

Studies on the Infrared Emitting ZnCdS:Cu, In, Cl Phosphors - Phosphors for Marking, Coding, and Identification

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ABSTRACT

Zn_{1-x}Cd_xS:Cu_{0.03%},Cl infrared emitting phosphors have been synthesized by an aqueous thermal decomposition method. It was found that the emission band at 1000nm was sufficiently far into the infrared region that visible emission was minimized. This makes such infrared emitting phosphors attractive for developing for covert marking applications. Co-doping Zn_{1-x}Cd_xS:Cu_{0.03%} with In³⁺ increased the infrared emission intensity by up to 50% over that of the equivalent Zn_{1-x}Cd_xS:Cu_{0.03%} phosphor with no indium co-doping, with the highest intensities being where x = 0.7-0.8.

1. INTRODUCTION

The widespread availability of near-ultraviolet light and high brightness visible light emitting diodes has made the remote excitation of infrared emitting phosphors a practical possibility. Infrared emitting powder phosphors have long been known to have potential uses in marking, coding and identification but their development for general use was restricted because of the lack of cheap mobile excitation sources. For security of high value articles the advent of such portable sources facilitates infrared emitting phosphors to meet some of these marking and coding

requirements, especially in low light and poor visibility.

Phosphors dominated the displays and lighting industries for the last six decades, but with the demise of the plasma displays their use in the former is much reduced, however both fluorescent and the replacement white LED lighting are both very dependent on phosphors. Indeed white LEDs are found in not only lighting for buildings and domestic use but also for car headlights, in white goods such as fridges and of course street lighting and all the lights used in airports on runways and in all the terminals. Infrared lighting would find uses in security zones at night and also as lights for green houses in cold climates at night.

Among the advantages of IR phosphor powders is that they can easily be deposited by conventional techniques to form large areas, if required, either by simple settling techniques, or by inclusion in a binder suitable for screen printing which is transparent over the required spectral ranges for the excitation and emission of the phosphor particles. Such layers, depending on thickness and particle size etc., can be used in a transmission or reflective mode with suitable UV or visible excitation sources.

It has been demonstrated that increasing the cadmium concentration in $Zn_{1-x}Cd_xS$ solid solutions shifted the photoluminescence emission band to longer wavelength because the band gap energy (E_g) decreases with increasing cadmium concentration, from 3.91eV for ZnS to 2.58eV in CdS.¹ Werring *et al* used $Zn_{0.4}Cd_{0.6}S:Cu$ with an emission peak at ~900nm in order to match with the absorption peak of a silicon thyristor for use in an infrared switching device.²

As it was found that in the $ZnCdS:Cu, In, Cl$ phosphors altering the zinc to cadmium ratio allows fine tuning of the wavelength of the photoluminescent emission band.³ The aim of this work was to shift the emission peak of the phosphor sufficiently far into the infra-red region so that visible light emission was minimized and the infra-red emission from the phosphor was clearly detectable by night vision systems. We have previously reported brief details of this infrared phosphor system⁴, but here we report a much more complete study dedicated solely to this system.

$Zn_{1-x}Cd_xS:Cu$ phosphors with higher cadmium concentrations than $Zn_{0.4}Cd_{0.6}S:Cu$ were selected for study with the aim that such increases would result in the emission band being moved sufficiently far into the near infrared region.

The indium co dopant has a direct effect on the emission intensity of the phosphor and increasing the In^{3+} concentration was also investigated with the aim of increasing the infrared emission intensity.

In our previous study on ZnS nanoparticles co-doped with Cu^{2+} and In^{3+} we found equal concentrations of copper and indium ions yielded the highest photoluminescence intensity compared with co-doping with other ratios of the two activators.⁴ However, a comparison of the photoluminescence intensities of the co-doped phosphor with ZnS doped with only Cu^{2+} was not reported and is a major point in this work.

2. RESULTS AND DISCUSSION

$Zn_{1-x}Cd_xS:Cu_{0.03},In_{0.03},Cl$ and $Zn_{1-x}Cd_xS:Cu_{0.03},Cl$ and (where $x = 0.5-0.9$) phosphors were synthesized by an aqueous decomposition method. A scanning electron micrograph of a typical sample is presented in Figure 1.

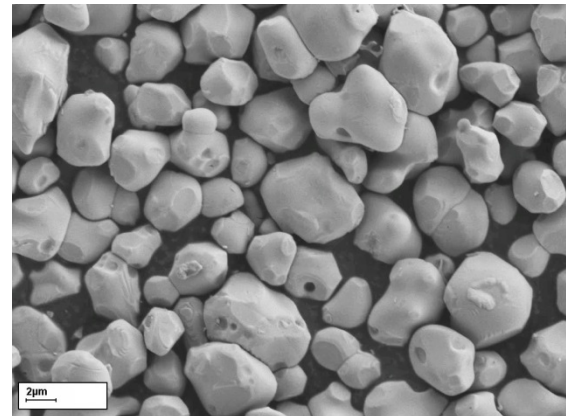


Fig. 1 SEM of a $Zn_{0.3}Cd_{0.7}S:Cu_{0.03},In_{0.03},Cl$ phosphor

All the particles are 2µm or larger in size; the mysterious holes were observed in all samples however their explanation is not part of this work.

The photoluminescent (PL) excitation spectra, (taken monitoring at 1000nm emission), of $Zn_{0.3}Cd_{0.7}S:Cu_{0.03},In_{0.03},Cl$ is presented in Figure 2.

