



## Local degradation of electroluminescent emission centers in ZnS:Cu,Cl phosphors

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### ABSTRACT

ZnS:Cu contains needle-shaped, CuS conducting nano-precipitates along the [111] planes which amplify the applied electric fields near the tips when the field is reversed, enabling AC electroluminescence for  $\sim 50 \mu\text{m}$  thick devices at AC voltages of  $\sim 100 \text{ V}$ . Unfortunately, the degradation process is poorly understood; previous studies using photodiode measurements were only able to determine the overall device degradation. Here, we analyze many individual emission centers using time-lapse microscope images of several degrading devices. We find that most of the individual emission centers have large, sudden, discrete drops in luminosity and many have a luminosity that actually increases significantly, minutes to hours after a drop. This suggests that there are two primary degradation mechanisms: gradual multi-step diffusion of single-atom trap states away from the high-field region (causing the gradual decrease in luminosity) and the sudden break-up and reformation of complex trap states within the high field region (causing the sudden decreases and increases, respectively).

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### 1. Introduction

Doped ZnS phosphors such as ZnS:Cu,Cl have been studied intensively since the 1950s and 1960s when it was discovered that these materials exhibit AC electroluminescence (AC EL) at much lower applied AC voltages than is required for DC EL [1,2]. For a relatively thick  $50 \mu\text{m}$  layer, the minimum AC square wave voltage for electroluminescence to occur is  $\sim 50 \text{ V}$  [3]; this corresponds to an applied electric field of about  $10^4 \text{ V/cm}$ , roughly two orders of magnitude lower than the  $2 \times 10^6 \text{ V/cm}$  threshold for DC EL in ZnS [4]. Since Cu has a very low solubility in ZnS,  $\sim 0.04\%$ , a majority of the Cu atoms precipitate out for higher concentrations and form needle-shaped conducting CuS nano-precipitates along [111] planes within the insulating ZnS host [5]. These CuS nano-precipitates enhance the local electric fields near their tips (especially during periods of field reversal), enabling low-voltage EL.

The remaining Cu dopants that do not precipitate out form hole-traps, at least some of which have been shown to be in Cu complexes, from Raman spectroscopy measurements which indicate  $C_{3v}$  symmetry [6]. Meanwhile, isolated Cl (or Br or Al) co-dopants form shallow electron-traps. The existence of more than one type of trap state helps to explain the presence of the four different emission lines that are seen [1,2,7,8].

It is believed that the optical emission is due to electron–hole recombination from the electron and hole trap sites which are in the high field region in the vicinity of the tips of the CuS

precipitates. With AC excitation, electrons and holes are injected into the ZnS in equal numbers via field emission from opposite ends of the CuS nano-precipitates and are trapped in their respective trap sites. Each time the field is reversed, some of these injected electrons recombine with holes trapped during the previous half cycle, emitting light [5].

Unfortunately, the usefulness of doped ZnS phosphors for high brightness applications is limited by the fact that the devices degrade to 10% of initial brightness over a short 20 h when run at 100 kHz [9,10]. Previous studies have shown that degradation proceeds faster at higher applied frequencies and when the device is run at higher temperatures [11–13,8]. After degradation, the devices can be rejuvenated back to 70–80% of initial brightness by annealing for about an hour at  $185^\circ\text{C}$ , with higher temperatures or longer times both resulting in a gradual decrease of EL. Further, devices can be degraded and annealed multiple times, each time permanently losing 20–30% of the initial brightness, until it is no longer worthwhile [8]. However, the degradation mechanism or mechanisms remains an unsolved problem even after more than 50 years.

The degradation and ability to subsequently rejuvenate, along with the fact that degradation of the material does not occur over long times under comparable applied DC fields ( $\sim 100 \text{ V DC}$ ) suggests that some type of electric-field enhanced diffusion during field switching in AC operation is primarily causing the degradation. Some popular degradation mechanisms include sharp CuS tips becoming blunted, decreasing numbers of hole and/or electron trap sites (Cl, Br, or Al co-dopant) in the high field region about the CuS nano-precipitates, Cu complexes (hole trap sites) becoming damaged, and local damage to the ZnS host.

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Previous studies of electroluminescent degradation focused on the device as a whole, using the entire light output from thousands of particles, each containing dozens of individual emission centers [8,14]. However, observing images taken during degradation, it was found that the number of visible emission centers decreased as the device degrades [8]. It is not known whether each emission center's light output decayed in the same way or if some sites decayed faster than others leading to the above observation. Due to the fact that the CuS nano-precipitates vary in size and orientation, the local electric fields must vary significantly throughout the device. Thus, it would not be surprising if individual emission centers simply degraded at different rates.

