

Mn-doped ZnS nanoparticles as efficient low-voltage cathodoluminescent phosphors

A. D. Dinsmore,^{a),b)} D. S. Hsu,^{c)} H. F. Gray,^{d)} S. B. Qadri,^{e)} Y. Tian,^{f)} and B. R. Ratna^{a)}
Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, DC 20375

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We have synthesized nanoparticles of ZnS doped with Mn for potential use as cathodoluminescent phosphors in field-emission displays (FEDs). We show that the cathodoluminescent efficiency of particles ≤ 100 nm in diameter is within 40% of that of a commercial (micron-sized) phosphor when the electron-beam energy ranges between 500 and 3500 eV. The nanoparticles exhibit less current saturation than larger-sized phosphors, an important feature for use in FEDs. Furthermore, the nanoparticles were annealed at just 535 °C, hundreds of degrees below the processing temperatures of standard phosphors. Finally, we discuss the effect of the particle surface on low-voltage luminous efficiency. © 1999 American Institute of Physics. [S0003-6951(99)02032-X]

A serious obstacle to the development of flat-panel field-emitter displays (FEDs) is the lack of phosphors with high cathodoluminescent efficiency at electron acceleration voltages near 1 kV.¹⁻⁴ Moreover, high-definition displays call for submicron particle sizes to maximize screen resolution and screen efficiency.⁵ Current commercial processes, which use mechanical milling to control the particle size, result in particles that are larger than about 2 μm . Nanoparticles can be synthesized with sizes ranging from 2 to 100 nm and thus easily fulfill the size requirement without mechanical milling. They also offer the necessary high crystallinity, can be doped with a variety of materials,⁶⁻¹¹ and potentially allow formation of smooth, tough films by relatively low-temperature sintering.¹² Some authors,^{13,14} however, have questioned whether it is possible to achieve high efficiency using particles that are less than approximately 1 μm in size. Some experiments¹⁴ have suggested (and it is commonly assumed) that as particles become smaller, the efficiency decreases because of the increasing surface area, which is thought to contain nonradiative recombination sites¹³ or some other kind of "dead layer." On the other hand, high cathodoluminescent efficiency has been obtained from particles with diameters as small as 0.2 μm .¹⁵⁻¹⁹ High cathodoluminescent efficiency has never been reported, however, for phosphors made from smaller nanoparticles [although high photoluminescent efficiency has been achieved in particles as small as 3 nm.^{6-9,11,20}

Here, we demonstrate 100-nm-diam particles of ZnS doped with Mn whose cathodoluminescent efficiency is similar to that of a commercial ZnS:Mn phosphor (Sarnoff Corporation, Princeton, NJ; comprised of particles 3–6 μm in diameter). The nanoparticles of ZnS:Mn are 40% as bright as the commercial product. The results demonstrate four important principles: (1) highly efficient cathodoluminescent phosphors can be made with particles as small as 100 nm; (2)

using nanoparticles as precursors, we obtain excellent luminous performance with very low annealing temperature (535 °C vs >1000 °C for standard materials); and (3) we obtain reduced current saturation. Finally, (4) we provide evidence that the "dead layer," which is blamed for the poor low-voltage efficiency of phosphors, does not completely surround the particles, but lies only at the surface first hit by the incident electrons. Hence, the small particle size is apparently not a hindrance to good low-voltage performance. We propose that these conclusions might also apply to nanoparticles of other phosphor materials with chromaticities suitable for full-color displays.¹⁹

Nanoparticles of ZnS:Mn were prepared by precipitation inside the nanometer-sized aqueous pores of the bicontinuous cubic phase of a water-surfactant mixture.^{8,21,22} All samples discussed here were made with the MnCl₂ to ZnCl₂ ratio set to 0.7 mol % in the initial aqueous solution and Na₂S provided the sulfide ions. Some samples were also doped with 0.06 mol % CuSO₄. (These concentrations have yet to be optimized.) The nanoparticles were capped by dispersing them in water and adding ZnCl₂ (one quarter the weight of the ZnCl₂ in the initial solution) and NaOH ($p\text{H} \sim 10$, for approximately 10 min before washing) to form a thin layer of ZnO around the particles. (Particles capped in this way were substantially brighter than uncapped particles. Details will be published later.)

