

The effect of In_2O_3 conductive coating on the luminescence and zeta potential of ZnS:Cu, Al phosphors

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Abstract

Phosphors used in CRTs have been coated with In_2O_3 conductive layer derived from the hydrolysis of indium chloride. It was found that brightness of the phosphors rises initially with the amount of InCl_3 , reaches a maximum at 10 wt.% InCl_3 and then decreases when more InCl_3 was added. With 10 wt.% InCl_3 coating, the brightness of ZnS:Cu, Al phosphor increases by 24% at 800 V and 1 μA while very little changes were observed in the luminescent emission peak and CIE color loci. The luminescence decay times increase with the increase of the conductive coating. However, they are shorter than 0.7 μs for samples with the amount of coating ranging from 0 to 20 wt.% InCl_3 and are suitable for display applications. Conductive coating affects the surface chemistry of the phosphor particles, enhances the zeta potential of ZnS:Cu, Al in IPA solution, and, consequently, increases the electrophoretic deposition rate of the phosphors onto substrate. The zeta potential of 10 wt.% InCl_3 coated ZnS:Cu, Al in isopropyl alcohol solution is 32 mV as compared to 1.2 mV of that of the uncoated ZnS:Cu, Al. Besides, the electrophoretic deposition rate of the 10 wt.% InCl_3 coated ZnS:Cu, Al (0.23 mg/s) is larger than that of the uncoated phosphor (0.17 mg/s).

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1. Introduction

Field emission display (FED) has been actively investigated for the development of the full color flat panel display in recent years. In the development of FED, it is important to develop phosphors with sufficient luminant efficiency at low voltages (<1 kV). In the design of phosphors for low voltage operations, there are three important factors to be considered: (1) the morphology and size [1]; (2) the stoichiometry and composition [2–6]; and (3) the surface of the phosphors [7–10]. As phosphors used in CRTs show high luminescence and efficiency, it is desired to use them for FEDs. However, the phosphors used in CRTs are difficult to be used at low voltages due to (1) the presence

of the non-emissive layer on the surface of the phosphors and/or the charging-up on the surface of the phosphors with high resistivities.

This is a continuing research. In the previous study, p22 phosphors, including ZnS:Cu, Al (green), ZnS:Ag (blue) and Y_2O_3 :Eu (red) were coated with In_2O_3 conductive layers derived from the hydrolysis of indium chloride [10]. It was found that the conductive coating retarded/eliminated charging-up on the phosphor surface and improved the cathodoluminescent (CL) brightness. However, the non-emissive conductive coating also degraded the CL brightness when it was too thick. A 20% increase of brightness at 500 V and 1 μA was obtained for phosphors with a 10 wt.% InCl coating [10].

In addition to brightness, CL spectrum, color and decay time are also critical issues to evaluate the phosphor. Besides, most deposition processes for phosphors require the preparation of a suspension of particles. The effect of

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coating on the surface chemistry of the phosphor particles affects their dispersibility in solution and adhesion to the substrate. In the present work, the effects of In_2O_3 coating on the CL spectrum, CIE color, decay time and zeta potential of phosphors are explored.

2. Experimental procedures

Phosphors used in this study were p22 series purchased from Kasei Optonix, Ltd. In_2O_3 thin layer was coated on the surface of the phosphor by hydrolysis of indium chloride. Indium chloride, InCl_3 , was dissolved in deionized water and then phosphor was added to the solution. The concentration of InCl_3 varies from 0 to 20 wt.%. The solution was stirred for 10 min and then filtered. The slurry was dried at 120 °C for 4 h and the filtrate was analyzed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES ICPA 9000, Jarrel-Ash, USA) for the concentration of In in the solution.

The as-received and coated powders were examined with a scanning electron microscope (SEM, Leica S440, Japan) to investigate the particle size, shape and surface morphology. The phosphor powder was further examined with a Laser particles sizer (Analysette 22, Fritsch) to evaluate the particle size distribution. The phase and crystal structure of the as-fabricated phosphor were identified with an X-ray diffractometer (Rigaku Ru-200, Japan) with a wavelength of $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$).

Screen printing method was employed to deposit the phosphor powders onto ITO glass. Paste consisting of polyvinyl alcohol (PVA, as a binder) and phosphor was printed onto ITO glass and baked at 450 °C for 1 h. The film thickness was about 100 μm .

