELDs) were investigated. In this work, we fabricated two kinds of ELDs, that is, yellow electroluminescent device (Y-ELD), blue electroluminescent device (B-ELD). The basic structures of Y-ELD and B-ELD are ITO (Indium Tin Oxide)/Phosphor layer/Insulator layer/Al electrode and ITO/Phosphor layer/Insulating layer/Carbon electrode, respectively. Another structures of ITO/Phosphor and Insulator mixture layer/Backelectrode are introduced. EL spectra and luminance of two types of ELDs were measured by changing voltage at fixed frequency 0.4 kHz, 1.5 kHz. Blue and yellow phosphors prepared in this work show 50 cd/m² and 30 cd/m² of luminance at 400 Hz, 150 V.

Key words : P-ELD (Powder Electroluminescent Devices), Phosphor, Luminance, CIE (Commission International de Enlumineure) coordinator, ITO (indium tin oxide)

1. Introduction

Recently display industry was in a new era for liquid crystal display (LCD) replace cathode ray tube (CRT). Small size, weight, slim type, high luminance and long life time is needed for the present display.^{1,2)} Electroluminescent (ELDs) attract public attention as a significant light sources because of its high efficiency. It can be divided into thin film type and powder type ELDs (P-ELD). In case of P-ELD, though it has been studied for a long time, it has a limit in generating luminance. But the thin film type EL has good prospect as a backlight in LCD. P-ELD is easy for fabricating device and low-cost, useful as a large area flat light emitter.^{3,4)}

ELDs are flexible, flat, thin and cold illumination sources that can be cut into complex shapes for lighting LCD displays, aircraft instrument panels, architectural accents, advertising signage, and special effects for movies, television, etc. The ELDs resembles a sandwich in that it is comprised of a light emitting material placed between two insulating layers. This structure in turn is then placed between two conducting electrodes. The phosphor material which is typically zinc sulfide doped with manganese is placed between the insulating layers.^{5,6)} Aluminum and indium tin oxide (ITO) which is a transparent conductive metal, are used as the

electrodes. When the voltage exceeds a well defined threshold, the emitter breaks down and conducts current. The current excites the activator and co-activator ions, which give off light. Electroluminescence generally comes from the light emission obtained by an electrical excitation energy passing through a phosphor layer under an applied high electrical field ($\leq 10^6$ V).^{7,8)} The preparation and characterizations of light emitting ACPEL (alternating-current powder electroluminescent) cells based on ZnS:Cu powder are discussed. The ACPELD is useful for constructing large sized flat panel display.

In this work, blue and yellow phosphor materials were successfully synthesized by the firing process. We designed P-ELD as ITO/phosphor layer/insulating layer/back electrode. The silk screen deposition method was adapted for fabricating ELDs. An optimal structure for EL cell was investigated. After considering the effect on electric and dielectric properties with emission properties, relationship of luminance and voltage was investigated by changing voltage. About 200 cd/m² of luminance was investigated with ZnS:Cu phosphor at 200 V, 1.5 kHz.

2. Experimental

2.1. Materials

For synthesizing a blue EL phosphor, ZnS as a host and

[†]E-mail: sgpark@trut.chungbuk.ac.kr

CuBr_2 as a activator and co-activator were purchased from High Purity Chemical Co. For the yellow EL phosphor, Mn as a co-activator was purchased from Aldrich Chemical Co. Flux agents also were introduced for aiding crystal growth. For fabricating ELD, high dielectrics BaTiO_3 powder was purchased from High Purity Chemical Co. CR-M which is mixed by CR-S (cyanoethyl pullulan) (70%):CR-V (cyanoethyl polyvinylalcohol) (30%) was purchased from Shinets Chemical Co. Dimethylformamide as a solvent and carbon as back electrode were used for fabricating ELDs. And other chemicals were from Junsei Chemical Co.

