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Characterization and conductive coating of phosphors for improved brightness

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Abstract

In this study, the phosphors used in CRTs are coated with In_2O_3 conductive layer derived from the hydrolysis of indium chloride. The conductive coating retards/eliminates charging-up on the phosphor surface during the bombardment of the electrons and improves the cathodoluminescent brightness of the phosphor. However, the non-emissive conductive coating also degrades the cathodoluminescent brightness when it is too thick. The cathodoluminescent brightness increases initially with the amount of coating, reaches a maximum at 10 wt.% $InCl_3$, and decreases with further increase of coating. It is found that with a 10 wt.% $InCl_3$ coating, the brightness of phosphor increases by 20% at 500 V and 1 μA.

Keywords: Brightness; $InCl_3$; Phosphor

1. Introduction

Recently, field emission display (FED) has been actively investigated in the development of full color flat panel display. In the development of FED, it is imperative to optimize phosphor properties to reduce power consumption and increase brightness [1–3].

In the design of phosphors for low voltage operations, there are three important factors to be considered: (1) the morphology and size [4]; (2) the stoichiometry and composition [5–9]; (3) the surface of the phosphors [10–12]. As phosphors used in CRTs show high luminescence and efficiency, it is desired to used 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.

The non-emission layers appear to result from non-radiative surface effects such as defects, contamination, and/or band-bending. When the applied voltage is low, penetration of electrons into the phosphor particles is shallow, consequently a lower luminescent

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efficiency is observed due to the loss of energy to non-radiative centers within the non-emissive surface layer. Hence, the control of the surface is one of the key factors in phosphor design.

Several methods have been employed to treat the surface of the phosphors for improved brightness. Previous works report that wet chemical etching of phosphor surfaces with a basic aqueous solution of sodium borohydride or a nitric acid enhance the cathodoluminescent (CL) efficiency of the phosphors [10,12]. Kominami et al. coated ZnS: Ag, Cl phosphor with In_2O_3 using indium-*iso*-propoxide by the sol–gel method and improved the luminance of the phosphor [11].

In this research, phosphors are coated with an In_2Cl_3 conductive layer obtained from the hydrolysis of aqueous solution of $InCl_3$. The effect of coating on the luminescence of the phosphors is studied. The phosphors employed in this study are P22 series from Kasei Optomix, Ltd., they are: ZnS: Cu, Al for green, ZnS: Ag for blue, and Y_2O_3: Eu for red.