The cathodoluminescence (CL) spectra were measured with an electron gun in a vacuum chamber. The chamber was pumped down to 5×10^{-2} Torr with a mechanical pump and to 5×10^{-7} Torr with a turbo pump. Samples were excited by electron beam with accelerating voltage of 1 kV and electron current of 10 μA . The cathodoluminescent emission light, passes through a lens to focus on an optical fiber, was converted to an electrical signal by Fourier transform analysis instruments. The cathodoluminescence intensity was measured with a CL-SEM system (Nicolet MX-1, Acton Research Corporation) with a voltage from 0 to 20 kV. The wavelength detection range was 300–700 nm. The accuracy of the measurement is estimated to be ± 3 nm.

The CIE color coordinates of phosphor were measured with a colorimeter (Minolta CS-100, Japan). The excitation source used in the CIE measurement was the electron gun employed in the CL measurement.

In the decay time measurement, a pulsed Nd:YAG laser (spectra physics DCR-2) was used as the excitation source. The wavelength of the exciting source was converted to 355 nm before exciting the sample. The photoluminescence was detected with a photon multiplier tube through a monochromator. The electrical signal was received by a photon counter through an amplifier. The photoluminescence spectra were analyzed by Asyst-4 software with a personal computer through the IEEE GPIB card. The wavelength detection range was 450–700 nm. An oscilloscope was connected to the measurement system to observe the decay of the photoluminescent intensity.

In the zeta potential measurement, the electrophoretic deposition bath of interest is a suspension of phosphor particles in isopropyl alcohol (IPA) which contains dissolved $\text{Mg}(\text{NO}_3)_2$. The IPA solution is composed of 0.01 g $\text{Mg}(\text{NO}_3)_2$, 1 ml $\text{H}_2\text{O}_{(l)}$, and 100 ml IPA.

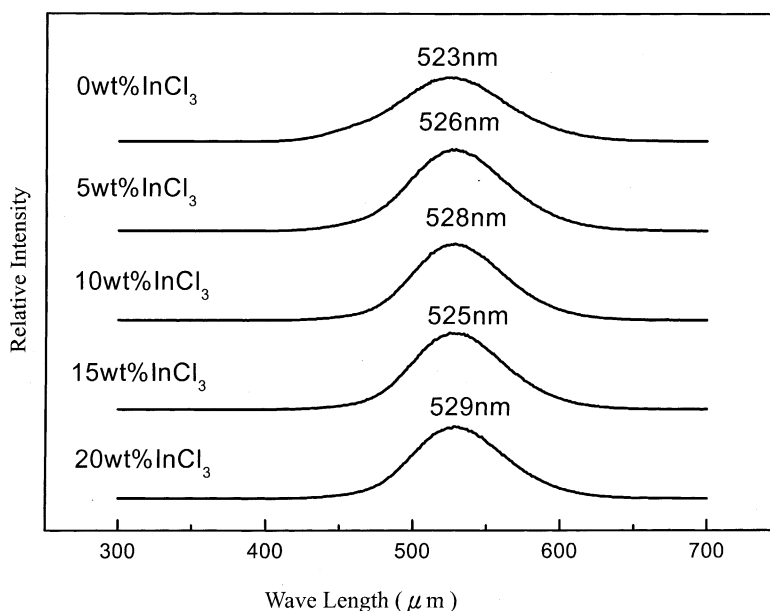


Fig. 1. Cathodoluminescence spectra of ZnS:Cu, Al phosphors coated with various amounts of InCl_3 . Samples measured at 7 kV and 20 μA .

