# The effect of ZnS content on the luminescence and electrical properties of ZnO : Zn phosphor

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Zinc oxide phosphors (ZnO : Zn) were prepared by solid state sintering of ZnO powders with ZnS and screen printed onto ITO-coated glass substrate. The effect of ZnS content and sintering temperature on the cathodoluminescence brightness, efficiency and electrical properties of ZnO : Zn were studied. Samples with 5 wt % ZnS and sintered at 1100 °C exhibit the highest brightness and efficiency among all the compositions studied. The brightness of phosphors increases linearly as the accelerating voltage $V$ and/or beam current $I$ increases. While the efficiency decreases initially and then reaches a constant value as $V$ and/or $I$ increases. Both the conductivity $\sigma$ and carrier concentration $n$ of the phosphor increase with the increase of ZnS content in the starting composition. Results of Hall measurement suggest that the ZnO : Zn phosphor is an $n$-type conductor with an electron mobility of around 175 cm$^2$/V-s. For specimen with 5 wt % ZnS, both $\sigma$ and $n$ increases initially with the increase of sintering temperature $T$, and reaches a constant value at $T \geq 1000$ °C. The unreacted ZnS found in samples sintered at $T < 1000$ °C explains the temperature dependence of $\sigma$ and $n$.
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## Introduction

Phosphor is defined as material that emits photons with high luminescence efficiency. The cathodoluminescent phosphors convert electron energy into visible light and are used in the display devices as the screen material. Zinc oxide phosphors have recently regained much interest because of potential use in new low voltage fluorescence applications, such as the field emission display technology [1, 2]. The practical use of ZnO prefers the powder form (or sintered layers of powder) to the single crystal form. There are many different conditions and methods of preparing luminescent ZnO powders [3, 4]. Pure ZnO emits a narrow luminescence band in the blue-violet spectral region [5]. However, upon incorporation of various dopants, a variety of emissions ranging from blue to orange spectral region occur [3].

This is a continuing research. In the previous study, ZnO doped with Zn (ZnO : Zn) phosphors were prepared by solid state sintering of ZnO powders with various amount of zinc sulphide (ZnS) at various temperatures in nitrogen atmosphere. Structural characterization carried out by X-ray diffraction analysis suggests that the Zn atoms from the decomposition of ZnS diffuse to occupy the oxygen vacancies in the host lattice. The cathodoluminescent (CL) spectra indicate a green emission band and the CIE color loci suggest that ZnO : Zn phosphor with 5 wt % ZnS can be used as a green primary for color picture tubes [6].

In addition to color, the brightness and conductivity are also critical issues to evaluate the phosphor. In the present work, the effects of ZnS content on the brightness efficiency, and electrical properties of ZnO : Zn phosphors are explored.

## Experimental procedures

Phosphor samples were prepared by solid state sintering of mixtures of ZnO and ZnS powders in N$_2$ atmosphere. Details of sample preparation, powder analysis and luminescence measurement were reported elsewhere [6].

The film thickness was measured with a stylus surface profile. The sheet resistance of the samples was measured with a four point probe and the resistivity of the film was calculated. Carrier concentration and Hall mobility were obtained from Hall effect measurement by the van der Pauw technique.