All samples discussed here were annealed in vacuum at 10^{-6} – 10^{-7} Torr in a ceramic crucible for 35 min at a maximum temperature of 535 °C. In contrast, commercial phosphors are typically fired at temperatures in excess of 1000 °C.²³ The as-synthesized nanoparticles exhibited the zinc-blende structure; after annealing to just 400 °C, approximately half of the sample had converted to wurtzite, which is the structure of the commercial phosphor. In bulk ZnS, however, the zinc-blende-to-wurtzite transition occurs at 1020 °C.²³ The significant reduction in the transition temperature appears to be another example of the remarkable thermodynamic properties of nanoparticles.²⁴ Further details of the structural changes of undoped ZnS nanoparticles upon annealing will be published.²⁵ Upon annealing the nanoparticles, we observed a dramatic increase (by a factor of several hundred) in luminescence, approximately coincident

^{a)}Center for Bio/Molecular Science and Engineering, Code 6930.

^{b)}Electronic mail: tdd@cblmse.nrl.navy.mil

^{c)}Chemistry Division, Code 6170.

^{d)}Electronics Science and Technology Division, Code 6844.

^{e)}Condensed Matter and Radiation Division, Code 6683.

^{f)}Current address: The Sarnoff Corp., 201 Washington Rd., Princeton, NJ 08543.

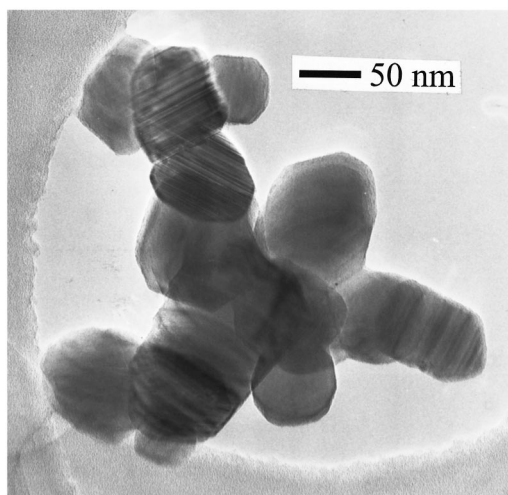


FIG. 1. Transmission electron micrograph (TEM, 200 kV) of ZnS:Mn/ZnO nanoparticles after annealing in vacuum to 535 °C. The average particle diameter ranged from 85 to 100 nm in different batches.

with the change in the ZnS crystal structure. The ability to anneal nanoparticles at low temperatures is an important technological advantage and potentially allows annealing in a fluidized bed or on a (glass) screen.

The annealed particles were regular in shape with average sizes between 85 and 100 nm (Fig. 1). Average crystallite sizes were 15–20 nm and were measured by fitting x-ray (Cu $K\alpha$ radiation) diffraction peaks to the Scherrer formula, as previously described.²² The annealed powder was light tan in color. Results of electron paramagnetic resonance (EPR), x-ray absorption fine-structure (XAFS), and x-ray photoelectron spectroscopy (XPS) measurements will be published later.

Cathodoluminescence measurements were performed on powder patches approximately 1 cm in diameter and 0.5–1 mm thick on indium tin oxide (ITO) coated glass plates. Plates were mounted in a grounded high-vacuum chamber (2×10^{-7} Torr) and excited with a beam of electrons from a filament electron gun with voltages between 0.5 and 3.5 kV. A bias voltage of +150 V was applied to the plate to recapture the secondary electrons. The electron-beam voltages will henceforth refer to the total acceleration voltage, equal to the 150 V bias plus the gun voltage (hence, 650–3650 V). The electron beam hit the sample from above and the emitted light was collected from the side. The sample plate was rotated so that it faced 45° from vertical. Electron-beam currents (dc) ranged from 1 to 40 μA and were measured using an electrometer attached to the indium tin oxide-coated plate. The area of the electron-beam spot was approximately 0.2 cm^2 . A calibrated Minolta CS-1000 spectroradiometer (diameter of detected spot: 0.3 cm) measured the emission spectra and the luminance in absolute units. In every case, the emission from the nanoparticles was compared to the emission from a similar-sized powder patch of a ZnS:Mn phosphor made by the Sarnoff Corporation. The peak wavelength of the cathodoluminescence from the nanoparticles was 582 nm (similar to the commercial phosphor, which peaked at 580 nm) and the Commission Internationale de l'Éclairage (CIE) 1931 color coordinates were $x = 0.53$ and $y = 0.47$. The luminance of all samples appeared yellow to the eye.