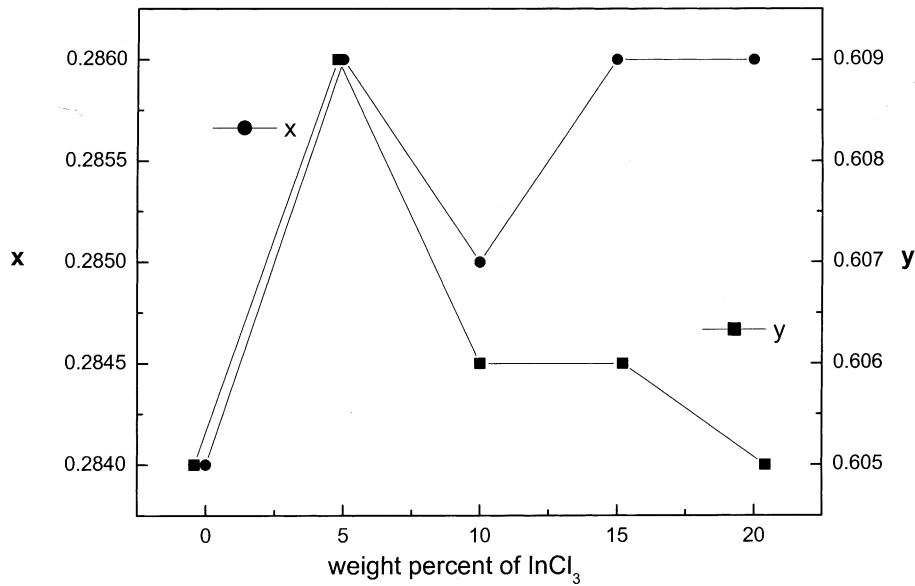


Fig. 2. *x*- and *y*-coordinate of CIE color coordinate of ZnS:Cu, Al phosphors coated with various amounts of InCl₃. Accelerating voltage: 800 V, beam current: 1 μA.

The experiments were performed by placing 0.4 g of phosphor and 101 ml of IPA solution in a glass jar. The zeta potential was determined by [11]:

$$\zeta = \frac{v\eta}{\epsilon E} \quad (1)$$

where *v* is the particle velocity, η and ϵ are the liquid viscosity and dielectric constant, respectively, and *E* is the applied electric field strength. $\epsilon_{r,IPA}$ is 18.3 and η_{IPA} was calculated assuming a linear temperature dependence between 20 °C ($\eta = 2.26$ cP) and 30 °C ($\eta = 1.72$ cP). The sample temperature, which was measured prior to zeta

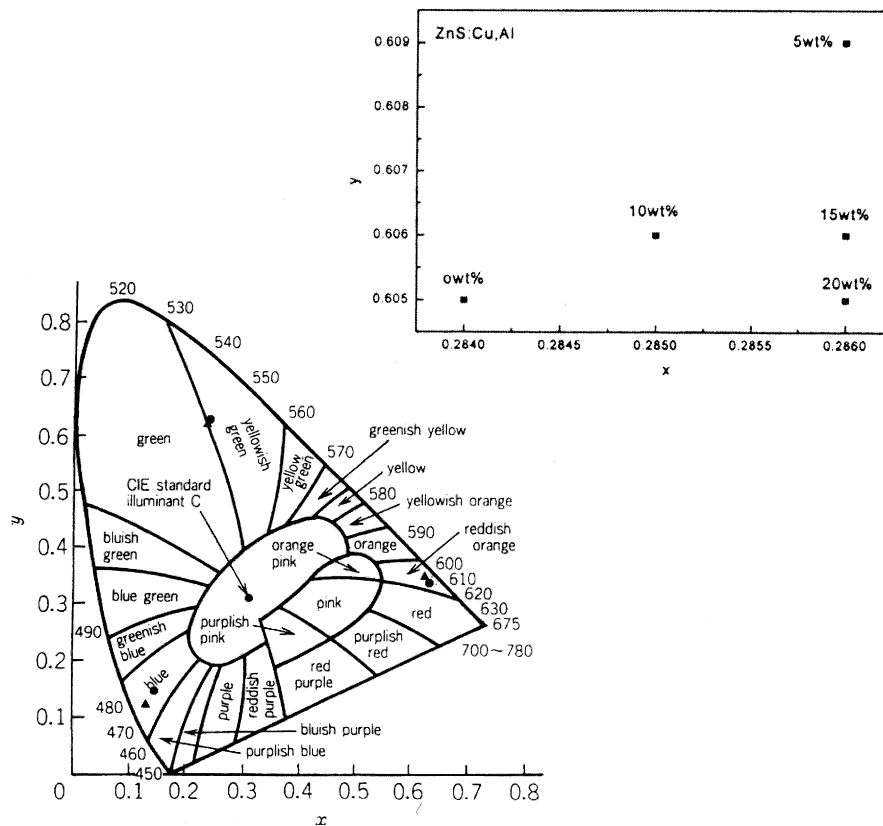


Fig. 3. CIE color loci of p22 phosphors with (●) and without (▲) 10 wt.% InCl₃ coating. Green: ZnS:Cu, Al. Blue: ZnS:Ag, and red: Y₂O₃:Eu. Inset is the exploded view of the *x*- and *y*-coordinate of ZnS:Cu, Al coated with various amount of InCl₃.

potential measurement, was approximately 27 °C. The cell voltage was 300 V, which corresponds to a field strength of 30 V/cm, for all measurements. The accuracy of the measurement is estimated to be ± 10 mV.