## Results and discussion

Zinc-activated zinc oxide ZnO : Zn films have been prepared by screen printing of solid state sintered $(100 - x)$ wt % ZnO $- x$ wt % ZnS ($x$ : 0–15) onto ITO-coated glass substrates. It was observed that the
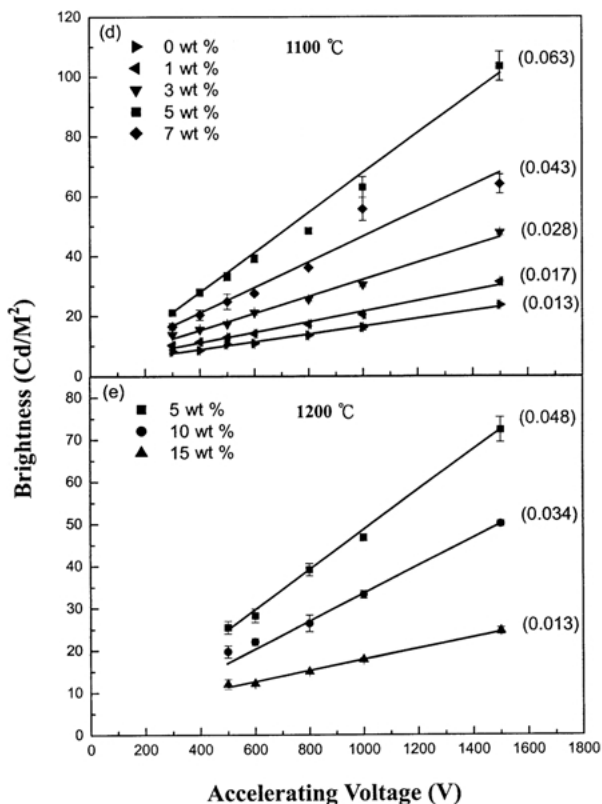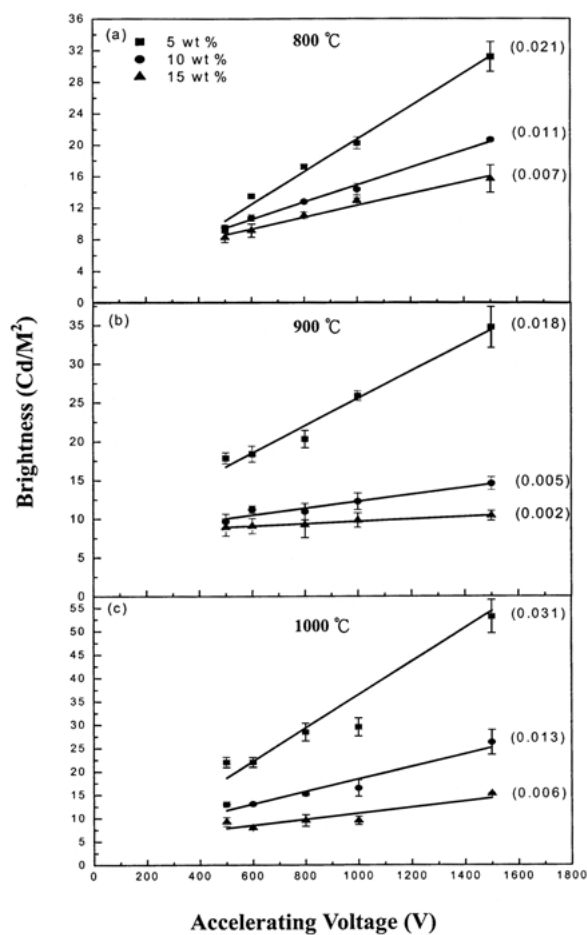
Figure 1 Brightness as a function of accelerating voltage of phosphors with various wt % ZnS sintered at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, and (e) 1200 °C for 1 h. Beam current: 1 μA. Data in the parentheses are the slopes of the plots.
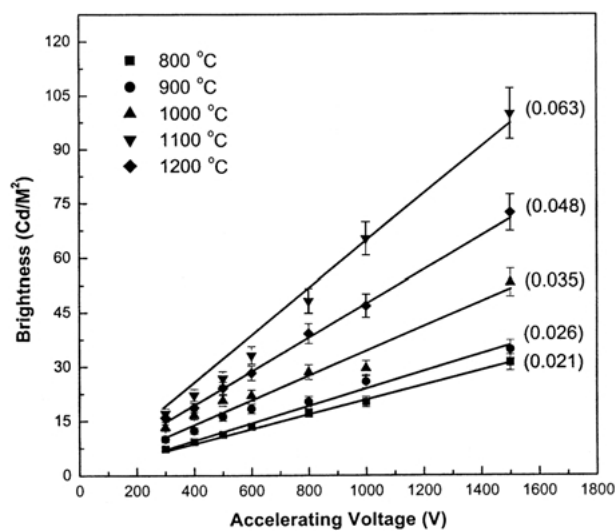


Figure 2 Brightness as a function of accelerating voltage of phosphor with 5 wt% ZnS sintered at various temperatures for 1 h. Beam current: 1 μA. Data in the parentheses are the slopes of the plots.

interstitial, the excess Zn atom occupied the oxygen vacancy of the host lattice. The CL spectra revealed the strongest emissions ranged from 494 to 508 nm, which is close to the green band of ZnO phosphor (510 nm). Both the deconvoluted CL spectra and the CIE measurement suggested that samples with 5 wt % ZnS exhibited a more ''green'' color than other specimens did [6].

