

# Cathodoluminescent properties of coated $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ and $\text{ZnS}:\text{Ag,Cl}$ phosphors for field emission display applications

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## Abstract

Field emission displays (FED) operate at lower voltages and significantly higher current densities than cathode ray tubes (CRTs). This makes it advantageous to consider how to adapt conventional CRT sulfur based phosphors, which have the highest luminescent efficiency, but which unstable under high electron bombardment, to FED applications. Thus to protect these phosphors from degradation it is necessary to develop thin layer coatings of stable materials, such as  $\text{MgO}$ ,  $\text{In}_2\text{O}_3$  or polyphosphate. The goal of this study is to investigate the influences of these coatings on the cathodoluminescent properties of the blue phosphor,  $\text{ZnS}:\text{Ag,Cl}$ ; and the green phosphor,  $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ . © 2000 Elsevier Science S.A. All rights reserved.

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Since the first Field Emission Display (FED) was demonstrated by LETI in 1990 [1], many new classes of phosphor materials for low voltage applications have been investigated [2–5]. Due to the short distance between the anode and cathode, the acceleration voltages used in a FED does not have to be as high as in a CRT (20–30 kV), and typically are in the range from 200 V to 8 kV. However, to achieve CRT levels of brightness in a FED, the current densities need to be increased at least 20 times. For these excitation conditions, most conventional sulfur-containing CRT phosphors are not appropriate for field emitter arrays. Also it has been shown that irradiation with an electron beam causes decomposition and generates harmful gases, such as  $\text{SO}_2$ , subsequently causing the cathode to deteriorate and the luminous efficiency of phosphors to decrease. In order to avoid these problems new coating techniques are being developed for sulfide phosphors to protect the phosphors from degradation. The published results demonstrated good aging behavior for  $\text{ZnS}$  phosphors with oxide or polyphosphate coating [6–10].

In this paper, we present the low voltage cathodoluminescent properties of the  $\text{ZnS}:\text{Ag,Cl}$  blue phosphor coated with  $\text{MgO}$  and polyphosphate, and the  $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$  green phosphor coated with  $\text{MgO}$  and  $\text{In}_2\text{O}_3$ . These two phosphors have excellent chromaticity and high luminous efficiency at low voltages [11]. The green emitting thiogallate used in this study was prepared at the Phosphor Technology Center of Excellence (PTCOE) and the blue emitting  $\text{ZnS}:\text{Ag,Cl}$  phosphor was purchased from Kyokko (P22-B1). All the coatings were prepared at the PTCOE of the Georgia Institute of Technology using a wet chemistry method.

The  $\text{MgO}$  and  $\text{In}_2\text{O}_3$  coatings were prepared by a sol-gel technique using magnesium ethoxide ( $\text{Mg}(\text{OC}_2\text{H}_5)_2$ ) and indium isopropoxide ( $\text{In}(\text{OC}_3\text{H}_7)_3$ ) as the precursors. The ratio of  $\text{MgO}$  to the strontium thiogallate was 0.5 wt.%, and to the zinc sulfide, 1.0 wt.%. The ratio of  $\text{In}_2\text{O}_3$  to strontium thiogallate was 0.5 wt.%. The precursors were first dissolved in ethanol, and then while continuous stirring, the phosphor materials were added to the ethanol solutions and mixed for  $\approx 10$  h. The final mixtures were evaporated and dried and baked at  $450^\circ\text{C}$  under an argon atmosphere. The polyphosphate coatings on zinc sulfide were prepared

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according to the process described by Haase [4]. To insure that pure MgO and In<sub>2</sub>O<sub>3</sub> coatings were obtained using these precursors, MgO and In<sub>2</sub>O<sub>3</sub> powders were prepared without phosphors. Both MgO and In<sub>2</sub>O<sub>3</sub> phases, respectively were identified from powder X-ray diffraction measurement (Rigaku D.MAX-B).