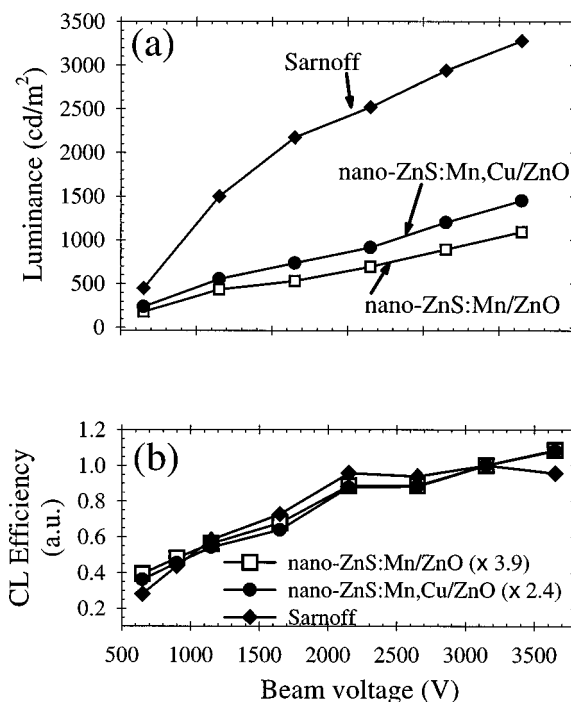


FIG. 2. (a) Luminance vs voltage for two annealed nanoparticle phosphors compared to that of the commercial phosphor (Sarnoff). The electron-beam current ranged between 25 and 40 μA . The nanoparticles were annealed at just 535 °C. (b) Luminous efficiency vs beam voltage at $\sim 2.5 \mu\text{A}/\text{cm}^2$. The efficiencies are scaled as indicated relative to the commercial Sarnoff material. The nanoparticles and large particles have very similar efficiency–voltage characteristics between 650 and 3650 V.

The measured luminance of our nanoparticle phosphors and the commercial ZnS:Mn phosphor are shown in Fig. 2(a). The luminance of the nano-ZnS:Mn/ZnO sample was 180 cd/m^2 at 650 V and 25 μA (approximately 125 $\mu\text{A}/\text{cm}^2$), within approximately 40% of the commercial phosphor. The luminous efficiency of our nanoparticles is 2.2 lm/W at 1 kV and 1 $\mu\text{A}/\text{cm}^2$, according to measurements by Penczek and Wagner of Georgia Technology Research Institute. Their measurements of the relative efficiencies of the commercial and nanophosphors at low current were consistent with those reported here. We found that adding 0.06 mol % CuSO_4 to the precursor solution to make nanoparticles of ZnS:Mn, Cu increased the luminance by approximately 30%, to 240 cd/m^2 at 650 V and 25 μA . The emission spectrum did not change. The added Cu is thought to improve the energy-transfer efficiency.²⁶

