

Degradation and local distortions in electroluminescent ZnS:Cu,Cl phosphors

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Abstract. We present time-lapsed microscopy and EXAFS/XANES data on size selected ground ZnS:Cu,Cl and ZnS:Cu,Mn,Cl phosphors to probe long standing problems in using these phosphors in high brightness applications. The time-lapsed study shows that many of the individual emission centers on each particle degrade via large step decreases while $< 50\%$ have a monotonic decrease. These large steps suggest a break-up of Cu aggregate centers and this degradation mechanism is likely irreversible. The Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption near Edge Structure (XANES) studies show that during grinding, the CuS precipitates within the ZnS host become highly disordered yet the host material shows no disorder, suggesting that the ZnS:Cu,Cl materials cleave through the CuS precipitates during grinding.

1. Introduction

The doped ZnS phosphors (ZnS:Cu,Cl and ZnS:Cu,Mn,Cl) have been used in commercial low-light applications for many years following extensive studies of these materials in the 50's-70's[1, 2]. They have the unusual property that electroluminescence can be excited by relatively low AC E-fields, whereas the E-fields required for DC excitation are about two orders of magnitude larger. The low E-field operation is attributed to a large E-field enhancement around the tips of conducting CuS needle-like precipitates[3]. For typical particles 20-30 μm in diameter in a layer 30-50 μm thick, AC voltages of order 100V are required.

The AC electroluminescence (AC EL) for ZnS:Cu,Cl is blue-green for low AC frequencies (500Hz) but becomes bright blue at high frequencies $\sim 50\text{-}100$ kHz[3, 4, 5]. The brightness at first increases nearly linearly with AC frequency but saturates by 100 kHz[6]. Although very useful for low-light applications, two long standing problems have limited the usefulness of these phosphors for a broader range of applications. First, the devices age with the number of AC cycles[7, 8] so for high brightness operation (high AC frequencies) the emission from a typical device can decrease to 20% in less than a day; surprisingly the degradation can be partially reversed by a thermal anneal near 180 $^{\circ}\text{C}$ [6]. Second, the particle sizes presently in use (20-30 μm) are a compromise between obtaining good brightness and keeping the required voltage relatively low. It would be desirable for many applications to operate at lower voltages ~ 10 V; however decreasing the particle size by grinding, such that much thinner devices can be made with the same internal fields, leads to poorer emission[2]. Because of the increased need for low-voltage, low-energy-consumption, solid state lighting, we have reconsidered these problems with a goal to circumvent them once the mechanisms are better understood.

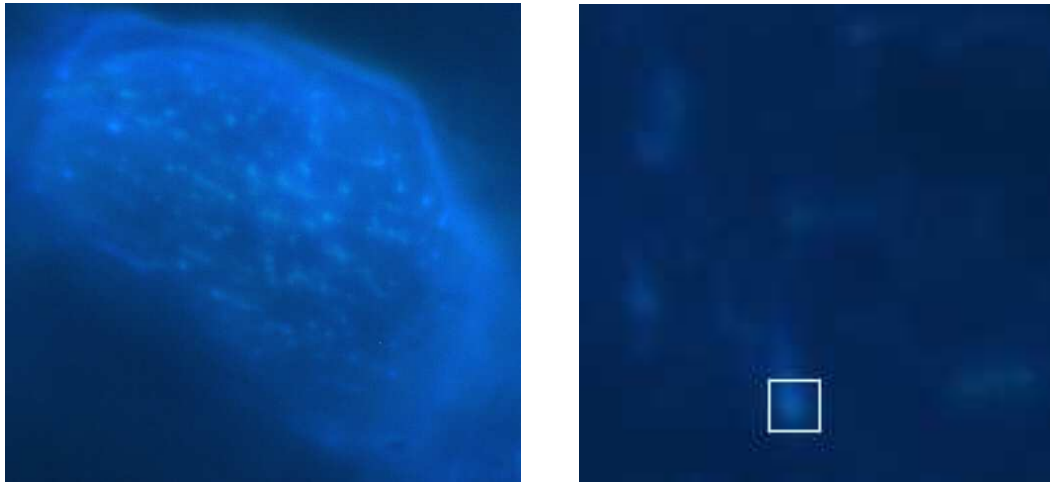


Figure 1. Left: An oil immersion microscope picture of a few particles inside an active device operating at 100 kHz; the size of the picture is $\sim 30 \mu\text{m}$ square. Right: a high magnification picture (different particle) showing the area of integration (white box) around a bright spot. Picture size: $\sim 10 \mu\text{m}$ square.