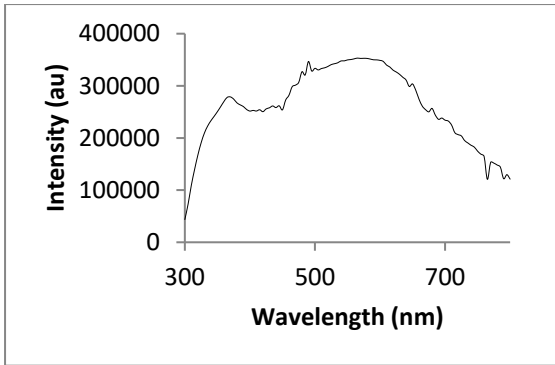


Fig 2 PL excitation spectra, at 1000nm emission of Zn_{0.3}Cd_{0.7}S:Cu_{0.03},In_{0.03},Cl phosphor

All of the Zn_{1-x}Cd_xS:Cu_{0.03},In_{0.03},Cl (where x =0.5-0.9 phosphors have similar excitation spectra to that of Zn_{0.3}Cd_{0.7}S:Cu_{0.03},In_{0.03},Cl presented in Figure 2.

Each has a broad band centered at ~365nm and a more intense sharp peak between ~460-505nm which shifted to longer wavelengths with increasing cadmium concentration, and an intense very broad excitation band between ~520nm and ~645nm. The broad excitation in the blue region facilitates excitation by blue light emitting LEDs between 440nm and 480nm, and the relatively strong excitation band at ~365nm allows excitation by long wavelength UV lamps or UV emitting LEDs and thus both sets of lights could be readily used as backlights for the infrared emission panels

The emission spectra of the Zn_{1-x}Cd_xS:Cu_{0.03},In_{0.03},Cl (where x =0.5-0.9) phosphors are presented in Figure 3.

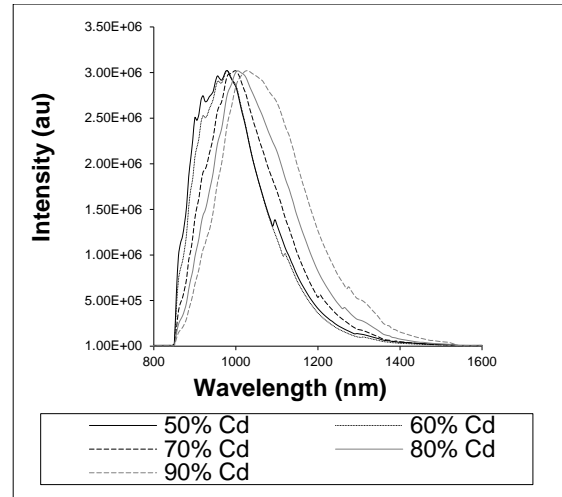


Fig. 3 PL Normalised PL emission spectra, under 580nm excitation, of Zn_{1-x}Cd_xS:Cu_{0.03},In_{0.03},Cl (where x =0.5-0.9) phosphors

As the cadmium concentration increases the emission peak moves to lower energy and the total wavelength change across the cadmium concentrations studied is around 100nm, with the center of the emission band moving from around 950nm to 1050nm. The full width at half height of the emission peaks are around 250nm.

A comparison of the emission brightness of Zn_{1-x}Cd_xS:Cu_{0.03},In_{0.03},Cl and Zn_{1-x}Cd_xS:Cu_{0.03},Cl (where x =0.5-0.9), is presented in Figure 4.

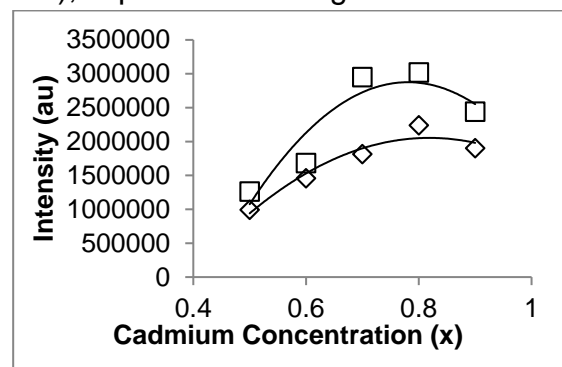


Figure 4 PL emission intensities of Zn_{1-x}Cd_xS:Cu_{0.03},Cl phosphors (◇) and Zn_{1-x}Cd_xS:Cu_{0.03},In_{0.03},Cl phosphors (□) with increasing cadmium concentrations (x)

For the phosphors which did not include indium as a co-dopant, there was a small increase in emission intensity with increasing cadmium concentrations; this reached a plateau at the highest cadmium concentrations. In contrast, the presence of indium resulted in a significant increase in the PL emission intensity as the concentration increased up to $x = 0.8$ concentrations. The PL emission intensity where $x = 0.7-0.8$ was approximately 50% greater compared to the comparable phosphors which were not co-doped with indium. At these cadmium concentrations, PL emission which involved In-Cu donor acceptor pairs resulted in significantly brighter PL emission compared to PL emission from Cl-Cu donor-acceptor pairs.

3. Conclusions

The ease of fabrication and the wide excitation spectra efficiency of the $Zn_{1-x}Cd_xS:Cu_{0.03},Cl$ (where $x = 0.5-0.9$), phosphors was demonstrated. The addition of In^{3+} resulted in an improvement in the PL emission intensity by up to 50%.

Acknowledgements

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