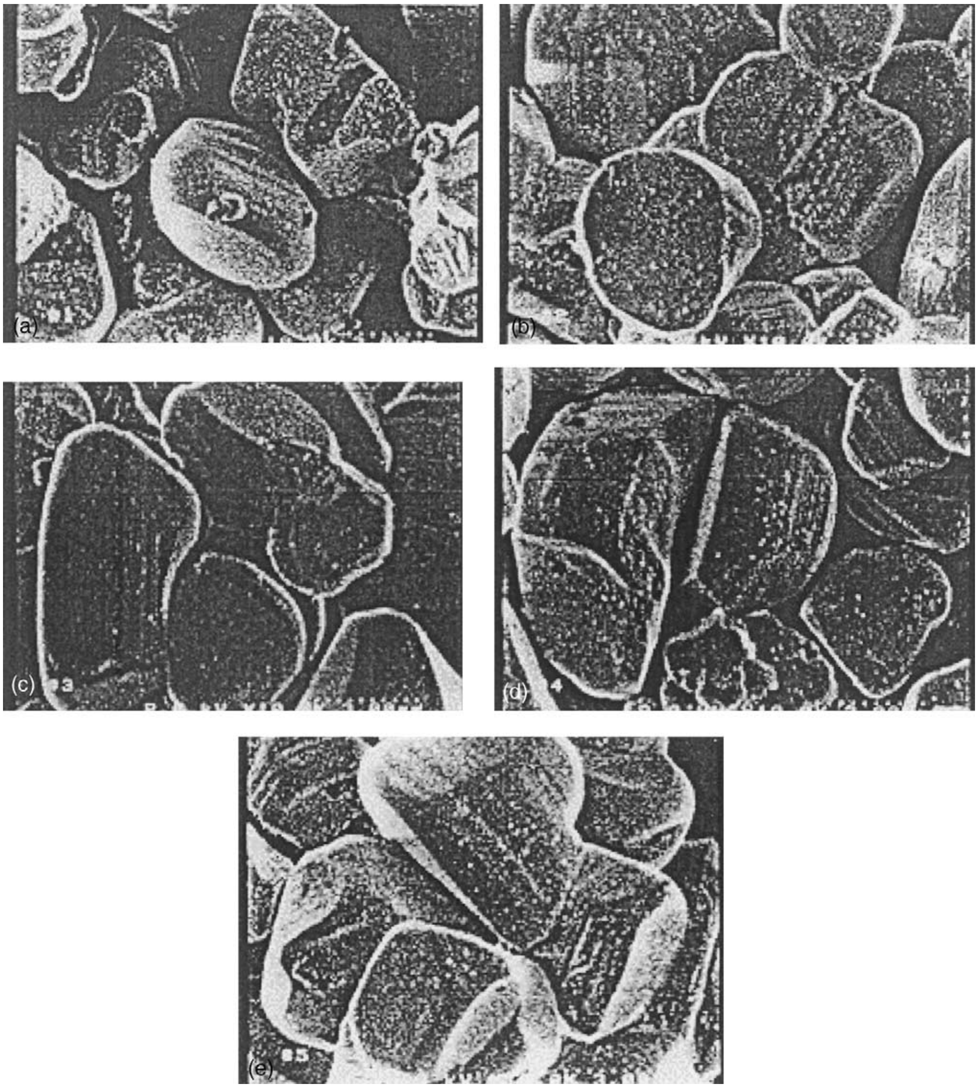


Fig. 1. SEM images of ZnS: Cu, Al phosphors coated with: (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, (d) 15 wt.%, and (e) 20 wt.% $InCl_3$.

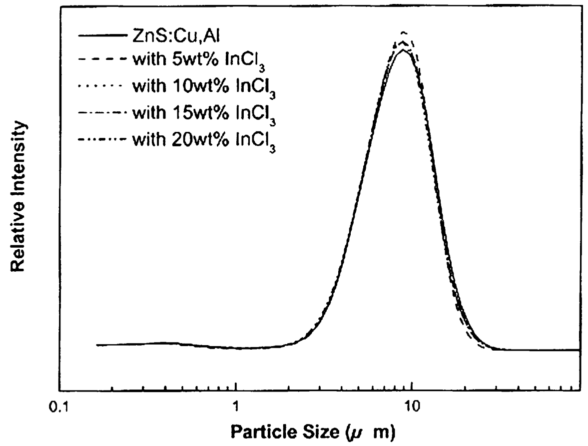


Fig. 2. Particles size distribution for ZnS: Cu, Al phosphors coated with various amounts of $InCl_3$.

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 Cu Kα (λ = 1.5406 Å).

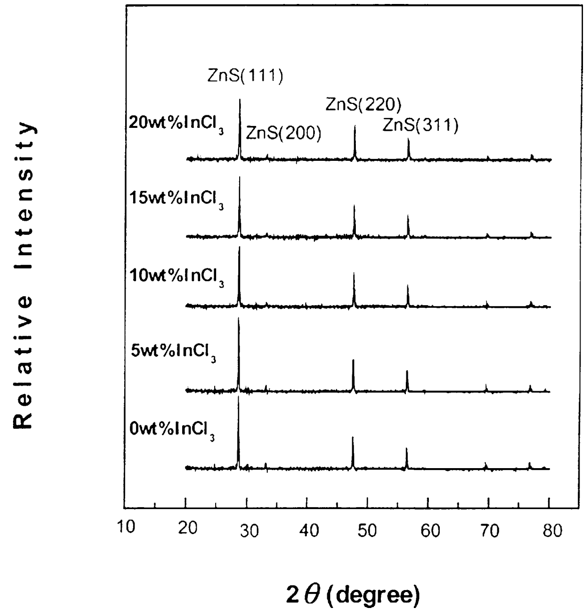


Fig. 3. The XRD patterns of ZnS: Cu, Al phosphors coated with various amounts of $InCl_3$.

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.