In addition to the CIE color coordination, the brightness is also a critical issue to evaluate the phosphor. Figs 1 and 2 give the brightness as a function of accelerating voltage of ZnO : Zn phosphors as a function of ZnS content and sintering temperature. The cathodoluminescence brightness of phosphor increases linearly as the energy of the irradiated electrons increases, especially for samples with 5 wt % ZnS sintered at 1100 °C, as exhibited in Fig. 2. The higher the applied voltage to the phosphor, the more amounts of luminescence are excited to emit the light. The depth of penetration of beam electrons into a particular specimen is determined by the energy of the beam electron. The higher the energy the greater the penetration. The number of inelastic events increase as the energy of the electron increases, resulting in less deflection of the electron beam on scattering and deeper penetration of the electrons into the phosphor sample. At higher accelerating voltage, the electrons can penetrate to greater depths since they retain a larger fraction of initial energy after traveling a fixed distance. Hence, more activator centers of phosphor are excited to emission by these high energy electrons, as shown schematically in Fig. 3 (a). However, the color of luminescence light does not shift with the increase of the applied voltage. There is no appreciable differences among spectra measured at different voltages.

The slopes of the brightness versus accelerating voltage (B-V) curves are also indicated in Figs 1 and 2. Specimen with 5 wt % ZnS, sintered at 1100 °C has the largest slope of the B-V curve, that is, the brightness of the 5 wt % ZnS − 1100 °C sintered specimen is most sensitive to the variation of accelerating voltage. Previous work reported that there were unreacted ZnS for compositions with a ZnS content of larger than
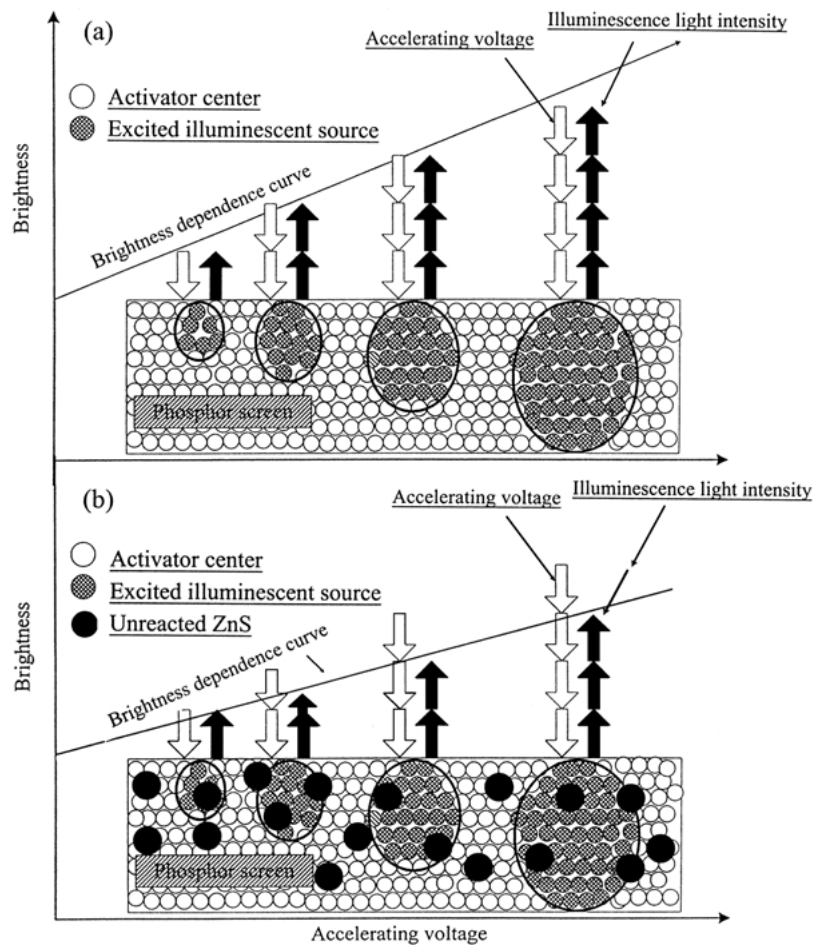
lattice parameter $a$ and $c$ of the hexagonal ZnO : Zn decreased slightly with the increase of ZnS content [6]. This suggested that, instead of remaining as an

*Figure 3* Schematic diagram of brightness as a function of accelerating voltage for phosphor (a) without and (b) with unreacted ZnS.