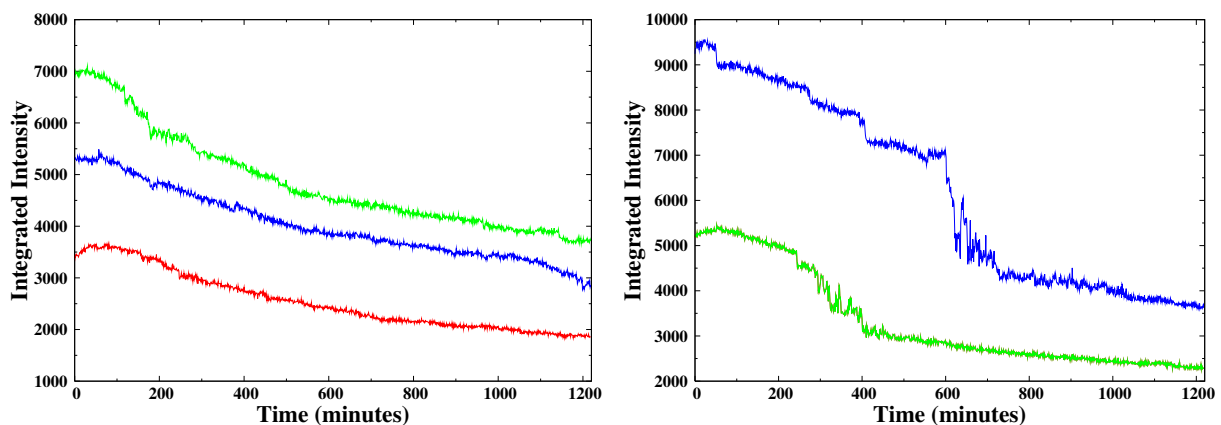


Figure 2. Left: The decay with time of the integrated intensity for three emission centers in the same particle (top to bottom: centers 5, 25, 4); here the decay is essentially monotonic and no large steps are observed. Right: Other examples from same device showing ragged steps in the integrated intensity vs time plots (top to bottom: centers 20, 24, 17). Most of the steps are downward but a few small upward steps are observed.

2. Time-lapsed microscopy

Earlier studies of “maintenance” [7, 8] and our previous studies of degradation and rejuvenation [9, 6] all used the entire light output from a large number of particles. The AC EL emission spectra are complex and the shape changes with the applied AC frequency. However for a given frequency – e.g. 100 kHz – the spectrum is unchanged as the emission output degrades down to 20% and also does not change when a degraded device is subsequently partially rejuvenated (via a 180°C anneal for 2 hours) and the output increases to 60-70% of initial brightness. From these studies we argued [6] that some type of E-field enhanced diffusion must be the main mechanism.

As shown in Fig. 1:Left, the brightness from a single ZnS:Cu,Cl particle is not uniform