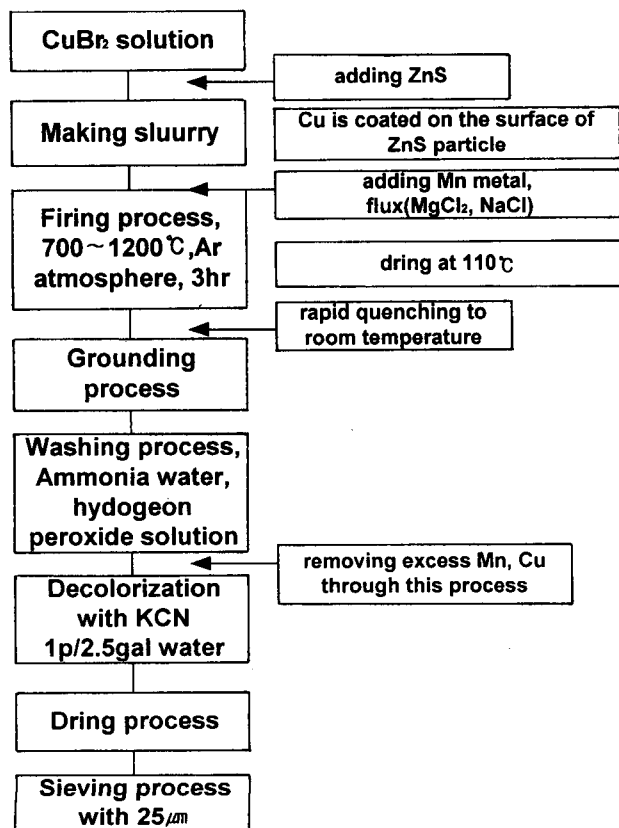
2.2. Substrate

30 Ω/S of ITO substrate were purchased from Samsung Corning Co. Etching process was introduced for easy fabricating with mixture of HCl and HNO_3 . After etching process, ITO was washed with ultrasonicator in acetone and ethyl alcohol then dried in oven.

2.3. Phosphor Preparation

Firing process was introduced with Lanton Furnace by changing composition and temperature. Phosphor preparation process was shown at scheme 1. After firing process, grinding, washing and sieving were performed. 25~30 μm phosphor was used as a EL phosphor material.

2.4. Fabricating ELD



Scheme 1. Flow diagram for preparing phosphor. Flow diagram of washing process of phosphor prepared. Excess of activator and co-activator was removed through this process.

EL cell was fabricated with ITO/Phosphor layer/Insulator layer/Back electrode. As shown in Fig. 1, fabricated device in this work had a multilayer structure. Phosphor and insulating layers were 20~30 μm , 10~30 μm , respectively. Silk screen method was introduced for deposition each layer. Each layer were mixed with binder. Viscosity of binder was adapted 8 and 11 poise for easy fabricating. After silk screen, ELDs were dried in 110°C oven.

2.5. Analysis

XRD (X-ray diffractometer) was performed for investigating phosphor crystal structure. For dielectric loss analysis, dielectric constant of each layer were investigated with Impedance Analyser (Hewlett Packard IA). EL spectra and luminance was investigated with high speed power amplifier (Me4015) which was set with Spectrometer (PMA-10) and Luminancemeter (Dr 2550 Millab) and Universalsource (HP3245A).

3. Results and Discussion

3.1. Phosphor analysis

XRD indicate phosphor prepared in this work has a hexagonal and cubic structure. Main peaks are at $2\theta=29, 48, 57.5^\circ$ (Fig. 2). Hexagonal show more strong luminance when applied electric field. For blue and yellow phosphor, proper firing temperature for hexagonal structure are 800°C, 1050°C, respectively. $2\theta=47^\circ$ peak is strong at 800°C compared with $2\theta=28^\circ$. Phosphor composition was investigated by energy dispersive x-ray spectroscopy (EDS) analysis. EDS showed phosphor has 1.3 wt% of Mn and 0.71 wt% of Cu. wt% of co-activator and activator should be below 1% for EL phosphor.