Table 1

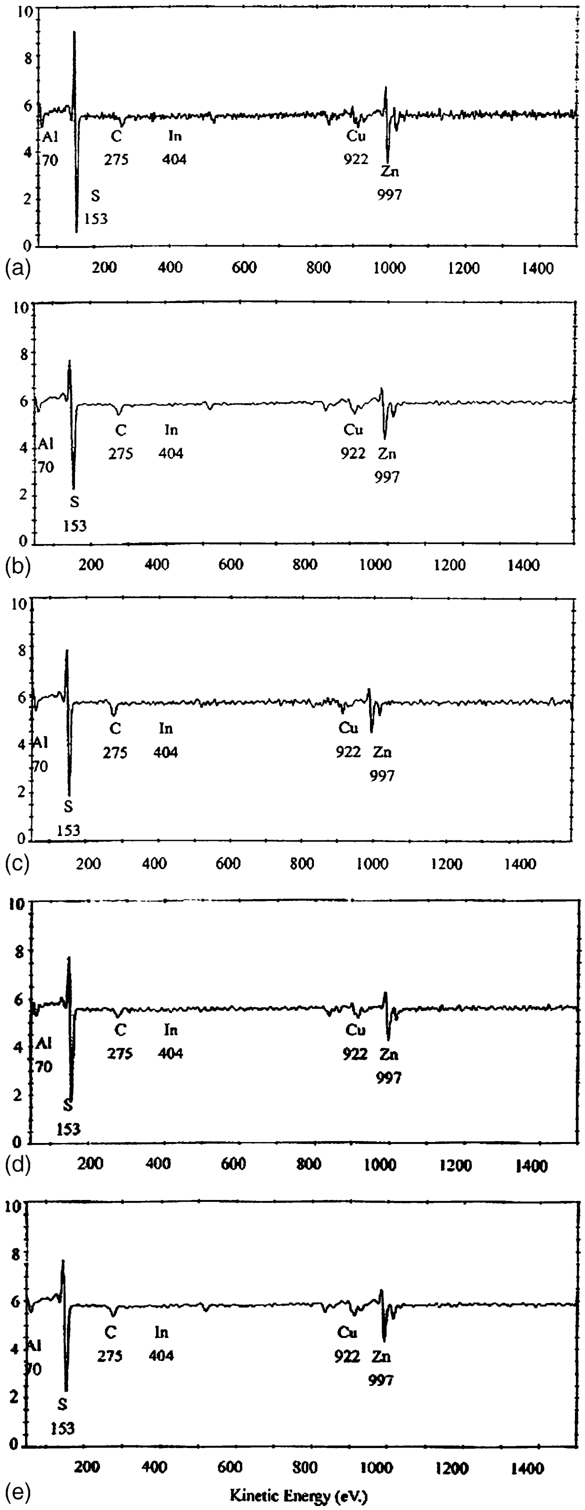
Total, remnant, and coated indium for ZnS: Cu, Al phosphor coated with various amounts (wt.%) of $InCl_3$

$InCl_3$ (wt.%)	0	5	10	15	20
Total In (g)	0	0.1307	0.2614	0.3920	0.5227
Remnant In (g) (In in filtrate)	–	0.054	0.144	0.253	0.344
In coated (g) (total-remnant)	–	0.0767	0.1174	0.1390	0.1787
Thickness of coating[a] (nm)	–	17.6 (29)[b]	27.4 (59.7)	33.9 (93.9)	45.2 (130.7)

Data obtained on the basis of ICP–AES analysis.

[a] Assuming spherical phosphor powders with a diameter of 9 μm.

[b] Data in the parenthesis is the calculated thickness assuming all the In are coated onto phosphor.



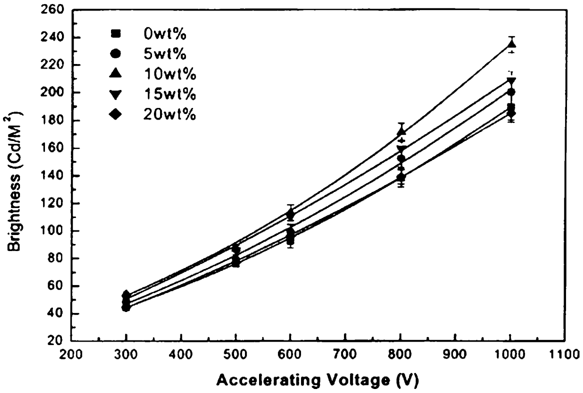


Fig. 5. Brightness as a function of accelerating voltage of ZnS: Cu, Al phosphors coated with various amounts of $InCl_3$. Beam current: 1 μA.

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 an accelerating voltage of 1 kV and an 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.

3. Results and discussion

$InCl_3$ is employed as the precursor for the coating of phosphor in order to reduce the resistivity of the phosphor. $In(OH)_3$ is formed after hydrolysis of $InCl_3$. $In(OH)_3$ is an unstable material, and polymerization occurs at once as follows:

$$2In(OH)_3 \rightarrow In_2O_3 + 3H_2O \quad (1)$$

H_2O molecules adhered to surface of phosphor, and those chemical reactions occurred on the phosphor surface. Thus, In_2O_3 was formed on the surface of phosphor.

