Luminescent mechanism of bulk and nano ZnS: Mn$^{2+}$ phosphors

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ABSTRACT

ZnS nanophosphors, with or without different concentrations of Mn$^{2+}$ activator ions, were synthesized by using the chemical precipitation method. Micron sized ZnS:Mn$^{2+}$ powder was obtained from Phosphor Technology in the United Kingdom. Structure, morphology and particle sizes of the samples were determined by using XRD, TEM and SEM. The average particle size was ~3 nm in diameter. The band gap of ZnS nanophosphors, estimated from the UV-Vis data, was 4.1 eV. Luminescent properties of the samples were determined by photoluminescence (PL) measurements. Two emission peaks at 450 nm and 590 nm were observed from the micron sized sample. The 590 nm peak was red-shifted by 10 nm in the case of ZnS:Mn$^{2+}$ nanophosphors used in this study. In this work a luminescent mechanism for both bulk (micron sized) and nano sized ZnS:Mn$^{2+}$ is proposed, and the red-shifting is explained using the configuration coordinate model for Mn$^{2+}$.

Keywords: ZnS:Mn$^{2+}$, nanophosphors, luminescence, luminescent mechanism

1 INTRODUCTION

Although ZnS:Mn$^{2+}$ is a well known phosphor used in display panels, solar cells and also in biological imaging together with CdS [1],[2], the excitation and emission mechanism of the nano sized ZnS is still not well understood. Most of the reported mechanisms attribute the 450 nm peak to emission from shallow traps in the band gap [3],[4] and the 590 – 600 nm peak to the $^2T_1 - ^2A_1$ transition of Mn$^{2+}$ [3],[4],[5]. None of these mechanisms differentiate between emission processes of bulk and nano scale ZnS or explain the red–shifting of the 590 nm peak. Some reports explain the mechanism in terms of the configurational coordinate model for a Mn$^{2+}$ impurity in ZnS [6],[7],[8], without explaining the red shift in the peak position. In this work a luminescent mechanism for both bulk and nano ZnS:Mn$^{2+}$ is proposed. This mechanism accounts for a blue shift in the excitation and absorption spectra of nano ZnS:Mn$^{2+}$, a PL peak that were observed at 450 nm , a peak at 590 nm for the bulk sample and one at 600. This red shift in the peak can be explained by the configuration coordinate model for Mn$^{2+}$. Understanding the mechanism could lead to development of high quality nanoscale ZnS:Mn$^{2+}$ phosphor for a variety of lighting applications.

2 EXPERIMENTAL SETUP

2.1 Synthesis

ZnS:Mn$^{2+}$ sols were prepared by using the chemical precipitation method described by Lu et al. [9]. The synthesis was carried out using Zn(CH$_3$COO)$_2$.2H$_2$O, Mn(CH$_3$COO)$_2$ and Na$_2$S as starting materials. Zn(CH$_3$COO)$_2$.2H$_2$O and Mn(CH$_3$COO)$_2$ were dissolved in ethanol with stirring at 150°C. A 1:1 ratio of ethanol to deionized water solution of Na$_2$S was added to the Zn$^{2+}$ and Mn$^{2+}$ solution drop by drop with vigorous stirring at 75°C. The resulting white precipitate was centrifuged and washed using a mixture of toluene and ethanol in a 2:1 volume ratio. The precipitate was dried at 120°C for two hours.

2.2 Characterization

The structure and morphology of the samples were determined by XRD and TEM and SEM using a Siemens Diffractometer D5000 equipped with a Cu Kα source and JEM 2100F TEM and JEM 7500F SEM. The bandgap of ZnS was determined from the UV-Vis data collected by a Shimadzu UV-1700 PharmaSpec UV-Vis spectrophotometer. The PL data was collected using a 15 W Xenon flash lamp and 325 nm HeCd (26mW) laser as excitation sources.