5 wt % and/or fired at a temperature lower than $1100\,°C$ [6]. The existence of the unreacted ZnS may be one of the reasons which reduces the slope of the B-V curve. In the presence of ZnS, the concentration of activator centers are diluted and the numbers of excited illuminescent sources decrease and, consequently, the slope of the B-V plot decreases, as shown schematically in Fig. 3(b).

The absolute radiative efficiency of a phosphor is the energy given off in the form of radiation divided by the energy incident upon the phosphor. Both the brightness and the color coordinate of phosphor were measured with a colorimeter. The brightness efficiency of the phosphors can be calculated from the measured brightness:

$$\eta = B \times A \times \pi / I \times V \qquad (1)$$

where $\eta$ represents the efficiency with a unit of lm/W, $B$ is the brightness in $Cd/m^2$, $A$ is the luminescent area $(m^2)$, $I$ is the substrate current, and $V$ is the electron accelerating voltage. The brightness efficiency calculated from Equation 1 is plotted as a function of accelerating voltage for samples with various ZnS contents and sintering temperatures as illustrated in Figs 4 and 5, respectively. Samples with 5 wt % ZnS sintered at $1100\,°C$ have the highest efficiency among various specimens studied, and the efficiency is around 0.4 in the voltage range of measurement, i.e., 300 V to 1500 V. The efficiency of the specimens decreases with the increase of accelerating voltage. Figs 1 and 2 indicate that the brightness is linearly proportional to the accelerating voltage. Hence one would expect that the
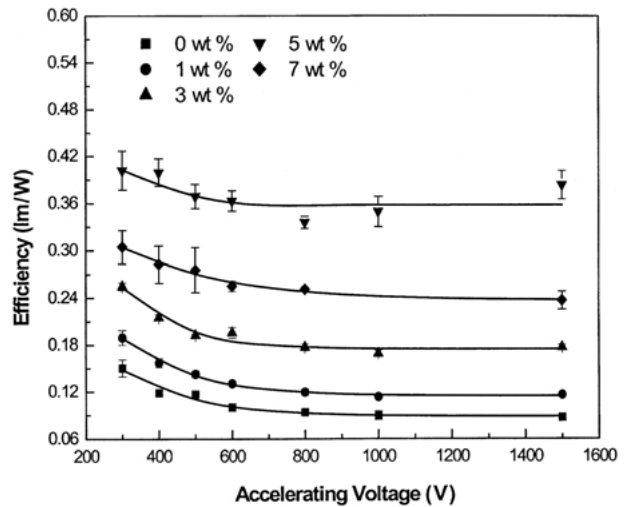


*Figure 4* Efficiency as a function of accelerating voltage of phosphors with various wt % ZnS. Samples sintered at $1100\,°C$ for 1 h. Beam current: 1 μA.

efficiency be independent of the applied voltage on the basis of Equation 1. It is not clear at this moment why the decrease of efficiency with the increase of voltage is observed for some specimens, as exhibited in Fig. 4. The luminescence efficiency determines the basic make-up of a phosphor in the sense that it defines the resolution and contrast as well as luminescence. Hence, an optimization of the process to obtain a maximum efficiency is essential. Fig. 6 gives the brightness as a function of beam current of phosphor with 5 wt % ZnS sintered at various temperatures. The cathodoluminescence bright-
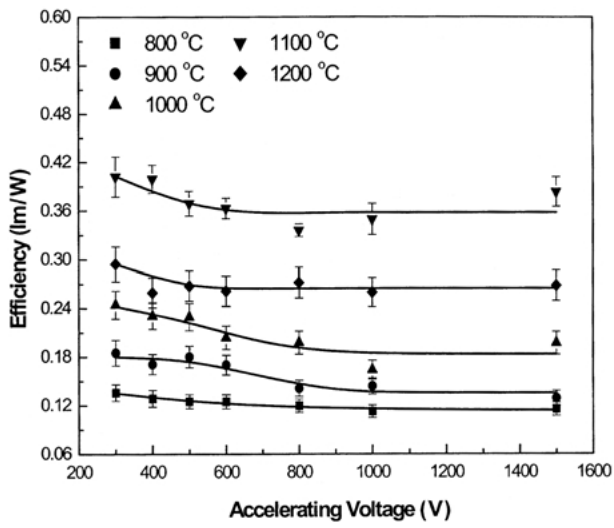
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*Figure 5* Efficiency as a function of beam current of phosphor with 5 wt % ZnS sintered at various temperatures for 1 h. Beam current 1 μA.
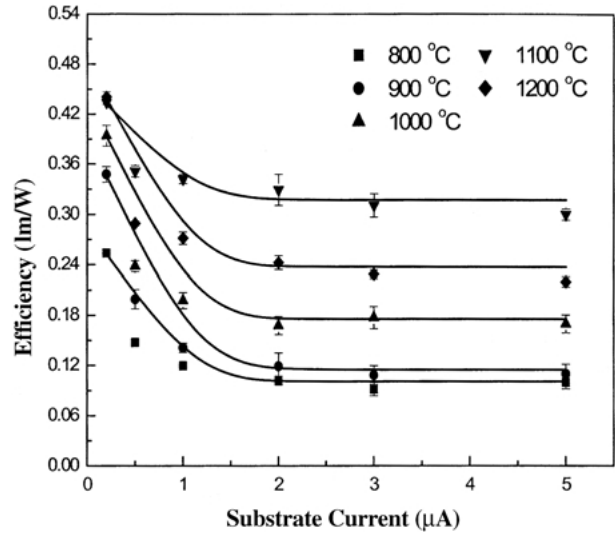