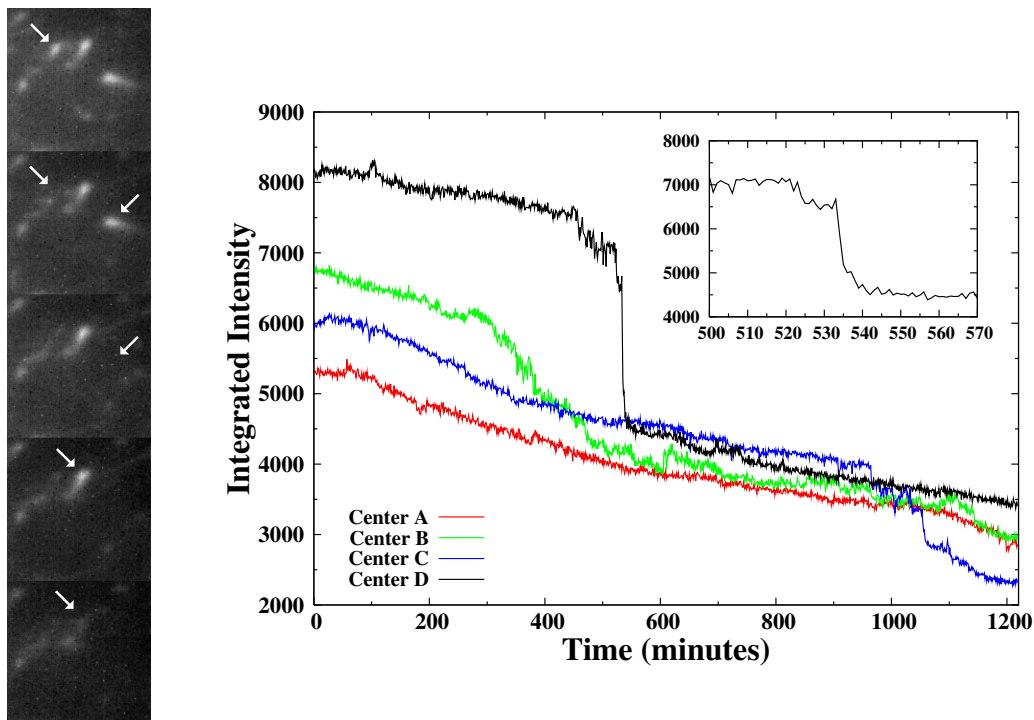


Figure 3. Left: Series of microscope time-frame pictures, showing sequences where a bright emission center turns off; times 300, 500, 700 900 and 1100 min. Right: Plots of integrated intensity vs time for four of these centers, showing the drop in intensity for three of them (centers B, C, and D). The inset shows a zoomed image of the very sharp drop-off for center D at 534 minutes.

across the particle; instead, the blue light emanates from a few bright points within each grain. It was not clear whether all emission points decay at nearly the same rate. Since the CuS needle-like precipitates likely have varying sizes and do not have the same orientations, the local E-fields are not expected to be the same and some variation in the output decay with time was expected. However, we had noted previously[6] that from a few microscope pictures, the number of observable bright spots (that were above the camera threshold) decreased with time at a rate comparable to the decay of the total integrated intensity.

To address the decay mechanism for individual emission points we took a large number (~ 1500) of microscope images of a few particles over a 20 hr period while the device was degrading. This was repeated for several devices. For the data shown here each frame is an average over four sec. and the frame spacing is 1 min. In all cases we found large variations in the decay vs time for bright spots within the same particle. To quantify the brightness, the intensity was integrated over a small square or rectangular area that enclosed the bright spot; such an area is shown in the enlarged image shown in Fig. 1:Right.

Some bright spots did decay monotonically with slightly different rates (Fig. 2:Left) – such decays must correspond to incremental changes – likely from simple hole or electron trap states diffusing slowly out of the local high E-field region about the tip of a CuS needle. However fewer than 50% of the bright spots decayed in this (likely reversible) manner. Most had some