The luminous efficiencies and the spectral properties of the phosphors were measured as a function of accelerating voltage (500–10 000 V) on deep powder patches using DC electron gun excitation at current densities  $\approx 1 \mu\text{A}/\text{cm}^2$ . Aging tests on phosphors settled without binders on ITO/glass screens were also performed. The excitation conditions used for these measurements were 2 kV with 400  $\mu\text{s}$  current pulses at 60 Hz with a peak current density of  $\approx 12 \text{ mA}/\text{cm}^2$ . Both the coated and un-coated phosphors were tested in a high vacuum

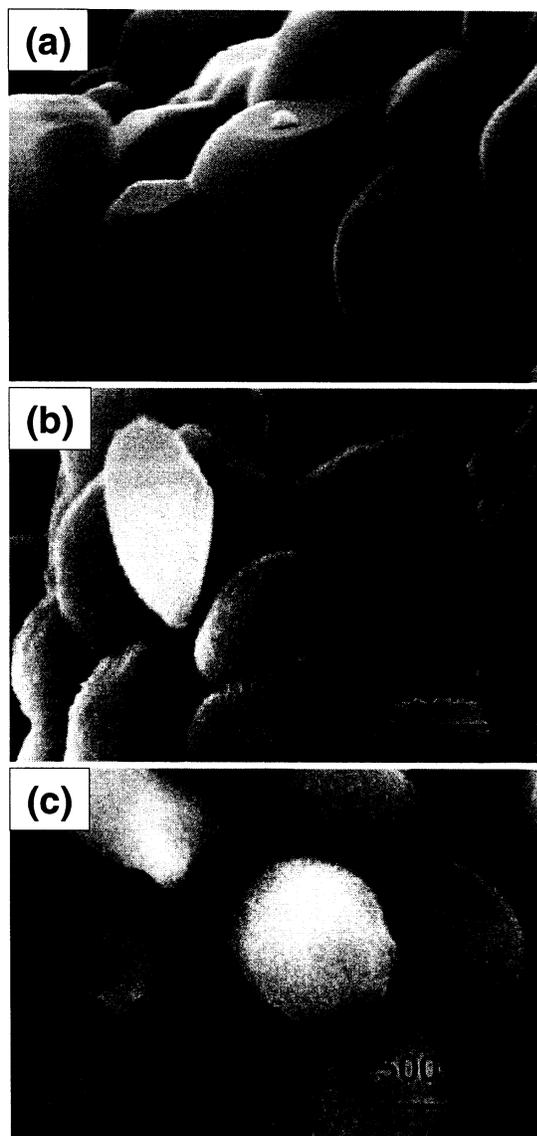


Fig. 1. Secondary electron micrographs of the SrGa<sub>2</sub>S<sub>4</sub>:Eu phosphor, (a) un-coated; (b) coated with MgO; and (c) coated with In<sub>2</sub>O<sub>3</sub>.

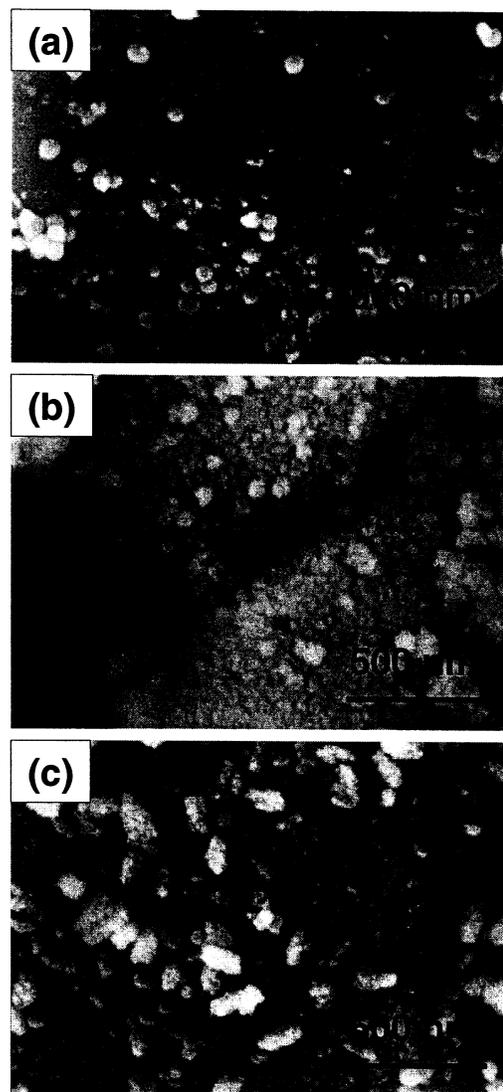


Fig. 2. Secondary electron micrographs of the ZnS:Ag phosphor, (a) un-coated; (b) coated with MgO; and (c) coated with polyphosphate.

chamber at the same time and under the same conditions to insure high accuracy. The electron beam was deflected from one sample to the other after each pulse, and the luminance of each sample was measured using two well-calibrated photometers.

