

# Luminescent mechanisms of ZnS:Cu:Cl and ZnS:Cu:Al phosphors

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## Abstract

ZnS:Cu:Cl and ZnS:Cu:Al phosphors are fabricated by a flux fusion method to be used in cathode ray tube (CRT) monitors for green emission. The emission spectra of the phosphors depend on the Cu concentration. A series of luminescence measurements have been conducted, and several models are applied to explain the luminescent phenomenon of these phosphors. It is revealed that ZnS:Cu:Cl and the ZnS:Cu:Al phosphors exhibit green emission yet their luminescence mechanisms are different. The emission spectrum from the as-fabricated green phosphors is not a typical Gaussian distribution. The combination of blue and green band luminescence is attributed to the green-luminescence quenching derived from the interstitial Cu<sup>+</sup> ions. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Phosphor; Dopant; Luminescence mechanism; Emission spectra

## 1. Introduction

The current status of computer technology is toward the multimedia, and might gradually replace the conventional television and audio. Intel Inc. once announced the Pentium Central Processing Unit (CPU) with an extra and practical memory multiplex (MMX) system which could drastically improve the function of multimedia in the personal computer. To meet the requirement for multimedia applications, the colorful and diversified display is also required in the feature. So far, the CRT display is commonly used as a computer monitor. However, to meet the demands of high speed and true color images for multimedia displays, the properties of the phosphors employed on CRT have to be modified and improved.

The ZnS activated with Cu ions is the most efficient cathodoluminescence phosphors. There has been a steady market for CRT application, because of their good stability against chemical and physical treatments during CRT operation processes [1]. Furthermore, ZnS-based phosphors are extensively employed on other displays such as field emission display (FED) [2], plasma display panel (PDP) [3], and electron luminescence (EL) [4]. Particularly, blue and green emitting ZnS:Cu:Cl and ZnS:Cu:Al phosphors used in CRT are well-known phosphors. The direct evidence of high efficiency was reported using the infrared absorption spectrum induced by ultraviolet irradiation and using the characteristic decay curve [5]. The origin of the luminescence of the practical ZnS phosphors can be explained with the donor–acceptor recombination model.

Kuboniwa [6] et al. explained the saturation effects of the ZnS:Cu:Al phosphors under pulse excitation, and the mechanisms of concentration quenching of the

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green-Cu luminescence in ZnS:Cu:Al under cathode-ray excitation were discussed by Kawai et al. [7]. However, only a limited number of papers have been devoted to investigations on the detailed cathodoluminescence properties. Green and blue emission in Cu doped ZnS have been recognized as a result of electron-hole recombination of donor-acceptor pairs. Excess or less impurity-doped concentrations (copper) might reduce the luminescent efficiency and discolor the luminescence of the phosphors. In this study, the cathodoluminescence spectra, and brightness of the as-fabricated green and blue phosphors were measured. In addition, the dependence of the activator-doped concentration to the luminescent behavior and the optical-electrical properties of the phosphor were discussed.

## 2. Experimental procedure

Fluxes of eutectic NaCl–MgCl<sub>2</sub> composition are a feasible way to fabricate the ZnS:Cu:Cl phosphor. With appropriate Al<sup>3+</sup> ion addition into ZnS fired by the mixture of NaI and NaBr, ZnS:Cu:Al phosphors can be fabricated [8]. The blended powder was transferred to a crucible, followed by firing at 850°C for 1 h and then the furnace was cooled down to room temperature.

After the firing process was completed, the phosphors were washed by water and dilute HCl. In the washing process, the sintered rod of phosphors from the furnace was soaked in the hot water at 70°C with stirred action for 2 h, and then the water was removed after the powder was sedimented. The phosphors were again washed with a 2 wt.% dilute HCl solution. Finally, the phosphors were washed with hot water to remove the residual HCl solution.