Fig. 4. The Auger electron spectra of ZnS: Cu, Al phosphors coated with: (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, (d) 15 wt.%, and (e) 20 wt.% $InCl_3$. Phosphors were printed and fired on ITO glass substrates.

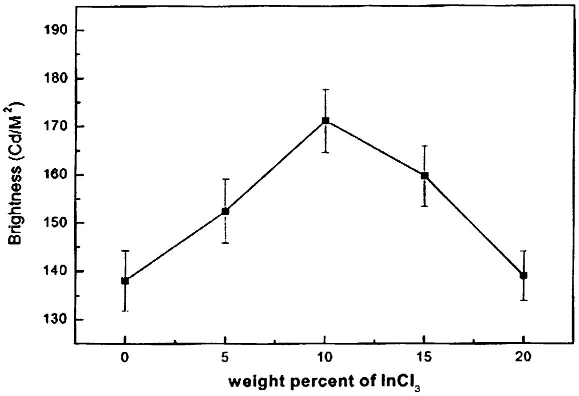


Fig. 6. Brightness of ZnS: Cu, Al phosphors coated with various amounts of InCl$_3$. Accelerating voltage: 800 V. Beam current: 1 μA.

The SEM images of the as received and coated P22-GN4 (ZnS: Cu, Al) phosphor are shown in Fig. 1. No apparent difference in particle shape and/or size is observed among the as-received powder and powders coated with various amount of InCl$_3$. The average particle size of as-received phosphor is ~9 μm, no apparent difference in particle size is observed for phosphor powders with various amount of InCl$_3$ (Fig. 2).

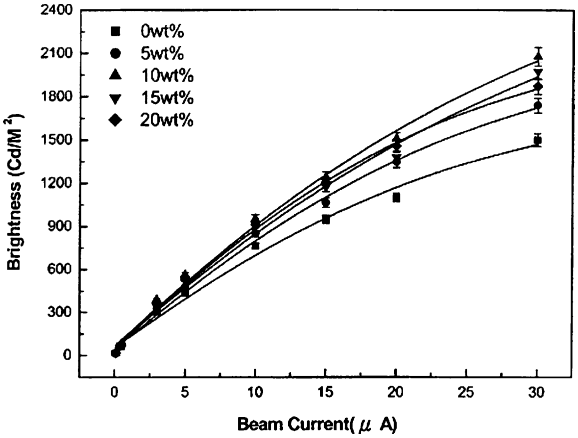


Fig. 7. Brightness as a function of beam current of ZnS: Cu, Al phosphors coated with various amounts of InCl$_3$. Accelerating voltage: 800 V.

The calculated thickness of the coating layer is ~45.2 nm for a spherical powder of diameter 9 μm coated with 20 wt.% InCl$_3$, hence one would not

