

Cu²⁺-addition effect on luminescence of ZnS:Cu,Cl blue-green phosphors

Tae-Yeon Cho^{1,2}, Ja-Il Park^{1,2}, Sang-Do Han¹, Jihye Gwak^{*1},
Dong Hyuk Shin^{3,4}, Il-Su Chun¹, Chi-Hwan Han¹

¹Korea Institute of Energy Research, Daejeon, Korea

TEL: 82 42 860 3468, e-mail: bleucoeur@kier.re.kr

²Hanyang University, Seoul, Korea

³EL Korea Corp., Daejeon, Korea

⁴Dongguk University, Seoul, Korea

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Abstract

ZnS:Cu,Cl blue-green phosphors were prepared by conventional solid state reaction. Copper activator of different concentrations was doped into ZnS structure at two firing steps. The luminescence characteristics dependent on Cu²⁺ doping concentration of the phosphors has been investigated for inorganic electroluminescent device.

1. Introduction

ZnS:Cu,Cl phosphors have attracted great attention due to their excellent luminescence properties. They have been applied in electronic display devices, CRTs, military equipment, LED, etc [1]. They are also used in electroluminescence (EL) device which has various applications such as mobile phone key pad, military equipment, e-paper and medical instruments. EL may also potential applications in LCD back light. However, high-performance phosphors are needed for EL device to overcome limitations in luminous efficiency, brightness and chromaticity, understanding their luminescence characteristics dependent on the synthesis conditions [2]. EL and photoluminescence (PL) properties such as luminescence intensity and chromaticity of ZnS:Cu,Cl phosphors synthesized with different concentration of activator, Cu²⁺, was studied in this work.

2. Experimental

The powders of ZnS:Cu,Cl phosphor were synthesized by solid-liquid state reaction with two firing steps. The concentrations of Cu added at the 1st blending step were 0.03 and 0.13 mol% for blue and green ZnS phosphors, respectively, based on the

results of previous work [3]. Cu concentration added at the 2nd blending step differed in the range of 0.13 mol% and 0.66 mol% (relative to ZnS). A proper quantity of NaCl, MgCl₂·6H₂O and BaCl₂·2H₂O was mixed with ZnS host material and Cu²⁺ activator. These chloride materials are needed not only as flux but also as a co-activator. The mixed sample was heat-treated at 1100°C with an extra amount of sulfur, followed by washing and drying. After the resulting product was ground with Cu²⁺ precursor, it was treated at 750°C, washed, and dried.

The structure and morphology of phosphor particles and their PL properties were studied by means of X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and PL emission spectra. The phosphor samples were excited with UV light $\lambda_{exc} = 352$ nm. Emission spectra were recorded on Minolta CS-1000. Using the obtained phosphor powders, EL devices were fabricated by screen-printing method. PL and EL spectra of the phosphors with various copper concentrations were investigated.

3. Results and discussion

PL and EL spectra of ZnS:Cu,Cl blue-green phosphors with different amounts of copper activator added at the 2nd blending step were studied. Effect of the Cu concentration on the PL and EL intensities of the phosphors are shown in Fig. 1. ZnS:Cu,Cl blue phosphor with 0.26 mol% Cu addition at the 2nd blending step shows maximum EL (75 cd/m²) and PL (57 cd/m²) intensities. For the green phosphor, 0.4 mol% Cu addition resulted in maximum EL intensity of 119 cd/m².

Table 1 shows the luminescence data of the synthesized ZnS:Cu,Cl phosphor of different amounts

of copper added at the 2nd blending step. The appropriate amounts of the activator doping may reduce the migration of excitation energy to the emitting sites in the phosphors, so it is beneficial to the luminescence intensity.

Fig. 2 shows EL spectra with emission peaks (green: 503 nm, blue: 457 nm) and CIE color coordinates of green and blue phosphors at the maximum EL intensity.