3.2. EL Spectrum

EL spectra was investigated for blue-green, yellow and white ELD. Under 200 V, 1.5 kHz electric field, EL spectra was measured. Fig. 3~Fig. 6 show each color phosphor. Blue, yellow, red and white EL spectra were measured. Blue emission from Cu around 460 nm is proportional to

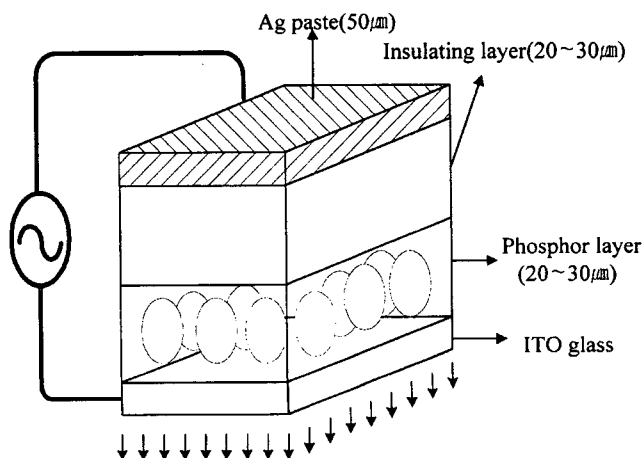


Fig. 1. Schematic structure of ELDs prepared in this work.

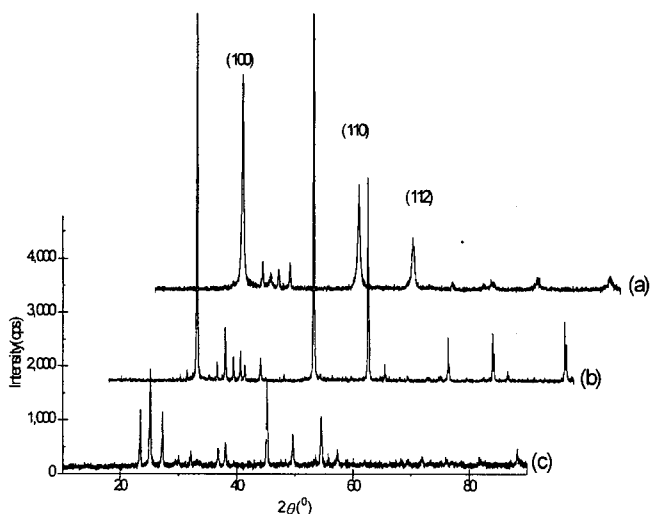


Fig. 2. XRD data for each phosphor.

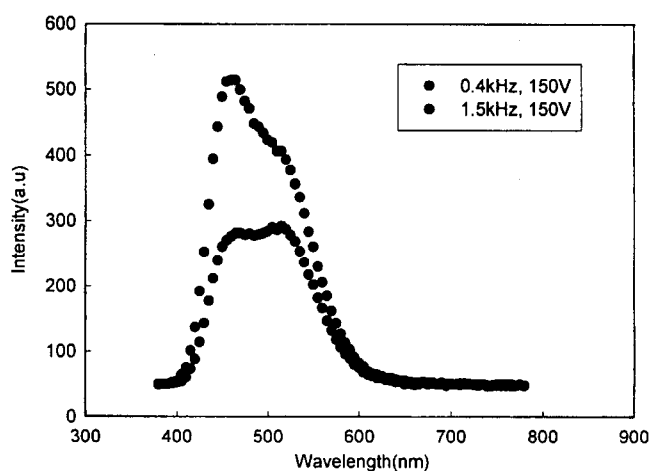


Fig. 3. EL spectra for blue phosphor prepared in this work.

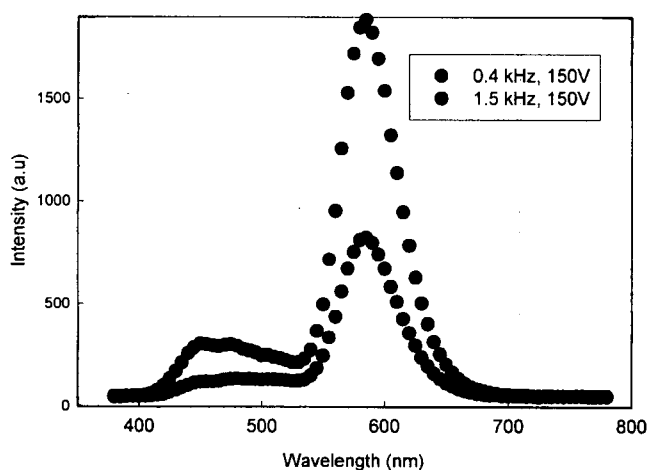


Fig. 4. EL spectra for yellow phosphor.