A screen method was employed to print the as-fabricated phosphors on the indium tin oxide (ITO) glass. Polyvinyl alcohol (PVA) acted as a binder. Fixed amounts of PVA and as-fabricated phosphors were homogeneously mixed. The as-fabricated phosphors were printed with an average thickness of 0.1 mm. To examine the intrinsic luminescence of phosphors, samples were fired at 450°C for 1 h to decompose the binder.

Phosphor samples were placed in the chamber at a pressure under  $5 \times 10^{-8}$  torr and excited by an electron beam with controlled accelerating voltage and probe current density. The emission spectrum was detected by Fourier transfer analysis (Nicolet MX-1, Acton Research Corporation), and the detecting range was from 360 to 830 nm. The sample temperature was kept at room temperature. The relative intensity of cathodoluminescence spectrum of phosphor was recorded with an in situ recorder. The Commission International de l'Éclairage (CIE) color coordinates of phosphor luminescence were determined with a Chroma Meter (Minolta CS-100, Japan). A pulsed

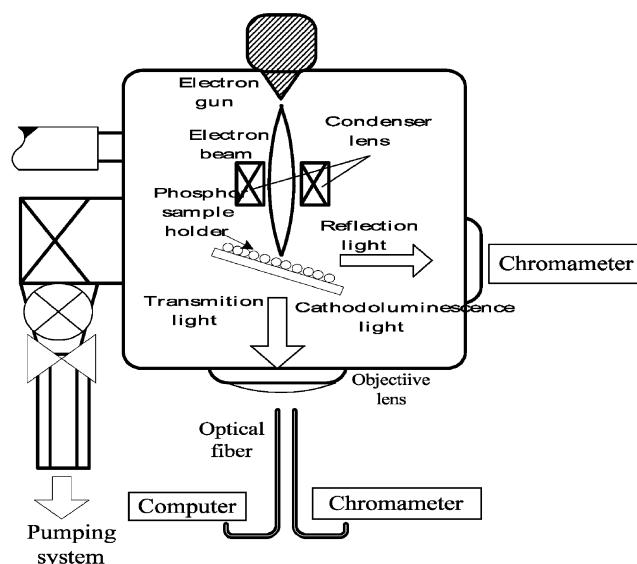


Fig. 1. Schematic diagram of the luminescence measurement system.

Nd:YAG laser (Spectra Physics DCR-2) was used as an exciting source for photo luminescence (PL) measurement. The repetition frequency was set at 10 Hz, and the mean duration of the exciting laser was approximately 10 ms. The wavelength of the exciting laser was 1046 nm, which was shifted to 355 nm after the laser passed through a harmonic generator (MODE HG-2, USA) to excite the sample. The photoluminescence was detected with a photo multiplier tube through a monochromator (Jobin-Yvon, USA) and a controller (Spectralnic, USA). The PL spectra were analyzed by Asyst-4 software in a personal computer. The detecting range of the wavelength was from 450 to 700 nm. The schematic diagram of the luminescence measurement system is shown in Fig. 1.

## 3. Results and discussion

ZnS:Cu:Cl with green luminescence was fabricated with fluxes of NaCl–MgCl<sub>2</sub>. Fig. 2 shows the emission spectrum of as-fabricated phosphors with various copper-doped concentrations. The wavelength of the green emission phosphor ranges from 475 to 525 nm. Powders with Cu-doped values of 120, 200, 400 ppm are close to the green emission. However, the emission of powders over 800 ppm turns to blue which ranges from 425 to 475 nm, while the phosphor less than 80 ppm exhibits emission from 450 to 550 nm. A further investigation indicates that the emission spectra of those phosphors are the combination of two main peaks, i.e. 450 and 500 nm.

