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:Cu0.03%Cl infrared emitting phosphors have been synthesized by an aqueous thermal decomposition method. Co-doping Zn_{1-x}Cd_xS:Cu0.03% with In^{3+} increased the infrared emission intensity by up to 50% over that of the equivalent Zn_{1-x}Cd_xS:Cu0.03% 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 most of the last six decades, but with the demise of the plasma displays there 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 headlamps, 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 greenhouses 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 well established been that increasing the cadmium concentration in Zn_{1-x}Cd_xS solid solutions shifts the photoluminescence emission band to longer wavelength because the band gap energy (E_g) decreases with increasing cadmium concentration, from 3.91eV for pure ZnS to 2.58eV in pure CdS.\(^1\) Werring et al demonstrated that Zn_{0.8}Cd_{0.2}S:Cu with an emission peak at ~900nm could be matched to the absorption peak of a silicon thyristor for use in an infrared switching device.\(^2\)

In 2002 Yang et al. reported that by altering the zinc to cadmium ratio in the ZnCdS:Cu, In, Cl phosphors 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 system\(^4,\) 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_{0.8}Cd_{0.2}S:Cu were selected for study with the aim of moving that the emission band significantly further into the near infrared region of the electromagnetic spectrum.

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.

One of the objections often used against cadmium containing phosphors is that the element is an environmental hazard due to its toxicity. It has been pointed out by Coe-Sullivan\(^5\) that in cadmium containing quantum dots (QDs) in QDLED displays that the amount present is both small and compared to the amount in the environment originating from burning fossil fuels is in fact minute and hence not a problem. Indeed cadmium containing QDs have been used/suggested for a range of applications in for example bio-imaging.\(^6,\)\(^7\)

In the last twelve years semiconductor nanocrystals with near-infrared (NIR) absorption
and emission spectra have been the subject of intensive research and development for biomedical imaging and diagnostics applications.\textsuperscript{8-11} Compared to visible emitting quantum dots (QDs), NIR nanocrystals with emission spectra in the 700–1700 nm spectral range have enhanced advantages including improved tissue penetration and reduced photochemical damage.

Because of inherent drawbacks such as their large sizes, broad emission spectra, low quantum yields, or poor photostability the resulting NIR nanocrystals have found only limited applications in biology and medicine. Moreover the more established multicolour emitting QDs have very different physical dimensions (they are smaller by a factor of 3–4 in diameter, and by a factor of 27–64 in volume), that cause large variations in signal brightness, steric hindrance, and binding kinetics in biological environments.\textsuperscript{12-14}

The fact that cadmium containing QDs are no longer considered as total environmental none starters could be seen as a justification to use other cadmium containing phosphors such as those reported in this work.

In our previous study on ZnS nanoparticles co-doped with Cu\textsuperscript{2+} and In\textsuperscript{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.\textsuperscript{4} However, in that work we did not compare the photoluminescence intensities of the co-doped phosphor with ZnS doped with only Cu\textsuperscript{2+} and this is a major aim of the work reported herein.

2. EXPERIMENTAL DETAILS

Zn\textsubscript{1-x}Cd\textsubscript{x}S:Cu\textsubscript{0.03},In\textsubscript{0.03},Cl and Zn\textsubscript{1-x}Cd\textsubscript{x}S:Cu\textsubscript{0.03},Cl (where x =0.5–0.9) phosphors were synthesized by an aqueous decomposition method.\textsuperscript{4}

3. RESULTS AND DISCUSSION

Zn\textsubscript{1-x}Cd\textsubscript{x}S:Cu\textsubscript{0.03},In\textsubscript{0.03},Cl and Zn\textsubscript{1-x}Cd\textsubscript{x}S:Cu\textsubscript{0.03},Cl (where x =0.5–0.9) phosphors were studied using scanning electron microscopy. A scanning electron micrograph of a typical sample is presented in Figure 1.

All the particles are 2μm or larger in size; the mysterious holes that are apparent in many of the particles in Figure 1 were observed in all the samples that we prepared. However, their explanation is not part of the current work.

The photoluminescent (PL) excitation spectrum, (taken monitoring at 1000nm emission), of Zn\textsubscript{0.3}Cd\textsubscript{0.7}S:Cu\textsubscript{0.03},In\textsubscript{0.03},Cl is presented in Figure 2. Each spectrum 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. Thus both UV and Blue LEDs could be readily used as backlights for the infrared emission panels.
The emission spectra of a series of Zn\(_{1-x}\)Cd\(_x\)S:Cu\(_{0.03}\),In\(_{0.03}\),Cl (where x = 0.5 - 0.9) phosphors are presented in Figure 3. In Figure 3 it is apparent that as the cadmium concentration increases the emission peak moves to lower energy. 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 the phosphors Zn\(_{1-x}\)Cd\(_x\)S:Cu\(_{0.03}\),Cl (○) and Zn\(_{1-x}\)Cd\(_x\)S:Cu\(_{0.03}\),In\(_{0.03}\),Cl (●) plotted as a function of increasing cadmium concentration is presented in Figure 4. It is apparent in Figure 4 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. 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.

4. CONCLUSIONS

The ease of fabrication and the wide excitation spectra efficiency of the Zn\(_{1-x}\)Cd\(_x\)S:Cu\(_{0.03}\),Cl (where x = 0.5 - 0.9), phosphors has been demonstrated herein. The addition of In\(_{3+}\) in the phosphors resulted in an improvement in the PL emission intensity by up to 50% over the equivalent phosphor that did not contain this sensitizer cation. 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\(_x\)S:Cu\(_{0.03}\),In\(_{0.03}\),Cl with In\(_{3+}\) increased the infrared emission intensity by up to 50% over that of the equivalent Zn\(_{1-x}\)Cd\(_x\)S:Cu\(_{0.03}\) phosphor with no indium co-doping, with the highest intensities being where x = 0.7 - 0.8.

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6. REFERENCES

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