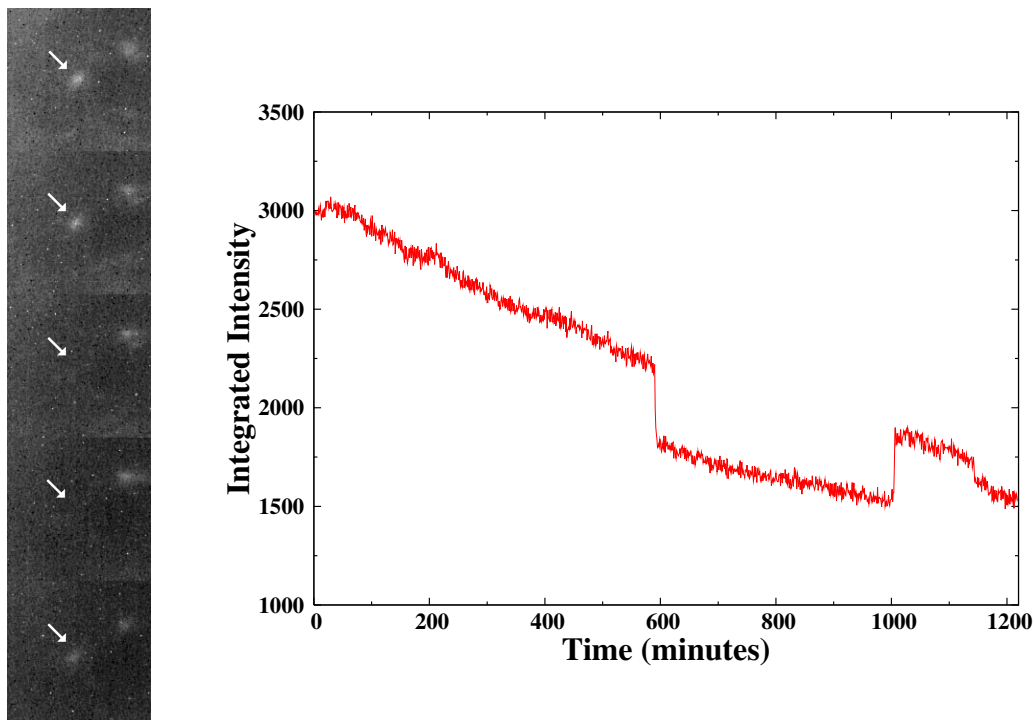


Figure 4. Left: Sequence of five frames, 200 min. apart showing an emission center (in middle of each frame) that disappears and then reappears. Right: the integrated intensity as a function of time showing the sharp drop near 580 min., and the rapid rise just above 1000 min.

type of step change as shown in Fig. 2:Right - some very fast, while other steps take place over many minutes (50-100 min.). In Fig. 3:Left we show a series of frames, (at 300, 500, 700, 900, 1100 min), that show three spots that disappear relatively quickly. Fig. 3:Right shows the time dependence of four emission centers; center B (green) that has a step between the first and second frames, center C (blue) that steps done between the fourth and fifth frames, and center D (black) the right hand spot that disappears in the third frame. The inset shows the very sharp drop for center D. Note that as in Fig. 2:Right, there are quite large fluctuations in these transition regions.

The results of the time-lapsed microscopy show that the local degradation of the AC EL is not a simple smooth decay. Although some emission centers in a particle do decrease monotonically, other centers within the same particle - only a few microns away, can have a rapid, but irregular decay over a short interval of time compared to the overall decay constant. Occasionally there can also be a significant step increase in the intensity - see Fig. 4 near 1000 min., but this is rare compared to the step decreases. This indicates at least two distinct mechanisms are present. To explain the very slow, nearly monotonic intensity decrease for some centers, some defects must diffuse slowly such that each step results in a small intensity change. It is likely that such a diffusion process is reversible and contributes to the rejuvenation observed after an anneal at 180°C. However the large step decreases likely indicate irreversible changes - such as the break-up of aggregate Cu centers. Although the large changes are occasionally reversible, large increases of the luminescence are rare.

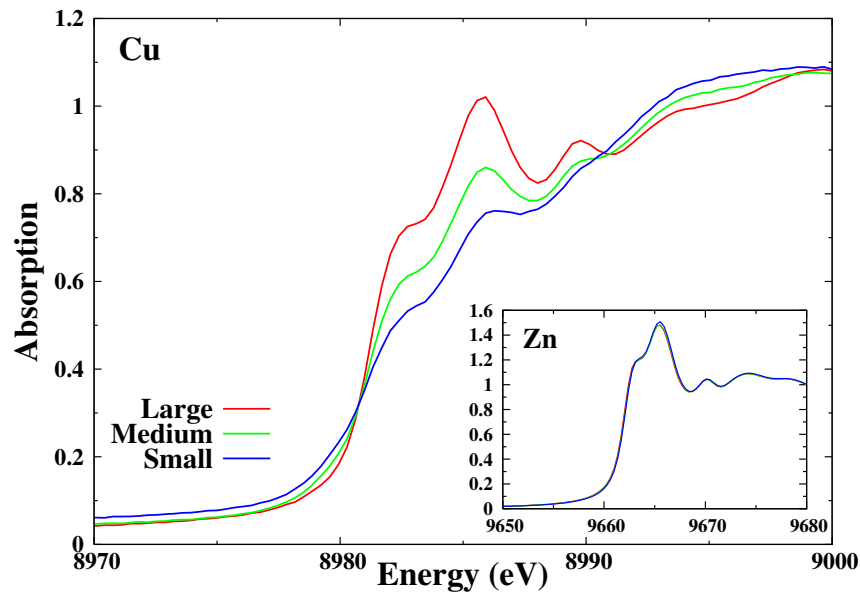


Figure 5. A plot of the XANES regions for the Cu K-edge showing the loss in detail as the particle size decreases from large to small. The inset shows similar data at the Zn K-edge of the host - there is no significant difference in the shape of the Zn-XANES for any of the samples. A similar negative result (not shown) was observed for the Mn dopant in ZnS:Cu,Mn,Cl.