3. Results and discussion

Fig. 1 exhibits cathodoluminescence spectra of ZnS:Cu, Al phosphor coated with various amount of InCl_3 . The wavelength of the emission peak ranges from 523 nm for the uncoated sample to 529 nm for the 20 wt.% InCl_3 coated specimens. However, no apparent correlation is found between the CL spectra and the amount of coating. A conductive coating is to retard/eliminate charging-up on the surface of the phosphor. It plays a role of non-luminescent foreign substance. The slight difference in wavelength between phosphors modified with various amounts of conductive coating suggests that coating has very slight effect on the energy levels of the luminescent centers and the luminescent mechanisms. The CIE color coordinate is employed to analyze the luminescence color. The x - and y -coordinate of CIE color, shown in Fig. 2, suggest that, among the compositions studied, ZnS:Cu, Al with 10 wt.% InCl_3 coating exhibits a color which is closest to that of the uncoated one. Fig. 3 gives the CIE color loci of p22 phosphors with and without 10 wt.% InCl_3 coating. Slight difference in color loci is observed between the coated and uncoated phosphors, however, the difference is too small to cause color shift especially in the case of ZnS:Cu, Al. The CIE color coordinates of p22 phosphors are summarized in Table 1.

The decay intensities of luminescence emitted from ZnS:Cu, Al with various amounts of InCl_3 as a function of

Table 1

CIE color coordinates of p22 phosphors with and without 10 wt.% InCl_3 coating

p22 phosphors	10 wt.% InCl_3 coating	x	y
ZnS:Cu, Al (green)	Uncoated	0.284	0.605
	Coated	0.285	0.606
Y_2O_3 :Eu (red)	Uncoated	0.632	0.346
	Coated	0.637	0.345
ZnS:Ag (blue)	Uncoated	0.157	0.145
	Coated	0.153	0.152

time are illustrated in Fig. 4. The decay time τ , defined as the time the intensity reduced to $1/e$ of the original value, increases with the increase of the conductive coating. Kuboniwa et al. reported that the decay time depended on the temperature of measurement as well as the activator concentration of the phosphor and proposed that non-radiative deactivation of the luminescent centers occurred during the early stages of the decay [12]. However, due to the absence of a theory to describe the decay curves with experimentally accessible parameters [13], no definite conclusion can be made on why the coating affects the decay time of the phosphor at present. The decay times are 0.62, 0.64, 0.67, 0.68, and 0.71 μs for samples with 0, 5, 10, 15, and 20 wt.% InCl_3 coating, respectively. They are short enough and suitable for display applications.

The deposition of a thin layer of phosphor particles in the manufacturing of screens used in display is an important process. Electrophoretic deposition is a method used in applying a thin layer of luminescent materials in the manufacturing of cathode ray tube (CRT) screens. Although the mechanisms for the transport and adhesion of the particles to the substrates are not well understood. The surface chemistry of the phosphor particles affects their

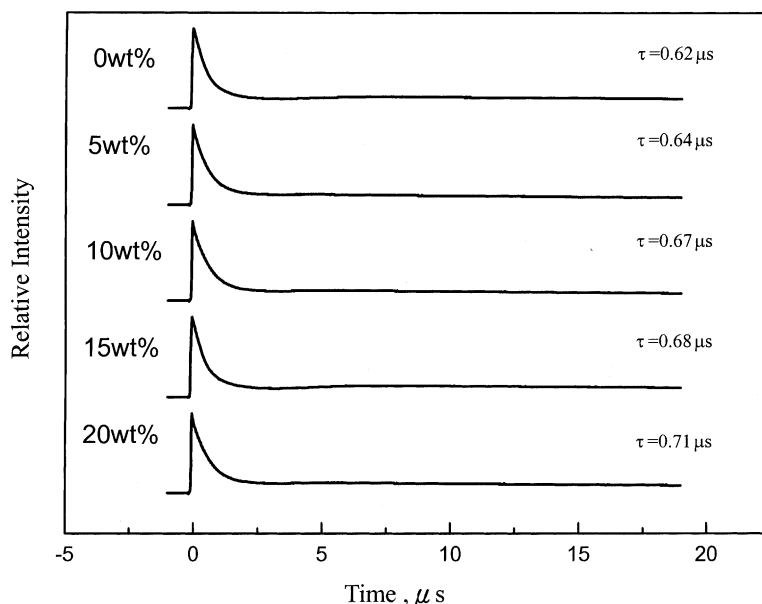


Fig. 4. The decay intensities of luminescence emitted from the ZnS:Cu, Al with various amounts of InCl_3 as a function of time.