frequency. As frequency increase, blue emission spectra was sharply increased. In case of yellow phosphor, Mn and Cu ion plays a role in emission. But Mn is more sharply increased by increasing frequency (Fig. 4). Mn is excited by

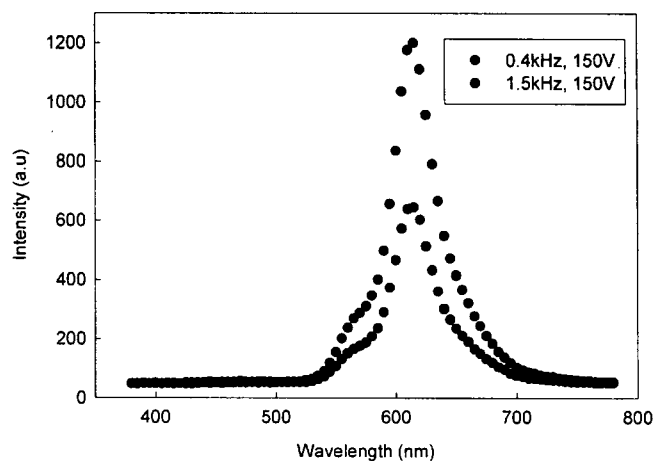


Fig. 5. EL spectra for dye doping yellow phosphor.

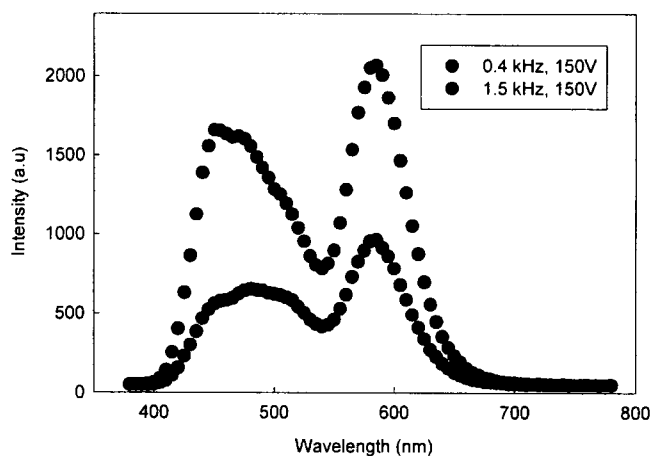


Fig. 6. EL spectra for white phosphor.

the electric field compared with Cu ion.

Another method to realize full color phosphor preparation, dye doping method was investigated. According to this phenomenon, optimal dye content did not have any effect on luminance. But dye can control its EL spectra (Fig. 5). In case of white phosphor, Cu, Mn show same increasing with frequency (Fig. 6).

3.3. Luminance

Luminance was measured for ELD fabricated in this work. Luminance was increased with voltage (Fig. 7). About 200 and 150 cd/m^2 of luminance for white and yellow ELDs was measured, respectively.

Applied voltage through multilayer was controlled by dielectric properties from this equation.

$$\frac{E_2}{E_m} = \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2 - V_2(\epsilon_2 - \epsilon_1)}$$

V_2 : phosphor concentration, E_m : applied average electric field, ϵ_1 : dielectric constant of binder, ϵ_2 : dielectric constant of phosphor, E_2 : electric field applied in phosphor.

After considering all above phenomena, EL devices were fabricated. According to above equation, even thickness

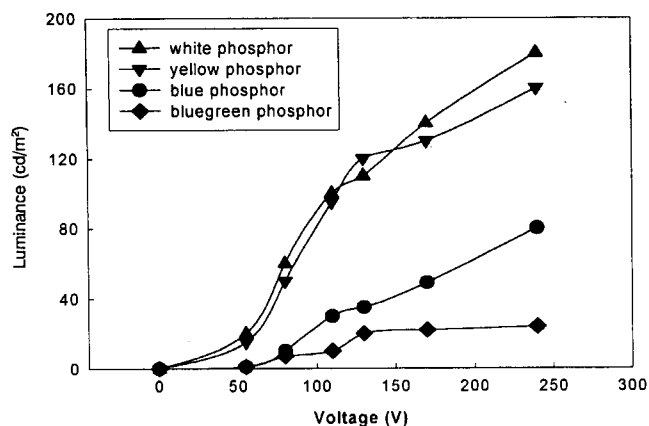


Fig. 7. Luminance-voltage characteristics for each phosphor.