3. XANES/EXAFS study of size separated particles

The second continuing problem for the use of ZnS:Cu,Cl in many bright light applications is the lack of small particles that have good AC EL efficiency. Particles of order 1 micron would reduce the required AC voltages by at least a factor of 10 (i.e. applied voltage could be ~ 10 V for a thinner device) and power consumption would go down. Although a slight reduction in size does allow somewhat lower voltages[10], we verified that using small particles $< 1 \mu\text{m}$) greatly reduces the AC EL emission, even for a relatively thick layers of such particles.

Our first Cu K-edge EXAFS and XANES studies on materials that had been ground for various times suggested some changes occurred in the local structure, but the results varied from one sample to another. To better address the particle size issue we size selected the particles into three groups; small ($< 1 \mu\text{m}$), medium ($\sim 10 \mu\text{m}$), and large ($\sim 20 \mu\text{m}$), either as made or very lightly ground. The XANES and EXAFS data then showed very clear changes and are presented here.

3.1. EXAFS/XANES technique

X-ray absorption data were collected at Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 10-2 using small slits (0.5 mm) and a Si (1,1,1) double monochromator, to obtain an energy resolution ~ 1.3 eV. The Zn K-edge data were collected in transmission mode while the Cu K-edge data were collected in fluorescence mode using a Ge multi-channel detector because of the very low Cu concentration – 0.15% Cu. For the ZnS:Cu,Mn,Cl samples which had an additional 5% Mn added, we also used the fluorescence technique for the Mn K-edge. For the XANES, the absorption data were normalized above the edge and then plotted over a small energy range about the edge. The EXAFS data were reduced using standard techniques, converted to k-space and then Fourier Transformed (FT) into r-space. The FT ranges are $4\text{-}13.5 \text{ \AA}^{-1}$ at the Zn K-edge and $3.5\text{-}11.35 \text{ \AA}^{-1}$ at the Cu and Mn K-edges.

3.2. XANES and EXAFS data

In Fig. 5 we plot the XANES data at the Cu K-edge for the three particle sizes. There is a clear change; the structure in the main edge decreases significantly as the particle size decreases. In contrast the Zn K-edge XANES for the host material shown in the inset, shows no change with particle size and a similar result (not shown) was also observed for the Mn K-edge in ZnS:Cu,Mn,Cl. The structure in the XANES spectrum usually arises from multi-electron scattering within an ordered cluster of atoms, typically 5-7 Å in radius. The calculated XANES for small clusters of 2-3 shells often has little structure. Thus the loss of structure for the Cu K-edge suggests that the CuS precipitates have been damaged by grinding, while the lack of change for the Zn K-edge (and also Mn) indicates that most of the small ZnS particles remain well ordered – the particle size is large enough that there is a negligible fraction of Zn sites in the surface layer of each particle. The results for the Mn K-edge suggest that few of the Mn sites are damaged via grinding, consistent with our previous result that Mn is a substitutional defect and therefore should substitute uniformly throughout the ZnS material.

Similar results are obtained from the EXAFS data shown in Fig. 6:Left. As the particle size decreases, the amplitude of both the first and second peaks decreases and in addition, there is also a shape change in the 2-2.5 Å shoulder region. In contrast the inset shows there is no observable change with particle size for Zn K-edge EXAFS (a similar lack of change is again observed for the Mn K-edge EXAFS in ZnS:Cu,Mn,Cl). The shoulder observed for the large particles (2-2.5 Å) is associated with well ordered CuS particles and observed for bulk CuS. The rapid disappearance of this shoulder is surprising.