The partition of both peak intensities closely depends on the Cu-doped concentration. The emission peak of 450 nm is significantly dominant in the spectrum of Cu-doped over 800 ppm, while the emission

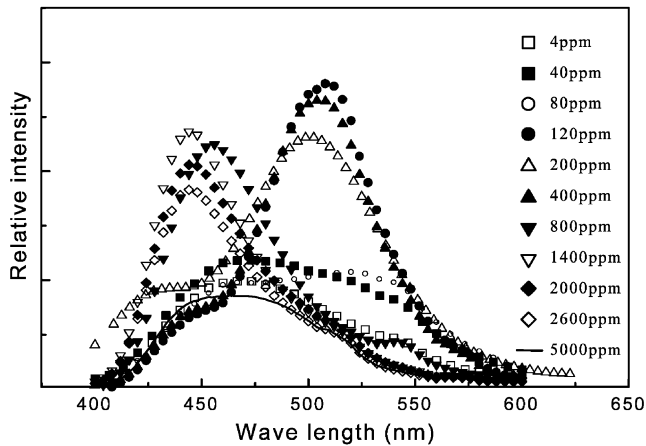


Fig. 2. The cathodoluminescence spectra of ZnS:Cu:Cl phosphors with various Cu-doped concentrations.

peak at 500 nm corresponds to the dominant peak for the spectrum of Cu-doped with 80, 120, 200, 400 ppm. However, both peak intensities emitted from 4, 40 and 80 ppm Cu-doped phosphors are equally weak and a broadening spectra is revealed.

The cathodoluminescence spectra are markedly dependent on copper concentrations. It is rather close to the intrinsic properties of pure ZnS powders with blue luminescence when copper concentrations are less than 80 ppm, while the blue emission occurs with copper concentrations greater than 400 ppm. The phosphors emit green luminescence with color coordinates of approximately  $x/y = 0.300:0.545$  in the range from 120 to 400 ppm of Cu-doped.

In a parallel study, the ZnS:Cu:Al phosphor was also fabricated with fluxes of NaI–NaBr, which shows a green luminescence. Fig. 3 represents the cathodoluminescent spectra of as-fabricated ZnS:Cu:Al phosphors with various copper-doped concentrations. The wavelength of green emission phosphor ranges from 475 to 525 nm. Powders with Cu-doped of 150, 200, 250 ppm exhibit the green emission with color coordinates of approximately  $x/y = 0.272:0.488$ . However, the emission of powders with Cu-doped above 300 ppm tends to the blue band, ranging from 425 to 475 nm. The emission peak of 450 nm is significantly dominant when the Cu-doped concentration is above 300 ppm, while the peak at 500 nm is predominated in the spectra of Cu-doped 150, 200, 250 ppm.

Von Gool [9] et al. employed a solid state model to explain the discolor mechanism in ZnS:Cu:Cl and ZnS:Cu:Al phosphors, and proposed that the luminescence color difference with copper activator concentrations is due to the ratio of the activator (Cu) and the coactivator (Al or Cl). The different wavelengths emitted are attributed to the copper activator concentration. It is summarized that the luminescence color difference with copper activator concentration is due to

the ratio of the activator to the coactivator. When the concentration of the Cu activator is equal to that ratio, the luminescence color should be green. If the activator concentration is higher than the coactivator concentration, the luminescence color will turn to blue. However, the blue emission occurs again if the activator concentration is much lower than the coactivator concentration. This implies that the self-luminescence properties of ZnS play a major role when low activators are doped.

In the study of Kawai et al. [7] the concentration dependence of the luminescence intensity is well explained by a model assuming complete pairing of the donor and acceptor. The concentration quenching of the green-Cu luminescence in ZnS:Cu:Al is derived if the interstitial  $\text{Cu}^+$  ions, due to excess Cu dopant, act as recombination centers for free carriers and provide the dominant non-radiative path for excitation energy when doped Cu is much greater than the Al ion.