The voltage dependence of the nanoparticles' luminous efficiency provides some insight into the mechanism of the nearly universally observed loss of efficiency at voltages below 2 kV. In Fig. 2(b), we plot the luminous efficiency (in arbitrary units) versus electron-beam voltage. The current density was $\sim 2.5 \mu\text{A}/\text{cm}^2$ and the efficiency was set to 1 at 3150 V for each sample. For the nanoparticles and for the larger commercial particles, the efficiency increased by a factor of approximately 3 when the voltage increased from 650 to 3650 V. We now discuss explanations for this behavior. The low efficiency at low voltages has been attributed to a nonluminescent “dead layer” on the surface of the particles or of the powder patch. The location and composition of the dead layer are not fully understood.^{13,23,27–32} At low voltage, much of the energy of the incident electrons is ab-

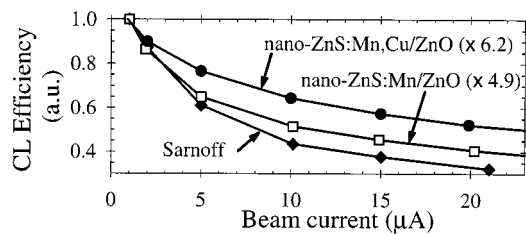


FIG. 3. Luminous efficiency (arbitrary units) vs beam current. The efficiencies are each defined to be 1 at $1 \mu\text{A}$ (although the Sarnoff is approximately $5\times$ more efficient at $1 \mu\text{A}$, as indicated by the scale factors on the plot). The beam voltage is 1150 V and the beam spot size is 0.2 cm^2 . The nanoparticles saturate less than the commercial phosphor.

sorbed inside the dead layer, so that the efficiency is low. Estimates of the penetration depth of electrons in ZnS are 2 nm at 650 V and 140 nm at 3650 V.³³ With *large, micron-sized* particles, as the beam voltage is increased, the electrons penetrate farther into the solid, thus depositing their energy farther from the surface dead layer and increasing the luminous efficiency. With *nanoparticles*, when the voltage is large enough so that the penetration depth exceeds the particle size, the incident electrons pass through multiple particle surfaces, and therefore, still deposit much of their energy near surfaces. Thus, if the dead layer completely surrounds the small particles, their efficiency should not increase with voltage as much as it does for the micron-size particles. If, on the other hand, the dead layer occurs only at the first surface encountered by the electrons (i.e., at the interface between the vacuum and phosphor screen), then the nanoparticles would exhibit the same efficiency–voltage characteristic as the larger particles. The latter model is consistent with our results.

Finally, the luminous efficiency is plotted versus electron-beam current (at 1150 V) in Fig. 3. We define the efficiency of each sample to be 1.0 at $1 \mu\text{A}$ in order to highlight differences in the saturation behavior. At high current densities, the luminescent centers tend to saturate, reducing the luminous efficiency. We find that the nanoparticles saturate substantially less than the commercial phosphor. At a current of $20 \mu\text{A}$, the nano-ZnS:Mn, Cu/ZnO efficiency decreased to approximately 52% of its $1 \mu\text{A}$ value, compared to 40% for the ZnS:Mn/ZnO nanoparticles, and as low as 30% for the Sarnoff phosphor. Thus, although the commercial phosphor is five times more efficient at $1 \mu\text{A}$, it is only 2.5 times more efficient at $25 \mu\text{A}$. With increasing current, the efficiency of the nanoparticles approaches that of the commercial phosphor. Reducing current saturation is very important for development of successful phosphors for FEDs, since they should operate under pulsed electron-beam excitation with average current densities up to $100 \mu\text{A}/\text{cm}^2$.³⁴

In summary, the cathodoluminescent efficiency of the reported ZnS:Mn nanoparticles (or nanophosphors) was within 40% of the commercial Sarnoff sample at 650 V and approximately $125 \mu\text{A}/\text{cm}^2$. Optimizing the Mn concentration and purity will yield further improvement in the nanophosphors' cathodoluminescence. Furthermore, the nanophosphors exhibited significantly reduced current saturation. Finally, the nanophosphors were fired to just 535°C , hundreds of degrees less than the firing temperatures used in

commercial processes. In short, using nanoparticles, one can attain the high luminous efficiency (which has frequently been associated only with larger particles) and also benefit from very low processing temperature and small particle size. These qualities should make nanoparticles attractive for use in new high-resolution display technologies.

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