*Figure 7* Efficiency as a function of beam current of phosphor with 5 wt % ZnS sintered at various temperature for 1 h. Accelerating voltage: 800 V.
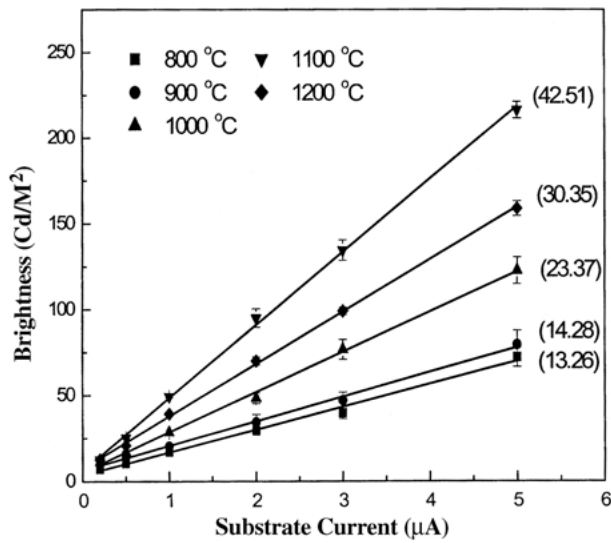


*Figure 6* Brightness as a function of beam current of phosphor with 5 wt % ZnS sintered at various temperatures for 1 h. Accelerating voltage: 800 V. Data in the parentheses are the slopes of the plots.
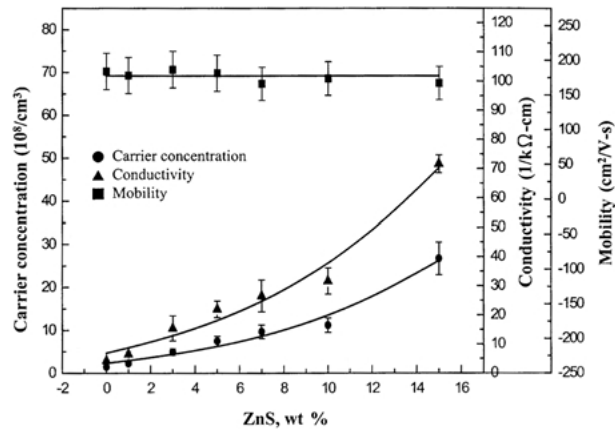


*Figure 8* Carrier concentration, mobility, and conductivity as a function of wt % ZnS for ZnO : Zn phosphors sintered at 1100 °C for 1 h.

ness of phosphor increases linearly as the beam current increases, especially for the specimen sintered at 1100 °C. The efficiency as a function of beam current for phosphor with 5 wt % ZnS sintered at various temperatures is shown in Fig. 7. The efficiency decreases initially with the increase of beam current and reaches a constant. A sudden drop of efficiency is observed at a beam current of around 0.5 μA.