In this work, we investigate the degradation of many individual emission centers in a number of bulk particles ( $\sim 20\text{--}30\ \mu\text{m}$ ) for several devices. Using an oil immersion optical microscope with a magnification of  $60\times$  and a depth of focus of  $\sim 10\ \mu\text{m}$ , we took 4 s exposures at intervals ranging from every 5 s (at the beginning of the degradation) to every minute (towards the end of the degradation) for 24–100 h, giving us about 2000 images per degradation. Some preliminary results from one run were presented in conference proceedings [15]. There we noted a few bright points that turned off and on. Here we show that this is a much more general behavior and occurs over most of each particle. We took two separate approaches in analyzing these extensive data sets.

AC EL devices were fabricated using commercially available blue-green emitting ZnS:Cu,Cl phosphor from Osram-Sylvania and Osram-Sylvania EL binder with a superstrate device structure on glass slides. Phosphor material was mixed with binder by mass at a ratio of  $m_{\text{ph}}/m_{\text{bi}} = 0.55 \pm 0.02$ . Layers silver paste contact, phosphor material, and transparent PEDOT contact were each applied using doctor blading using Scotch tape to control the wet film thickness. After applying each layer the devices were annealed in a vacuum oven at  $110^\circ\text{C}$  and  $\sim 1\ \text{Torr}$  for 30 min. Completed active device area was  $3\ \text{mm} \times 3\ \text{mm}$ .

## 2. Intensity measurements

We subsequently identified a large number of emission centers (40–80 per image) in each set of exposures by looking at several images—not just the initial image. Then, we integrated the number of counts within a  $0.5\text{--}1.0\ \mu\text{m}^2$  ( $\sim 150$  pixel) rectangle around each point, as shown in Fig. 1. We next plot the intensity as a function of time for each identified emission center. While the light output from some emission centers decayed in rough agreement with the exponential decay for the device as a whole [8], these accounted for fewer than 50% of the emission centers. Instead, most individual emission centers exhibit sharp changes in their light output.

In Fig. 2 we plot the intensities for several emission centers with monotonically decreasing luminosity, including sharp drops. In many cases (including the drop shown in Fig. 2B), all of the drop occurs in less than the time between exposures (5–60 s); even in cases (such as Fig. 2A) where the drop takes place over the course of several exposures, it is still quite short compared to the hours-long device degradation. However, these sharp drops were not the only unexpected behavior visible. Some of the emission centers also showed sudden increases in luminosity, often turning off and back on several times during the device degradation, as can be seen in Fig. 2C and D. In Fig. 2C, note that there are two small, rapid blinks, slightly later in the degradation (between 12 and 15 h) and two shorter blinks within the inset. In Fig. 2D, the increase in intensity near 30 h seems to be equal to several of the previous drops. Often, this blinking happens at the end of the life of that emission center, but in some cases (as in Fig. 2C) the emission center continues to emit light for a long time after blinking.

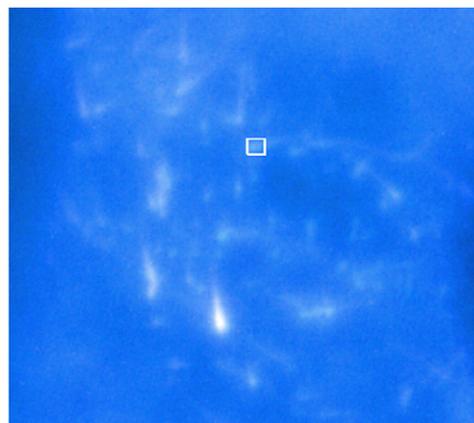


Fig. 1. A small phosphor particle from within a larger image. Note that the resolution of the emission centers is limited by diffraction; the actual emission centers are likely much smaller than they appear. The white box indicates an example integration region, of which this particle would contain about 20.