Fig. 1 shows the morphologies of the thiogallate phosphors before and after coating. Before coating the phosphor particles exhibited very clean and smooth surfaces (Fig. 1a). As shown in Fig. 1b and c, for the coating conditions described, the surfaces of the phosphor particles were covered uniformly with particulate-like MgO and In<sub>2</sub>O<sub>3</sub>, respectively. The thickness of the coatings were estimated to be in the range of 20–50 nm. In contrast with thiogallate phosphors, the as-received commercial zinc sulfide phosphors were already coated with particulate-like silicon oxide to improve its fluidity when making screens (Fig. 2a). Fig. 2b shows

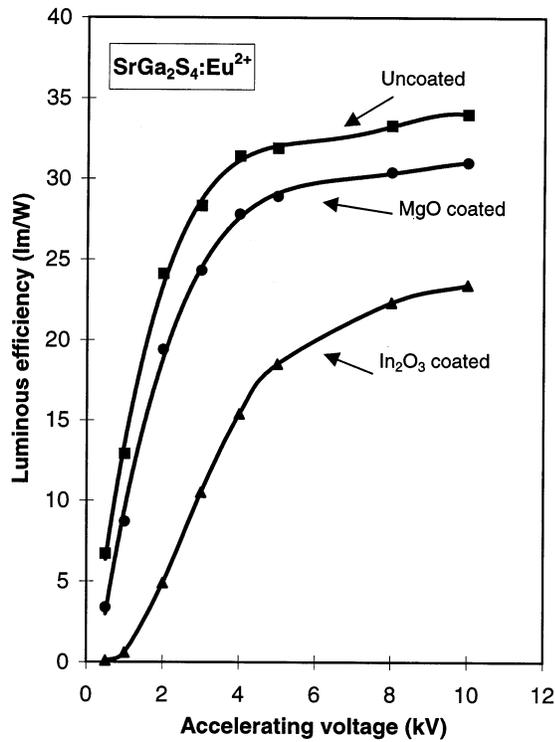


Fig. 3. Dependence of luminous efficiency on electron beam accelerating voltage for SrGa<sub>2</sub>S<sub>4</sub>:Eu phosphor, showing decrease of luminous efficiency after coating.

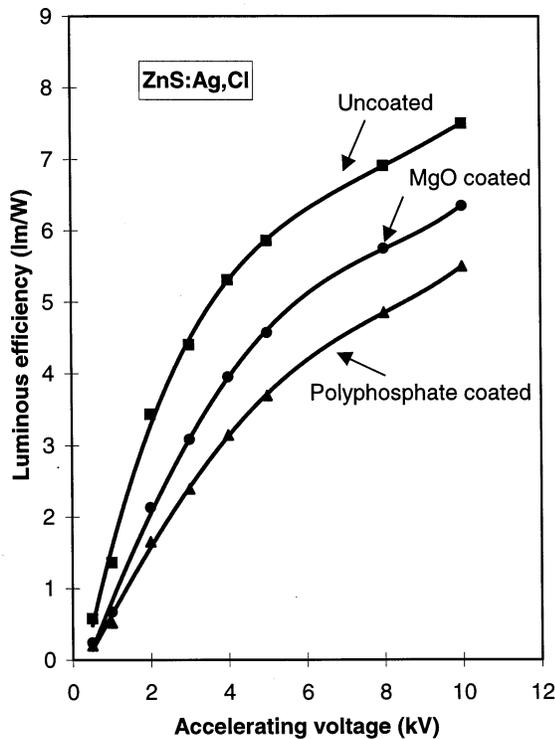


Fig. 4. Dependence of luminous efficiency on electron beam accelerating voltage for ZnS:Ag phosphor, showing decrease of luminous efficiency after coating.