Besides efficiency, electrical conductivity is also a critical issue to evaluate the phosphor. Fig. 8 gives the conductivity, carrier concentration and Hall mobility of ZnO : Zn phosphors as a function of wt % ZnS. Both the conductivity and carrier concentration increase as the amount of ZnS in the starting composition increases while a constant mobility ($\sim 175\,\mathrm{cm^2/V\text{-}s}$) is obtained for all samples. Pure ZnO has a conductivity of $10^{-4}\,\Omega$-cm. The room temperature mobility for holes and electrons in ZnO are 180 and $200\,\mathrm{cm^2/V\text{-}s}$, respectively [5]. The electrical conductivity of zinc oxide is provided by a high concentration of oxygen vacancies and/or interstitial cations, which can form

shallow donors. On the basis of Hall measurement the ZnO : Zn phosphor in this study is an *n*-type semiconductor with an electron mobility of $\sim 175\,\mathrm{cm^2/V\text{-}s}$ as compared to a mobility of $200\,\mathrm{cm^2/V\text{-}s}$ for that of pure ZnO. The decrease in mobility is attributed to defect scattering. The conductivity of ZnO phosphors is higher than that of pure ZnO as free charge carriers are created according to the following reaction [7]:

$$\mathrm{ZnO} + x\,\mathrm{ZnS} \rightarrow \mathrm{Zn(O_{1-x} \cdot x\,V_0)} + x\,\mathrm{SO} \\ + x\,\mathrm{Zn_1^{2+}} + 2x\,e' \tag{2}$$
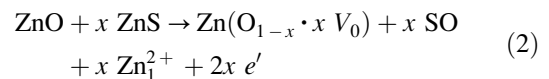
The defect formation behavior is one where the sulfide decomposes, reduces the host lattice and forms an oxygen vacancy plus two free electrons.

The carrier concentration *n* and conductivity σ increases initially as temperature increases and reaches a constant value at $T \geq 1000\,^\circ\mathrm{C}$, as exhibited in Fig. 9. No apparent dependence of mobility on the firing temperature is observed. Both *n* and σ increase with the decomposition/incorporation of ZnS into ZnO as
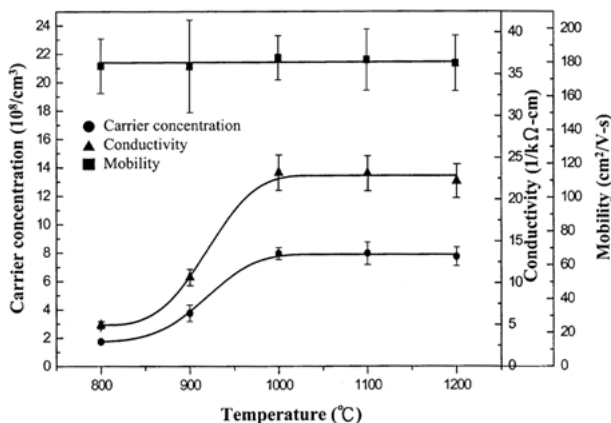
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*Figure 9* Carrier concentration, mobility, and conductivity of ZnO : Zn phosphors with 5 wt % ZnS as a function of sintering temperature.

manifested in Fig. 8 and Equation 2. Samples with a fixed amount of ZnS should have a constant $n$ and $\sigma$. In previous work, unreacted ZnS was found for 5 wt % ZnS specimen sintered at 800 °C or below [6]. Hence, specimens fired at lower temperatures have smaller $n$ and $\sigma$ as fewer ZnS are incorporated into ZnO. While for samples fired at $T \geq 1000$ °C, all the ZnS are reacted so that both $n$ and $\sigma$ reach a constant value.

## 4. Conclusions
In this work, the effect of ZnS contents and sintering temperature on the efficiency and electrical properties of sintered (ZnO + ZnS) phosphors are investigated.

The cathodoluminescence brightness of phosphors is linearly dependent on both the accelerating voltage and the beam current. A decrease of efficiency with the increase of the accelerating voltage and beam current is observed. Samples with 5 wt % ZnS sintered at 1100 °C have both the highest brightness and efficiency among various specimens studied. Combining the brightness and efficiency data with CL spectra and CIE color loci

obtained in previous work [6], one can conclude that ZnO : Zn phosphor with 5 wt % ZnS sintered at 1100 °C can be used as a green primary for color picture tubes.

The conductivity and carrier concentration of phosphors increase as the amount of ZnS in the starting composition increases. The ZnO phosphors are *n*-type conductors with an electron mobility of about $175 \, \text{cm}^2/\text{V-s}$ as compared to a mobility of $200 \, \text{cm}^2/\text{V-s}$ for pure ZnO. The reduced mobility is attributed to the scattering of defects formed upon decomposition of ZnS. No apparent dependence of mobility on the ZnS content or the firing temperature is observed.

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