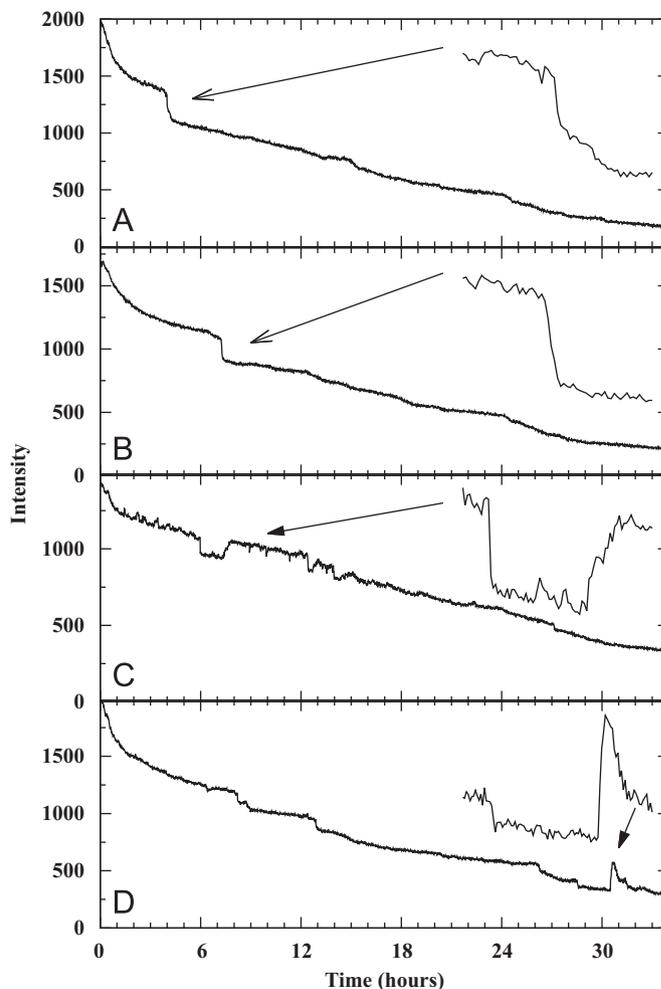


Fig. 2. Intensity for several emission centers, with enlarged inserts showing the occasionally abrupt behavior in detail. In A and B we see only gradual decay and sharp drops in luminosity, while in C and D we also see large increases in luminosity, or blinking.

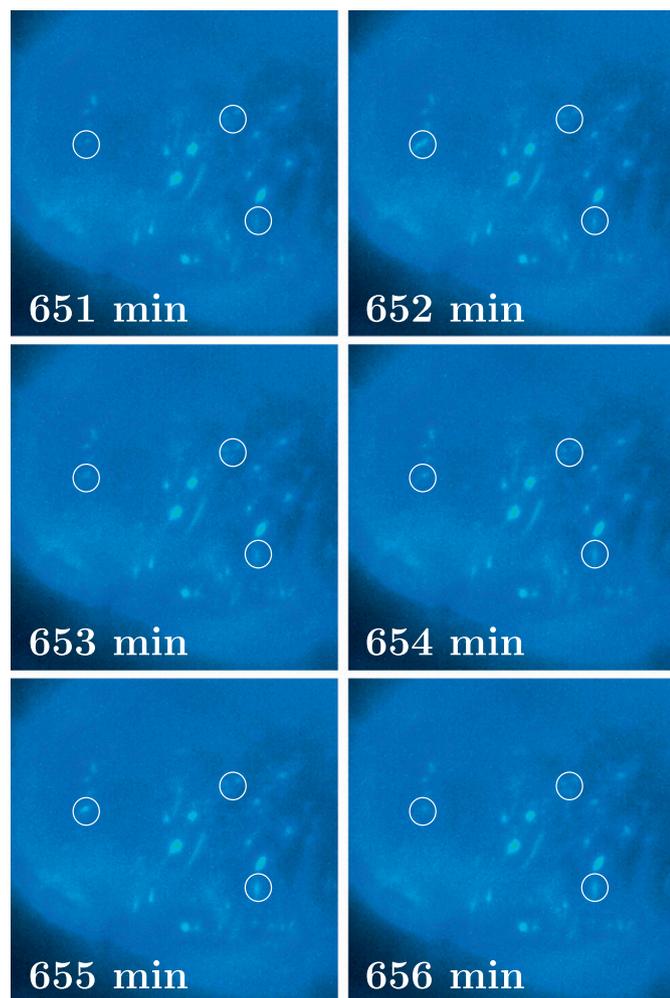
Unfortunately, the large variations in the scattered light within each particle result in a background which varies greatly with both time and locations, prevented us from being able to accurately subtract off the background to truly isolate the

individual emission centers. Thus, it is unclear how much of the smooth decaying behavior is due to the individual particle gradually dimming, versus scattered light from elsewhere in the device creating a slowly decaying background.