The emission spectrum measured from as-fabricated green phosphors is not a typical Gaussian distribution, yet it consists of blue and green band luminescence. This can be well explained by the model provided by Kawai [7] in which the green-luminescence quenching is derived from the interstitial  $\text{Cu}^+$ . Hence, it is important to estimate the concentration of interstitial  $\text{Cu}^+$ . In general, interstitial  $\text{Cu}^+$  centers are formed during the fabrication process and their concentrations can be determined through thermodynamic equilibrium with other defects at the firing temperature. In fact, the results from the study of Kawai et al. could be employed to estimate the concentration of interstitial  $\text{Cu}^+$ , only if the Cu ion with a positive charge can be identified in the as-fabricated ZnS:Cu:Al and ZnS:Cu:Cl phosphors.

Electron paramagnetic resonance (EPR) spectra are routinely obtained from paramagnetic transition ions in crystals. The peaks would be observed in EPR spec-

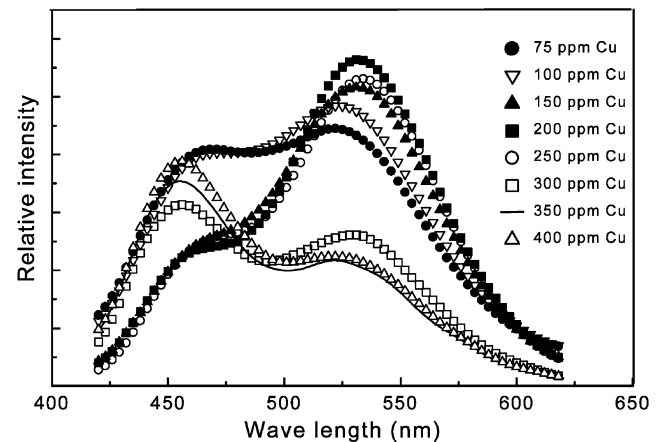


Fig. 3. The cathodoluminescence spectra of ZnS:Cu:Al phosphors with various Cu-doped concentrations.

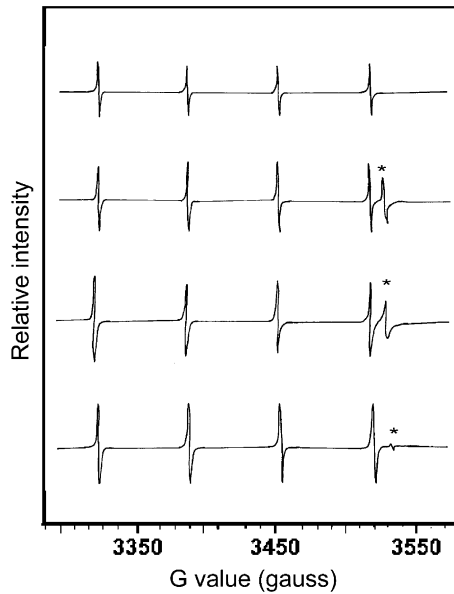


Fig. 4. EPR spectra of (a) 150 ppm Cu-doped ZnS:Cu:Al phosphor (b) 5000 ppm Cu-doped ZnS:Cu:Cl phosphor (c) 400 ppm Cu-doped ZnS:Cu:Cl phosphor (d) pure ZnS fired at 800°C.

trum when the transition metal ions possess an odd number of electrons. Fig. 4d shows the EPR spectrum of the pure ZnS powders fired with NaCl at 800°C. The separated peaks with regular space indicate that ZnS powder is completely crystallized. However, a weak peak appears where the mark \* is indicated (G value at approx. 3525) in Fig. 4d. The EPR spectra of ZnS:Cu:Cl phosphors with 5000 and 400 ppm are shown in Fig. 4b,c, respectively, which are almost identical to that of the pure ZnS powder fired with NaCl at 800°C (Fig. 4d) except the intensity of the \* marked peak is higher than that in Fig. 4d. EPR spectrum of ZnS:Cu:Al with 150 ppm Cu-doped is shown in Fig. 4a. The peaks separated by regular space are observed, however, the \* marked peak disappears.