To provide more insight we compare the disorder introduced via grinding (Fig. 6:Left) with thermally induced disorder for the “as-made” material in (Fig. 6:Right). The thermally induced disorder of the second main peak (mostly Cu-Cu) is comparable for the two figures. However for the ground and size separated samples (Fig. 6:Left), the shoulder in the 2-2.5 Å region completely disappears even for the medium size particles and in addition to the amplitude reduction, the shape of the main peak changes. We can fit the 100 and 200K traces using the 3K data as a reference file (1.1-2.1 Å) and obtain excellent fits. However, because of the shape change for the ground material, similar fits are poor; χ^2 for the fits are factors of 20-80 larger than for the thermally disordered samples. These results indicate a significant change in the local structure about Cu even though no obvious change occurs for Zn (or Mn), and is consistent with the large structural change inferred from the XANES data.

How can the local structure about Cu change dramatically with grinding and yet the local environment within the host material (Zn K-edge) and around another substitutional dopant, Mn, be unchanged? The most likely answer is that in the grinding process the crystallites of ZnS fracture through the CuS precipitates. It is well known that zinc blende crystals cleave easily along the (1,1,1) planes and earlier studies also suggest that the CuS-like needles appear to be oriented along [1,1,1] directions[2, 3]. Further we have found that an 18 Å thick layer of CuS can be inserted into the ZnS structure along the (1,1,1) plane with very little strain. However even a little strain will make cleavage along such a plane more likely. Cleavage through a CuS precipitate will reduce the size of the precipitate, introduce disorder, and leave parts of it on the surface, which will make those precipitates relatively inactive as emission centers.

4. Conclusions

The time-lapsed microscopy pictures and the XANES/EXAFS results for ground and size-separated particles of ZnS:Cu,Cl and ZnS:Cu,Mn,Cl clarify two outstanding problems that limit the usefulness of these phosphors for high brightness applications. The time-lapsed microscopy shows that the individual emission centers do not all degrade slowly and monotonically; instead a large fraction suddenly decrease at some point during the degradation, and only rarely is this reversed. Such large changes in the emission center intensity must correspond to the break-up

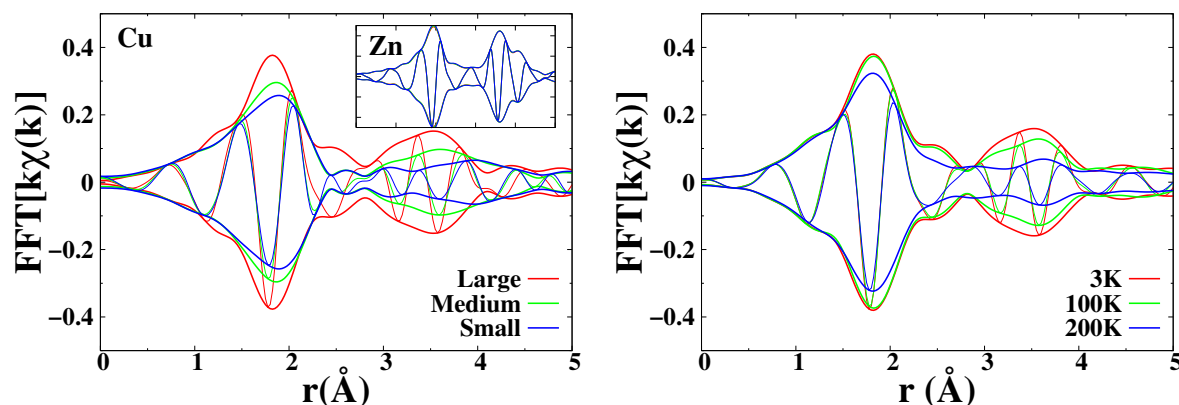


Figure 6. Left: A plot of the Cu K-edge EXAFS for the three sizes of particles; the amplitude decreases significantly. The plot for the large particles has a large shoulder at 2.5 Å which we previously identified with CuS precipitates. The inset shows corresponding data at the Zn K-edge; as for the XANES, there is no observable change in the Zn EXAFS with particle size. Right: The Cu EXAFS for the large particles as a function of temperature showing the effect of thermally induced disorder.

or change of some highly efficient luminescence centers. Our earlier rejuvenation studies show that the material can only be partially rejuvenated; it is likely that the break-up of complex aggregate Cu emission centers is the reason for this lack of reversibility.

For the size-separated ground samples, the large changes in the Cu XANES and EXAFS, but no change for Zn or Mn data, suggest that the phosphor particles cleave through the CuS precipitates. Consequently making smaller particles via grinding is not viable. We are presently making nano-particles of Cu-doped ZnS materials[11] to try to avoid some of the above problems.

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