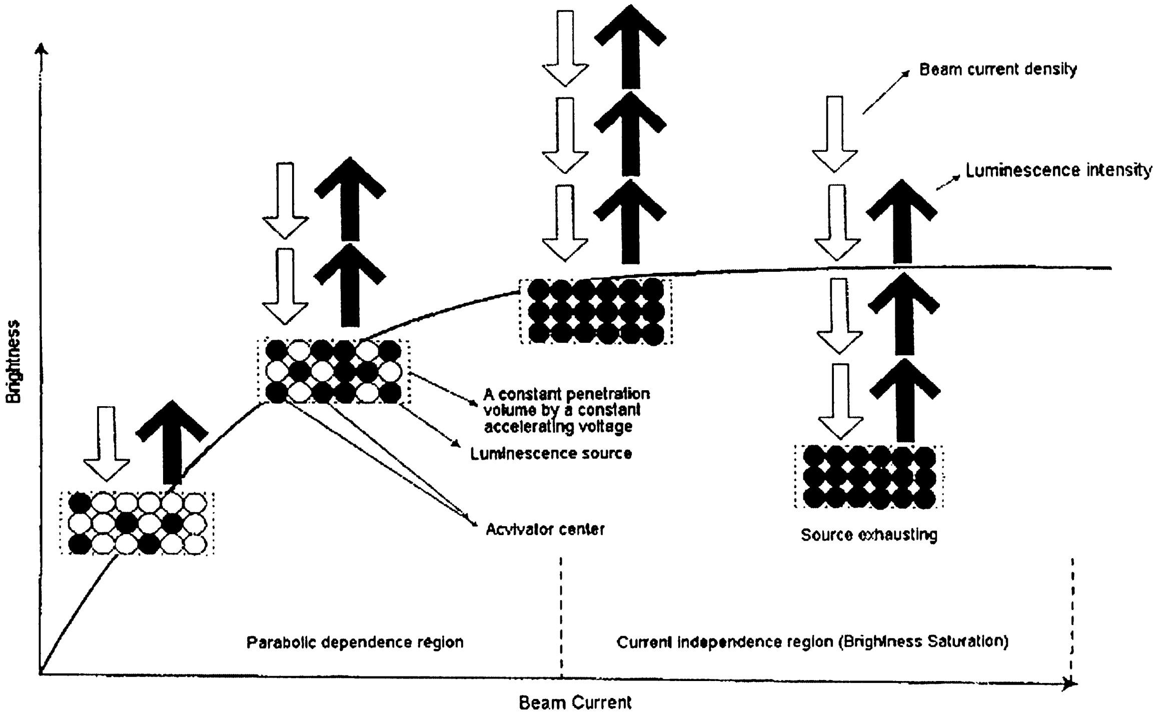


Fig. 8. Schematic diagram of brightness as a function of beam current.

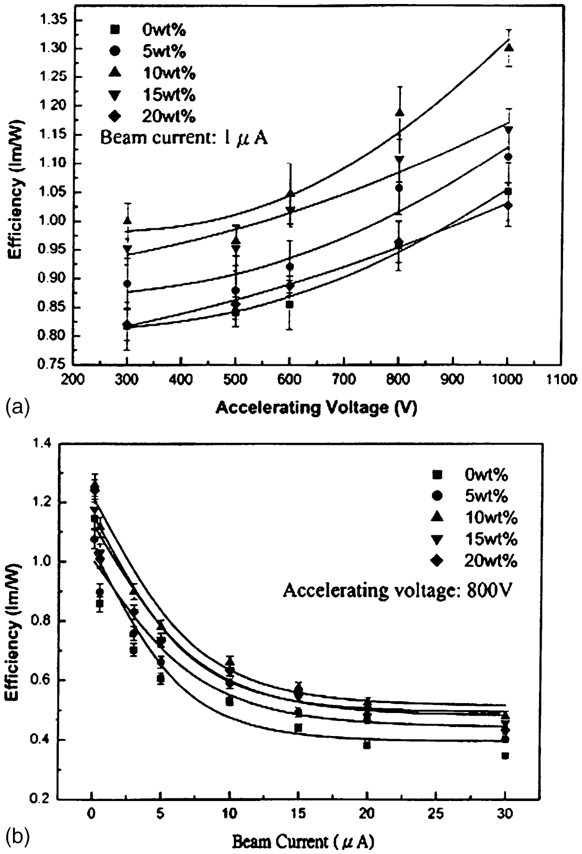


Fig. 9. Efficiency as a function of (a) accelerating voltage and (b) beam current of ZnS: Cu, Al phosphors coated with various amounts of $InCl_3$.

expect any difference in either the particle size or shape of the coated samples. Moreover, the ICP–AES analysis indicates remnant indium in the filtrate, as summarized in Table 1, the coated layer is even thinner than expected. Fig. 3 gives the XRD patterns of the as-received and In_2O_3-coated phosphors. It is seen that the phosphor after coating does not show any peaks of In_2O_3. This suggests that the In_2O_3 layer is very thin and/or that the layer is amorphous on the phosphor surface. In addition, the Auger electron spectra, shown in Fig. 4, do not reveal any obvious difference between the surface compositions of the as-received and the In_2O_3-coated powders. In order to clarify this fact, In_2O_3 powder only was made from indium chloride without phosphor, $InCl_3$ was dissolved in deionized water, dried, and then baked at 450 °C for 1 h, and the XRD patterns suggest formation of In_2O_3 particles.