The weak marked peak observed in Fig. 4d is attributed to two factors. First, it might be the residual flux containing Cl ion on the surface of phosphor. Secondly, the Cl ion is difficult to diffuse to the ZnS lattice due to the charge incompatibility of sulfur and chloride. Namely, a trace amount of Cl ions can replace the sulfur site in the ZnS lattice. Hence, the weak marked peak is observed and it can be recognized as the chloride ion in the EPR spectrum. The charge incompatibility will be vanished when the activator (Cu ion with one positive charge) is employed. The Zn and S sites in ZnS lattice can easily be replaced by Cu and Cl, respectively, at the same time, since the Cu ion with a positive charge is compatible with the chloride with a negative charge. The activation energy of diffusion for Cu and Cl ions to ZnS lattice is reduced, thus the intensity of the marked peak intensity is enhanced (Fig. 4b,c). It can be reconfirmed that the extra marked peak

is the paramagnetic transition for Cl ion, since there is no extra peak observed in the EPR spectra of ZnS:Cu:Al as shown in Fig. 4a. The electron configuration for one positive charge copper is  $4s^0 3d^{10}$ , so no EPR signal is revealed due to the even number of electron observed in the  $d$  orbital. It is argued that the Zn site is replaced by the Cu ion with a positive charge in ZnS:Cu:Al, since no other paramagnetic transition is observed in the EPR spectrum.

The results of EPR spectra illustrate that the Cu ion with a positive charge might diffuse to the ZnS lattice. An estimation of the concentration of interstitial  $\text{Cu}^+$  with the aid of Kawai study is approximately  $1 \times 10^{-10}$  g/atom per mole. Thus, the cathodoluminescence spectrum tends to the blue band due to interstitial  $\text{Cu}^+$ , which acts as the recombination center for free carriers and provides the non-radiative path for excitation energy.

The cathodoluminescence brightness of the phosphor is a function of both applied voltages ( $V$ ) and currents ( $I$ ) due to the basic principle in elementary electronics. The brightness and brightness efficiency of the ZnS:Cu:Cl phosphor of 120 ppm Cu-doped is plotted as function of the substrate current as shown in Fig. 5, which indicates that the brightness is a linear function of substrate current. However, no saturation behavior is observed when the substrate current exceeds 2000 nA in the as-fabricated ZnS-base phosphor. It is also indicated that the luminescence efficiency is reduced if more electron beams are applied on the as-fabricated phosphors.

The brightness and brightness efficiency of 200 ppm Cu-doped ZnS:Cu:Al phosphors as a function of substrate currents are illustrated in Fig. 6. The saturation behavior is observed when the substrate current exceeds 2000 nA in the as-fabricated ZnS-base phosphors. It appears that the luminescence efficiency is reduced as the substrate current is increased. To study

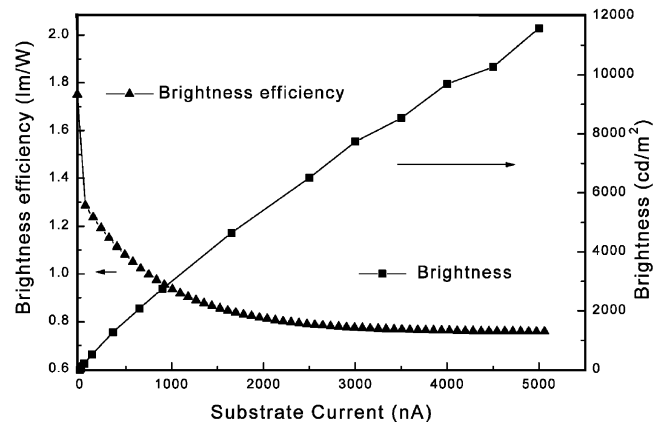


Fig. 5. The brightness and brightness efficiency of 120 ppm Cu-doped ZnS:Cu:Cl phosphors as a function of substrate current under an applied voltage of 10 kV.