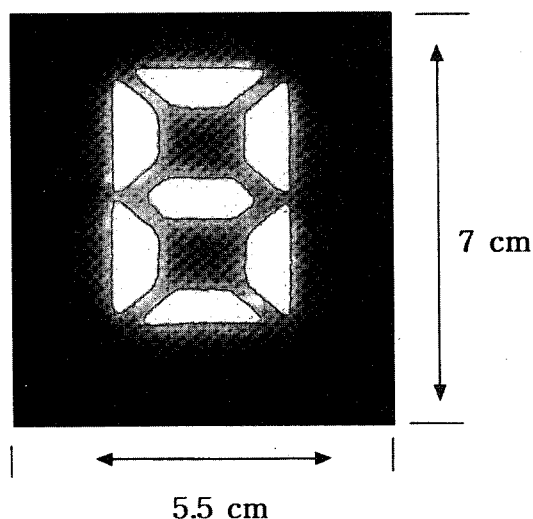


Fig. 8. EL emission phenomenon for white phosphor.

was acquired for realizing even surface emission. If the thickness of each layer is different for entire surface, different electric field come to be applied. From this results, irregular emission was investigated. Fig. 8 shows EL emission with seven segment for white phosphor. Time responses of EL emission intensity under square wave voltage were investigated. If the thickness of insulator is above 50 μm , EL emission intensity was reduced. When 200 V, 1.5 kHz rectangular wave was applied, emission wave was measured by time.

EL peak was shown with increasing and decreasing of voltage. When voltage ascended, this phenomenon could be explained like this.⁹⁾ Electron which is trapped near the elec-

trode is tunnelled when voltage is applied. Infused electron is accelerated by high electric field applied to a phosphor. Emission was occurred when accelerated electron excite copper emission center and trapped electron to ionized copper is transferred. Also when voltage descended, infused hot electron was accumulated by anode surface and this accumulated electron formed reverse direction electric field. This electric field excite electron trapped to shallow donor and acceptor levels. Maximum EL peak was measured when thickness of phosphor and insulator layer is 30, 25 μm , respectively. When rectangular wave is maximum, luminance is maximum. Also luminance is proportional to the applied frequency. This can be explained like this; AC voltage was applied to ELDs, 10^6 V/cm of electric field can be applied to ELDs. If frequency increase, an cycle of applied energy can be faster with proportional to frequency. By that result, applied energy to ELDs is increased. When voltage increased.

4. Conclusion

In this work, blue-green and yellow phosphor was synthesized through firing process. XRD indicate hexagonal structure show strong emission compared with cubic structure. EL spectra shows blue, bluegreen and yellow phosphor was synthesized successfully. ELD which is ITO/Phosphor layer/Insulating layer/Back electrode was fabricated using silkscreen method. 200 cd/m^2 luminance was investigated at 200 V, 1.5 kHz. Luminance is linearly increased by frequency but exponentially increased by voltage to reach its saturating value.

References

1. H. Ohinish, ICEE97 (1997).
2. Y. Qian, K. Hara, H. Munkata and H. Kukimoto, *J. Appl. Phys.*, **34**, 368 (1995).
3. Y. A. Ona, *Encyclopedia of Applied Phys.*, **5**, 295 (1993).
4. S. Tanaka, S. Morimoto, K. Yamada and H. Kobayashi, *Crystal Growth*, **117**, 997 (1992).
5. T. Tohda, Y. Fujita and T. Matsuoka, *Appl. Phys. Lett.*, **48**, 95 (1986).
6. T. Nakagawa, J. Yamaguchi, T. Usuki and Y. Hamakawa, *Jpn. J. Appl. Phys.*, **18**, 897 (1979).
7. A. G. Fisher, *J. Electrochem. Soc.*, **118**, 139C (1971).
8. H. F. Lvey, *Electro, Eletroluminescence and Related*, Academic press, New York and London, p.72 (1963).