This method clearly worked well when the device did not move throughout the data collection. However, due to the fact that many individual emission centers blinked off and on repeatedly, it was not feasible to implement drift-tracking and to produce graphs for those devices that, for one reason or another, had drifting of the optical system during the course of the data collection.

### 3. Video analysis

Our second approach was to take crops of 5–8 individual particles within each image and combine them into a video at 30 fps, speeding up the degradation by a factor of  $150\times$ . This made it easy for the naked eye to pick out emission centers – even dim or slightly unfocused ones – that are turning off, turning on, or blinking on and off. Excerpted individual (original) frames showing this blinking are presented in Fig. 3. Full videos can be found in Appendix A, which is available online.



**Fig. 3.** Several images of the same particle over a short period. The circles are around emission centers with significantly fluctuating intensities. The circle at the left, in particular, is an example of an emission center that turns on and off twice within 5 min (on in 652 and 655). The top right circle contains three emission centers until 656 when another turns on and it contains four. The bottom right circle increases in brightness gradually from 651 to 655. This 5 min example is typical of many particles over their entire degradation.

These videos show that over the entire area of each particle there are significant intensity fluctuations—i.e. at some point in the decay, nearly every emission center shows significant intensity fluctuations.

Thus the videos, and to a lesser extent the short sequence of still images in Fig. 3, make it clear that the phenomenon graphed in Fig. 2 is not limited to one or two of the strongest emission centers in a few particles or devices, but occurs for most emission centers in every phosphor particle – it is a universal behavior.

### 4. Discussion

The extensive plots of intensity versus time for hundreds of emission points provides a new assessment of the degradation and provides a means of evaluating several distinct proposed degradation mechanisms, listed in Table 1. The fact that there are two primary degradation methods (sudden changes, down and up, and gradual decay) suggests that at least two different degradation mechanisms play major roles, and at least one of them is rapid and can be reversible. The rapid changes suggest a threshold effect and the ability to spontaneously start emitting again suggests that randomness is a significant factor.

The proposed blunting of the tips of the CuS nano-precipitates, which would cause a decrease in the electric field amplification, would be gradual and irreversible. Local damage to the ZnS host would also be gradual and, while it is expected to be reversible by annealing, it would be extremely unlikely to occur spontaneously during degradation. Diffusion of the trap sites out of the high field region would be reversible, but not rapid enough (due to the fact that it would take many hops, each with a random component, to exit the high field region).

To a lesser extent, the long-scale fluctuation in the degradation, as in Fig. 2B at  $\sim 12$  h and Fig. 2C at  $\sim 24$  h, suggest a process that is gradual and has a random component, such as the migration of single-atom trap states. Thus, the smooth decay that can be seen in every emission center is probably due to single-atom trap states slowly diffusing out of the local high field region, and suggest that the migration of trap states plays a larger role in the gradual degradation of the phosphor than tip blunting or damage to the ZnS host.

If some of the trap states are complexes, formed of several atoms or vacancies, the movement of a single atom or vacancy only a short distance away from the complex center might damage a complex site and thereby quench emission. Thus, the large rapid changes are most likely caused by damage to complex sites. Further, if a complex can be turned off by one of the atoms moving away from the cluster, then rapid blinking could easily occur if that atom hops back and forth. However, if one of the complex atoms/vacancies diffuses several lattice sites away from the complex, the site may become permanently damaged and not easily rejuvenated even by annealing. In addition, it has been proposed that if another defect diffuses to an active emission center, it might quench the strong emission. One suggestion [16], for example, is that if  $\text{Cl}^-$  diffuses close to a Cu, that site might become inactive. Such a quenching would also be rapid if it takes a single hop for the extra defect to join the active site; one

**Table 1**

Summary of the features of proposed degradation mechanisms. Only damage to complexes can be both rapid and reversible, due to individual atoms hopping short distances.

Proposed mechanism	Rapid?	Reversible?
Tip blunting	No	No
Trap migration	No	Yes
Damage to complexes	Yes	Partially
Host damage	No	Only under anneal

cannot differentiate between an atom leaving or joining a Cu complex – thereby causing a rapid quenching – or blinking if that atom hops back and forth between two sites.

Of the various degradation mechanisms proposed to date, only damage to the Cu complex is rapid and can be reversible, and thus we conclude that it must play the primary role in the apparent blinking off and on of individual emission centers and likely plays a significant role in the degradation of the device as a whole.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version of <http://dx.doi.org/10.1016/j.jlumin.2012.08.037>.

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