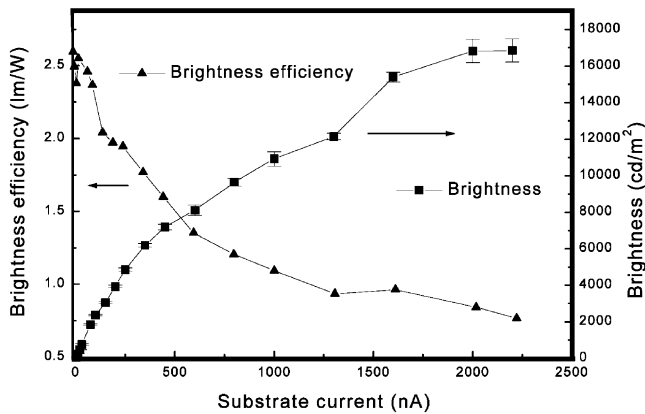


Fig. 6. The brightness and brightness efficiency of the 200 ppm Cu-doped ZnS:Cu:Al phosphor as a function of substrate current under an applied voltage of 10 kV.

the green emission efficiency, the green phosphors with various Cu-doped concentrations were employed to make a comparison. Since the Cu 150 ppm doped ZnS:Cu:Al phosphor did not exhibit purely green luminescence as shown in Fig. 3, the comparison was made between the Cu 200 ppm ZnS:Cu:Al green phosphor and 120 ppm ZnS:Cu:Cl green phosphor. Only between the identical green emission phosphors that the comparison of brightness efficiency makes sense. Observation of Figs. 5 and 6 indicates that the brightness efficiency of 200 ppm ZnS:Cu:Al green phosphor is higher than that of the 120 ppm ZnS:Cu:Cl phosphor.

A preliminary measurement reveals that the brightness is independent of the applied current in the ZnS:Cu:Al phosphor when the substrate current is above 2000 nA due to the saturation behavior. The saturation behaviors take place in the ZnS:Cu:Al phosphor (Fig. 6), however, it is not observed in the ZnS:Cu:Cl phosphor even when the substrate current is increased to 2000 nA (Fig. 5). This fact leads to a conclusion that the saturation behavior takes place due to a limited number of luminescent centers. At high excitation densities, an excited donor–acceptor pair can easily find a filled donor or acceptor in the near neighborhood and the saturation is induced when the donor–acceptor recombination reaches the steady state. Both atoms of Al and Cu are positively charged, therefore the solubility of the Al ion in the ZnS lattice is much lower than that of Cl in ZnS. The number of luminescent centers is limited in the ZnS:Cu:Al phosphor, while that of ZnS:Cu:Cl phosphor is so large that no saturation behavior is observed. This implies that no saturation behavior is observed since the applied current density is not sufficient to completely promote all the donor–acceptor pairs to an elevated energy level.

The ZnS:Cu:Al phosphor with a limited number of luminescent centers is easily excited by applying a rather low current. Conversely, the ZnS:Cu:Cl phos-

phor with a large number of luminescent centers are not able to excite efficiently since the large number of the luminescent centers might disperse the energy when the applied current is weak. The substrate current dependence of luminescence efficiency and the saturation behavior of both phosphors can be clearly demonstrated by the fact that saturation is derived from the limited luminescent centers.

According to the solid state kinetics, the population of luminescent ions in the excited state,  $Ne(t)$  after an excitation pulse can be expressed as

$$Ne(t) = Ne(0) \times \exp(-t/\tau R) \quad (1)$$

where  $Ne(0)$  is the initial population;  $\tau R$  is the decay time, indicating that the population in the excited state has decreased to  $1/e$  after time  $\tau R$ . The decay intensities of luminescence emitted from the as-fabricated phosphors as a function of time are illustrated in Fig. 7. The decay time for the ZnS:Cu:Cl and ZnS:Cu:Al phosphor are evaluated to be 0.05 and 0.035 s, respectively. The commercial Kasei-Optonic phosphor is also shown in Fig. 7a for comparison. It seems that the luminescence is decayed as the measuring time increases for all the phosphors. However, the decay curves