Table 1  
Measured Commission International de l'Eclairage (CIE) coordinates

Phosphor	x	Y
SrGa <sub>2</sub> S <sub>4</sub> :Eu uncoated	0.25	0.69
SrGa <sub>2</sub> S <sub>4</sub> :Eu coated with MgO	0.25	0.69
SrGa <sub>2</sub> S <sub>4</sub> :Eu coated with In <sub>2</sub> O <sub>3</sub>	0.25	0.69
ZnS:Ag,Cl: uncoated	0.1495	0.0498
ZnS:Ag,Cl coated with MgO	0.1522	0.0585
ZnS:Ag,Cl coated with polyphosphate (1)	0.1519	0.0485

the morphologies of MgO coated zinc sulfide phosphor. Just as in the case of thiogallate phosphor, the MgO coating was particulate and some extra MgO agglomerates were found on the surface of the phosphors. The morphology of ZnS phosphors coated with polyphosphate (Fig. 2c) showed that the coating was not as uniform as the MgO coating for ZnS and thiogallate, but that most of the phosphor surface was covered. Some extra polyphosphate agglomerates were found on the phosphor surface as well.

Figs. 3 and 4 show the luminous efficiencies of the strontium thiogallate and zinc sulfide phosphors measured as a function of excitation voltage. As expected, the intrinsic luminous efficiencies of the coated phosphors were lower than those of the un-coated phosphors, and the difference between these two luminous efficiencies decreased as the accelerating voltage was increased. This was attributed to the fact that as the electron energy was increased, it can more easily penetrate the coating layers and excite a larger interaction volume in the phosphor. For the In<sub>2</sub>O<sub>3</sub> coating on the thiogallate and for the polyphosphate coating on zinc sulfide, the luminous efficiency at low voltages (< 1000 V) was much lower. This was probably due to a continuous coating on the phosphors.

Table 1 lists the measured chromaticity coordinates of the coated and un-coated phosphors. These measurements were performed at low voltages in order to sample the surface region. It was shown that these coating produced only a very small change in the chromaticity coordinates of the ZnS:Ag,Cl emission, indicating that no contamination occurred.

Fig. 5 shows the normalized brightness as a function of irradiation time for the coated and un-coated thiogallate phosphors. During the 15 h of electron bombardment, a continuous decrease in the efficiency was observed for the un-coated phosphor, which dropped to 74% of the original value. In contrast the luminance from the MgO coated sample decreased only ≈ 10% and the In<sub>2</sub>O<sub>3</sub> coated sample in fact increased by ≈ 13% with respect to the initial brightness, respectively. Thus both of the coated thiogallate phosphor showed better aging behavior. These results suggested that both MgO and In<sub>2</sub>O<sub>3</sub> protect the thiogallate from degradation, and that the In<sub>2</sub>O<sub>3</sub> coating has a strong

positive effect on the stability of the thiogallate phosphor screen under electron bombardment. This effect could be due to protection or to a reduction in the charging behavior of the phosphor.

In contrast to the thiogallate sample, the MgO coating had only a small effect on increasing the stability of the ZnS:Ag,Cl phosphor (Fig. 6), and the brightness of both the MgO coated sample and the un-coated sample showed a continuous decrease during the aging test. On the other hand, it was found that the polyphosphate coating had a strong positive effect on increasing the stability of the ZnS:Ag,Cl phosphor as reported previously by Haase<sup>4</sup> at higher voltages. The initial reduction in the brightness was compensated by a better behavior during the aging test. Thus the polyphosphate coating showed a promising effect to preserve ZnS:Ag,Cl from degradation under electron bombardment.

In summary, the cathodoluminescent properties of the ZnS:Ag,Cl blue phosphor coated with MgO and polyphosphate, and the SrGa<sub>2</sub>S<sub>4</sub>:Eu<sup>2+</sup> green phosphor coated with MgO and In<sub>2</sub>O<sub>3</sub> have been investigated. Preliminary work has shown that it is possible to improve the stability of these phosphors under electron bombardment by coating. Good results were obtained for the europium doped thiogallate phosphor coated with In<sub>2</sub>O<sub>3</sub> and for the ZnS:Ag,Cl phosphor coated