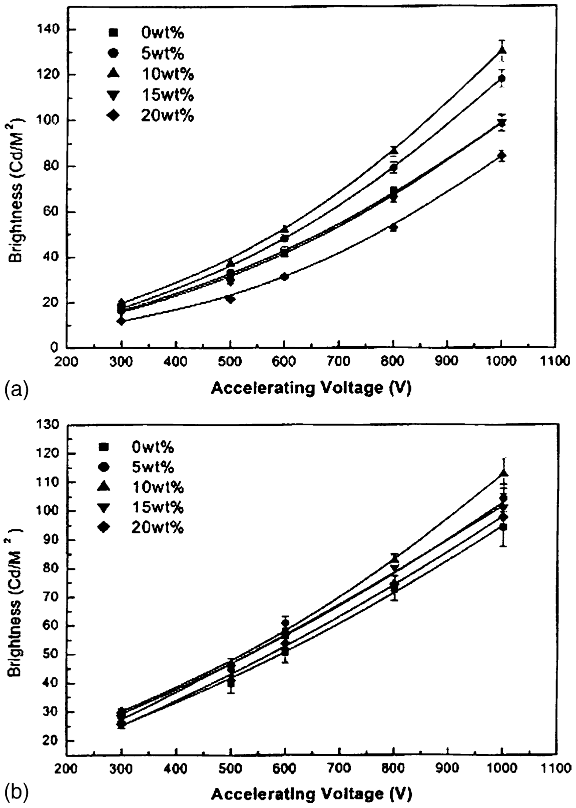


Fig. 10. Brightness as a function of accelerating voltage of (a) Y_2O_3: Eu and (b) ZnS: Ag phosphors coated with various amounts of $InCl_3$. Beam current: 1 μA.

The brightness data suggest the indium coating on the phosphors. Fig. 5 gives the brightness as a function of accelerating voltage of ZnS: Cu, Al phosphors coated with various amounts of $InCl_3$. The cathodoluminescent brightness of phosphors increases as the energy of the irradiated electrons increases, especially for samples coated with 10 wt.% $InCl_3$. The brightness increases with the wt.% of $InCl_3$ coating, reaches a maximum at 10 wt.% $InCl_3$, and then decreases with the further increase of $InCl_3$, as indicated in Fig. 6. The initial raise of the brightness is attributed to the presence of the conductive In_2O_3 coating which retards/eliminates charging-up on the surface of the phosphor. However, because In_2O_3 is a non-emitting material, the more $InCl_3$ coating, the thicker the non-emissive layer, hence, the brightness decreases. Fig. 7 shows the CL brightness as a function of beam current.

The brightness increases initially as the beam current increases, and reaches a plateau with the further increase of beam current. Before the saturation of brightness occurs, the relationship between brightness and beam current is parabolic dependence. It is argued that the total amount of activator centers is a constant in a restricted volume of spot, as the current density exceeds the limit, which all the activator centers are activated, the luminescence source is exhausted under the high energy density and a near saturated region is achieved as illustrated in Fig. 8.

The brightness efficiency of the phosphors can be calculated from the measured brightness:

$$\eta = \frac{B \times A \times \pi}{I \times V} \tag{2}$$

where η represents the efficiency with a unit of 1 m/W, B the brightness in Cd/m^2, A the luminescent area (m^2), I the substrate current, and V is the electron accelerating voltage. The brightness efficiency calculated from Eq. (2) is plotted as a function of accelerating voltage and beam current is exhibited in Fig. 9. Phosphors coated with 10 wt.% $InCl_3$ have an efficiency of ~1.3 lm/W at 1 μA and 1 kV as compared to η of ~1.04 lm/W of the uncoated phosphors. The efficiency increases with the increase of the accelerating voltage, while decreases initially and reaches a constant with the increase of beam current.

Similar trend is observed for the brightness as a function of amounts of $InCl_3$ coating of Y_2O_3: Eu and ZnS: Ag phosphors. As illustrated in Fig. 10, the brightness increases with the wt.% of $InCl_3$ coating, reaches a maximum at 10 wt.% $InCl_3$, and then decreases with the further increase of $InCl_3$. Appropriate coating of conductive layer is effective in enhancing the low voltage cathodoluminescence as shown in Figs. 5, 9, and 10.

4. Conclusions

Indium chloride has been used as a precursor for the conductive coating of In_2O_3 on the phosphor surface. Although no appreciable difference is observed in particle size, shape, morphology, and surface composition between the as-received phosphor and the coated ones. Appropriate coating of conductive layer does enhance the low voltage cathodoluminescent brightness of the phosphors. The conductive coating retards/eliminates charging-up on the surface of the phosphor, and increases the brightness of the phosphor. However, since the coating is a non-emissive layer, the brightness decreases when the coating layer becomes too thick. The optimum condition found in this study is a 10 wt.% $InCl_3$ coating of which the brightness of ZnS: Cu, Al phosphor increases 24 and 20% at 1 kV, 1 μA and 500 V, 1 μA, respectively.

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