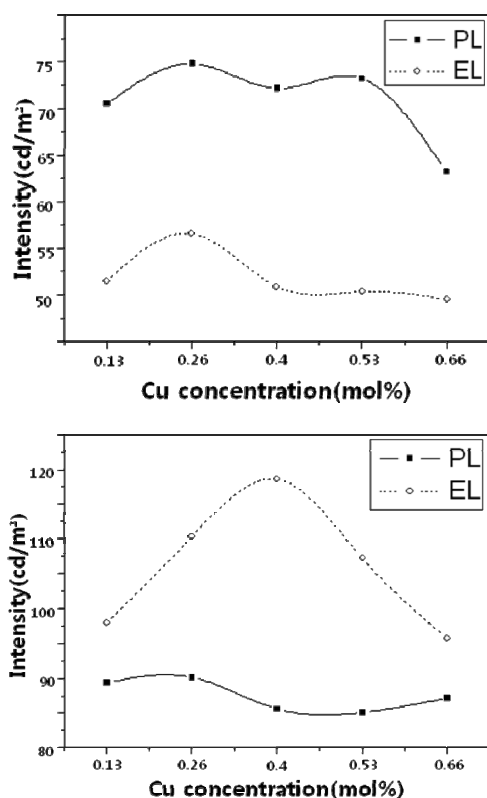


Fig. 1. EL and PL intensities of ZnS:Cu,Cl phosphors dependent on different Cu concentration: blue phosphors (up) and green phosphors (down).

TABLE 1. EL and PL intensities of ZnS:Cu,Cl phosphors with different Cu concentrations

Cu ²⁺ conc. (mol%)		0.13	0.26	0.4	0.53	0.66
Blue (cd/m ²)	PL	70.52	74.80	72.14	73.19	63.20
	EL	51.44	56.55	50.89	50.37	49.51
Green (cd/m ²)	PL	89.36	90.12	85.60	85.12	87.18
	EL	97.97	110.3	118.6	107.2	95.69

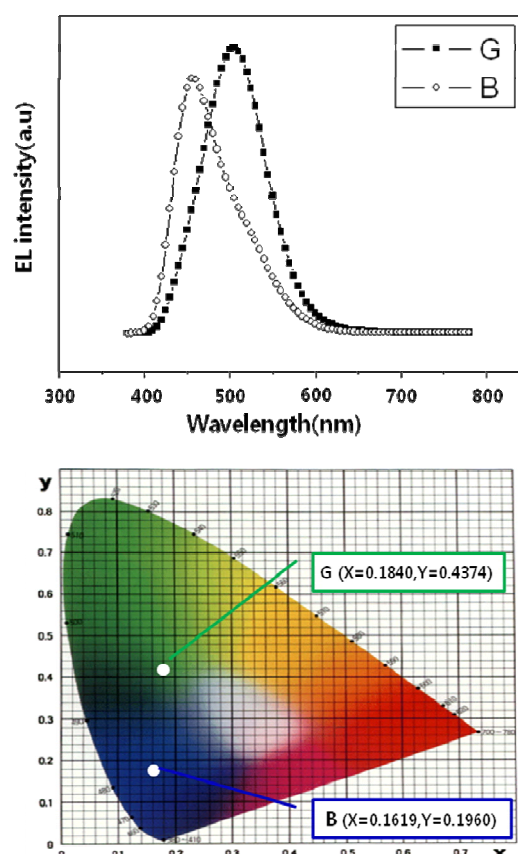


Fig. 2. EL spectra (up) at the maximum EL intensity and the CIE color coordinates (down) of green and blue phosphors.

4. Summary

Copper concentration added at the 2nd blending step of the synthesis process affected PL and EL intensities of ZnS:Cu,Cl phosphors. ZnS:Cu,Cl blue phosphor with 0.26 mol% Cu addition showed maximum EL (75 cd/m²) and PL (57 cd/m²) intensities, while 0.4 mol% Cu addition at the 2nd blending step gave maximum EL intensity of 119 cd/m² for the green phosphor.

5. References

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