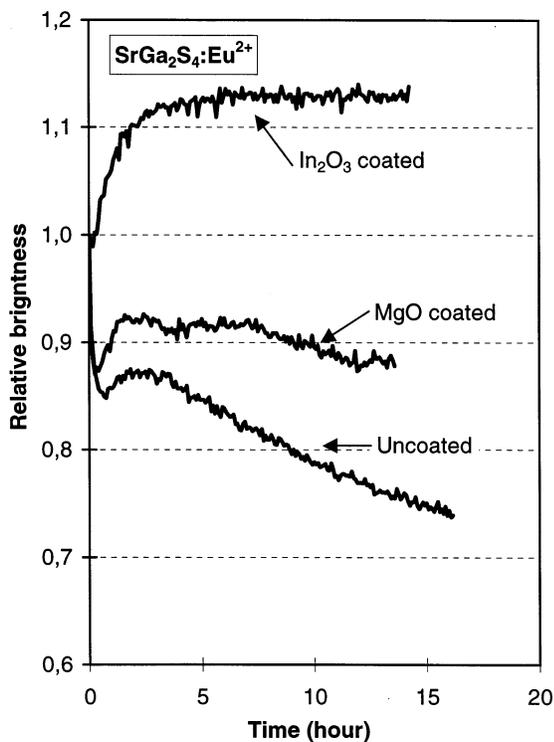


Fig. 5. Relative luminance of uncoated and MgO and In<sub>2</sub>O<sub>3</sub> coated SrGa<sub>2</sub>S<sub>4</sub>:Eu as a function of time when irradiated by a pulsed electron beam at 2 kV, showing improved aging performance after coating.

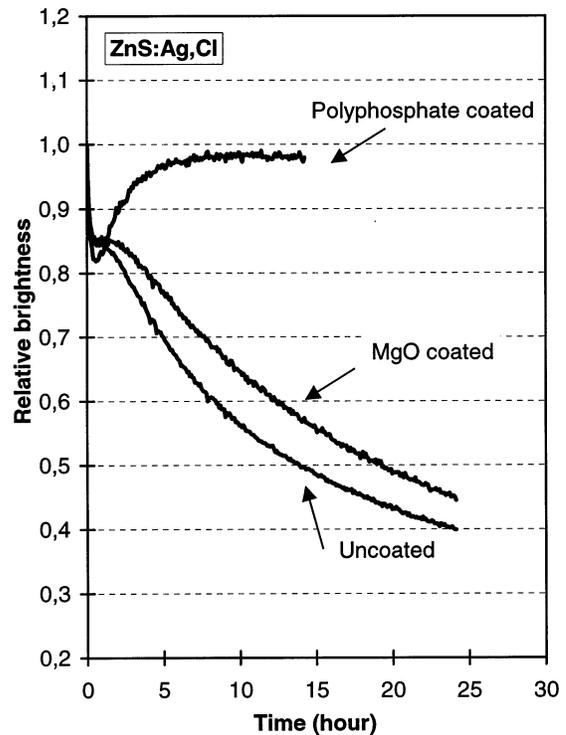


Fig. 6. Relative luminance of uncoated and MgO and polyphosphate coated ZnS:Ag as a function of time when irradiated by a pulsed electron beam at 2 kV, showing improved aging performance after coating.

with polyphosphate. However, at low voltage (< 1000 V) the coatings strongly reduced the initial luminous efficiency. Further research is needed to find the optimum coating conditions, so as to achieve minimum luminous efficiency loss with maximum stability.

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#### References

- [1] R. Meyer, Jpn. Display (1986) 513.
- [2] R.O. Petersen, Inform. Display 3 (1997) 22.
- [3] H. Yamamoto, J. SID 4 (3) (1996) 165.
- [4] L.E. Shea, Interface 24 (1998).
- [5] Y.D. Jiang, Z.L. Wang, F.L. Zhang, et al., J. Mater. Res. 13 (1998) 2950.
- [6] A.O. Dmitrienko, Tech. Digest of IVMC (1997).
- [7] H. Kominami, Jpn. J. Appl. Phys. Part 2 35 (1996) L1600.
- [8] M. Haase, H. Bechtel, Patent P4442706.9.
- [9] T. Nakamura, M. Kamiya, H. Watanabe, J. Electrochem. Soc. 142 (1995) 949.
- [10] C.N. Chau, US Patent 5 196 229.
- [11] J. Penczek, IDW'97, Nagoya, Japan, November 19–21, 1997, p. 625.