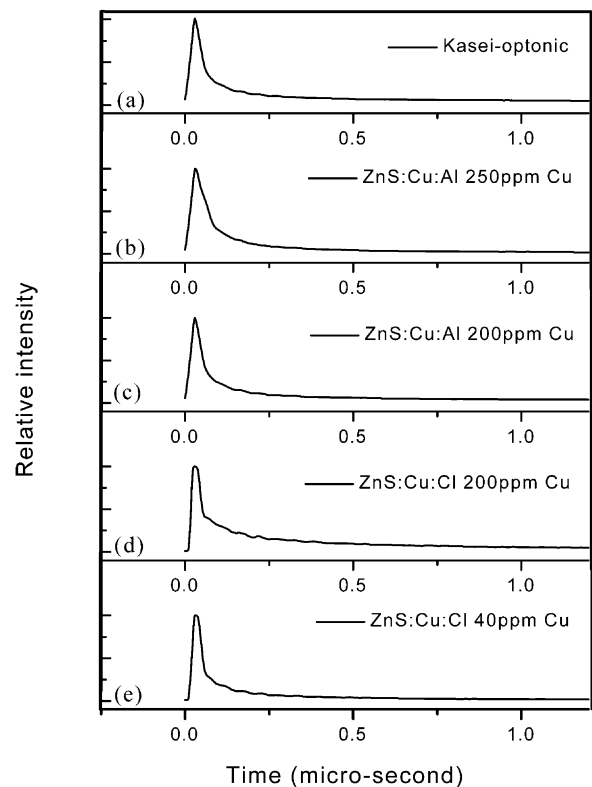


Fig. 7. The decay intensities of luminescence emitted from the as-fabricated phosphors as a function of time (a) Kasei-optonic commercial phosphors (b) 250 ppm Cu-doped ZnS:Cu:Al (c) 200 ppm Cu-doped ZnS:Cu:Al (d) 120 ppm Cu-doped ZnS:Cu:Cl (e) 40 ppm Cu-doped ZnS:Cu:Cl.

of ZnS:Cu:Cl phosphors with 40 and 200 ppm doped Cu in Fig. 7e,d are a little different from ZnS:Cu:Al phosphors with 200, 250 ppm doped Cu in Fig. 7c,b. It appears that the curve of the ZnS:Cu:Al peak is very sharp, while that of ZnS:Cu:Cl is rather broad. It is concluded that the decay time of phosphors with the Cu co-dopant are relatively longer, since the emission of Cl co-doped phosphors can last for longer periods in its highest brightness.

#### 4. Conclusions

ZnS-based green phosphors have been successfully fabricated with the flux of eutectic NaCl–MgCl<sub>2</sub> and NaBr–NaI. A series of luminescence measurements are carried out under various applied voltages and currents. The spectra measured from as-fabricated green phosphors, including both ZnS:Cu:Cl and ZnS:Cu:Al, are not a normal Gaussian distribution. The Cu dopant concentration plays a major role in the luminescence behavior and the green-luminescence quenching might be derived from the interstitial Cu<sup>+</sup> that can be identified by EPR analysis. The concentration of interstitial Cu<sup>+</sup> in the as-fabricated phosphor can be estimated at approximately  $1 \times 10^{-10}$  g/atom per mole. Various optoelectronic behaviors and decay curves are observed in the Al and Cl co-dopant phosphors. The brightness efficiency of ZnS:Cu:Al is higher than that of the ZnS:Cu:Cl phosphor at low substrate current, due to a limited number of luminescent cen-

ters in the phosphors. The substrate current dependence of luminescence efficiency and saturation behavior of both phosphors can be elucidated by the fact that saturation is derived from the limited luminescent centers.

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