Table 2
The zeta potential and luminescent properties of ZnS:Cu, Al with various amount of InCl₃

	Brightness ^a (Cd/m ²)	$(B_x^b - B_0)/B_0 \times 100$ (%)	Color coordinate ^a (x/y)	Decay time (μs)	Zeta potential ^c (mV)
ZnS:Cu, Al	138 ± 6.2	0	0.284/0.605	0.62	1.2
With 5 wt.% InCl ₃	152.4 ± 6.6	10	0.286/0.609	0.64	–
With 10 wt.% InCl ₃	171.2 ± 6.5	24	0.285/0.606	0.67	32
With 15 wt.% InCl ₃	159.7 ± 5.8	15	0.287/0.609	0.68	–
With 20 wt.% InCl ₃	138.9 ± 5.2	0	0.286/0.605	0.71	39

^a Accelerating voltage: 800 V, beam current: 1 μA.

^b Brightness of the sample with the wt.% of InCl₃.

^c The estimated accuracy of measurement is ±10 mV.

dispersibility in solution and adhesion to the substrate. Thus, measurement of zeta potential of phosphors is fundamental to understanding the stability of suspensions against coagulation and settling for coating of these powders. In electrophoretic deposition, the zeta potential also affects the particle deposition rate. Table 2 summarizes the zeta potential and luminescent properties of ZnS:Cu, Al with various amounts of InCl₃. The brightness increases with the wt.% of InCl₃ coating initially, reaches a maximum at 10 wt.% InCl₃, and then decreases with the further increase of InCl₃ as shown in Table 2. As mentioned previously, the conductive coating is a non-emissive layer. The initial raise of the brightness is attributed to the presence of the conductive coating which retards/eliminates charging-up on the surface of the phosphor. However, the more coating, the thicker the non-emissive layer, hence, the smaller the brightness. It should be noted that In₂O₃ results from the hydrolysis of InCl₃ and that the more InCl₃, the more In₂O₃ in the final product. Although there is no direct evidence that the resultant In₂O₃ exists as coating on phosphor instead of as separate particles free from the phosphors. The initial increase followed by a decrease of the brightness with the increase of InCl₃ does suggest that the more InCl₃ the thicker the non-emissive layer, that is, more InCl₃ results in more In₂O₃ coating.

As exhibited in Table 2, the zeta potential of uncoated phosphor particle in IPA solution is 1.2 mV while those coated with 10 and 20 wt.% InCl₃ are 32 and 39 mV, respectively. Shane et al. studied the zeta potential of phosphors in IPA containing dissolved nitrate salts and water. They reported that the zeta potential was negative (–45 mV) at very low salt concentrations (<10^{–6} M). As the concentration of Mg(NO₃)₂, Y(NO₃)₃, or Al(NO₃)₃ increased, the zeta potential increased and became positive [14,15].

A negative zeta potential suggests that cations from the phosphor surface are preferentially dissolved in IPA, leaving the particle with a non-negative charge. While a positive zeta potential indicates that the cations from the nitrate salts are adsorbed into the stern layer around the particles to reverse the zeta potential [11]. In this study, the enhanced positive zeta potential could be due to that the cations of the conductive coating adsorbed onto the phosphor particles created a net positive zeta potential. However, the root cause for the increase of the zeta potential is subjected to further investigations.

The zeta potential affects the particle deposition rate and is important for the evaluation of the particle substrate interactions during the coating process. A larger zeta potential should provide a higher deposition rate, since the deposition rate is proportional to the phosphor mobility which, in turn, is proportional to the zeta potential [15]. The electrophoretic deposition rates of the 10 wt.% InCl₃-coated ZnS:Cu, Al (0.23 mg/s) is larger than that of the uncoated phosphor (0.17 mg/s), as expected.

4. Conclusions

Indium chloride has been used as a precursor for the conductive coating of In₂O₃ on the phosphor surface. Slight differences in the cathodoluminescent emission peak and CIE color coordinates are observed between the uncoated and conductive coated phosphors. However, the differences are too small to cause color shift. The luminescence decay time increases from 0.62 to 0.71 μs as the amount of coating increases from 0 to 20 wt.% InCl₃. Coating affects the surface chemistry of the phosphor particles and, consequently, the dispersibility of particles in solution and the adhesion of particles to the substrate. The zeta potential of 10 wt.% InCl₃ coated ZnS:Cu, Al in IPA solution is 32 mV as compared to 1.2 mV of the uncoated ZnS:Cu, Al. The cations of the conductive coating may enhance the zeta potential. The electrophoretic deposition rate of the coated particles is larger than that of the uncoated ones.

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