3 RESULTS AND DISCUSSION

The XRD pattern of ZnS:Mn$^{2+}$ nanoparticles is shown in Figure 1. The three diffraction peaks indexed as (111), (220) and (311) (JCPDS 5-566) match the lattice planes of the zincblende ( sphalerite) ZnS crystal structure. Manganese impurities did not contribute to any additional diffraction peaks or shifts in the peak position and it indicates that the Mn$^{2+}$ ions were well dispersed in the ZnS matrix [10] and their concentration was relatively low. The particle sizes were calculated using Scherrer’s equation [11] by making use of the (111) diffraction peak. The average particle size was determined as 3 ± 1 nm in diameter. The TEM image in Figure 2 shows a cluster of agglomerated nanoparticles as indicated by the circle. The SEM image of the sample showed a similar cluster of agglomerated nanoparticles. The average particle size estimated from the TEM image was ~2-4 nm in diameter, which is consistent with the particle size calculated from the XRD data. The band gap of synthesized nano ZnS was determined from the UV absorption data and found to be 4.1 eV. This band gap
is blue shifted from the band gap of bulk ZnS (3.6 eV) [17]. The band gap of ZnS nanoparticles has thus enlarged probably due to quantum confinement effects. Figure 3 shows the PL excitation spectra for synthesized ZnS:Mn$^{2+}$ with different doping concentrations of Mn$^{2+}$. Two peaks are observed at 450 and 600 nm. The 450 nm peak corresponds to excitonic emission of ZnS and the 600 nm peak corresponds to the characteristic $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ ions [12]. There was an intensity increase with an increase in Mn$^{2+}$ from 2 – 5 mol% and a decrease in intensity for the 10 and 20 mol% Mn$^{2+}$ doping. This may be due to concentration quenching effects [13]. Figure 4 shows possible electron transitions that could lead to the orange emission from the Mn$^{2+}$ ions. These transitions were explained in terms of Tanabe-Sugano diagrams for the $d^5$ level and the Ligand field theory by different researchers [14]-[18]. It is known that Mn$^{2+}$ has a $d^5$ electron structure with a tetrahedral symmetry. When doped into ZnS, it occupies the sites of Zn$^{2+}$. The ground state of Mn$^{2+}$ is $^6A_1(6S)$ and the first excited state is $^4G$. Under tetrahedral symmetry, the excited state can be split into $^4T_1$, $^4T_2$, $^4A_1$, and $^4E$ multiplets whose energies were reported by McClure [17]. The d electron states of the Mn$^{2+}$ ion acts as efficient luminescent centers while interacting strongly with the host crystal’s s-p electronic states at which the external electronic states are normally directed [18]. Figure 4 describes (a) the excitation mechanism of bulk and nano ZnS (b) the emission mechanism of ZnS and ZnS:Mn$^{2+}$ (c) the emission mechanism of ZnS:Mn$^{2+}$ using the configurational coordinate model.

**Figure 4 (a):** The energy dispersion for a bulk semiconductor and a nanoparticle is described in ref [3]. In the case of a nanoparticle the band gap ($E_g$) is blue shifted. The band gap for bulk ZnS is 3.6 eV [19] and from UV-Vis measurements the band gap for ZnS nanoparticles was determined as 4.1 eV. The insert (i) in Figure 4 shows the excitation spectra of bulk and nanoparticles of ZnS. This corresponds to excitation over the band gap. A hole is created in the valence band by the incident photon and the electron is excited over the band gap to the conduction band. In the case of bulk ZnS the energy of this excitation is 3.6 eV and for ZnS nanoparticles it is 4.1 eV, that is the excitation energy of the ZnS nanoparticles is blue shifted.

**Figure 4(b):** The excited electron immediately transfers to the shallow traps (dashed line in Figure 4). This shallow trap-state is delocalized over the entire nanocrystal, because of the quite small effective mass of the electron. Because the hole has a much higher effective mass it will initially remain in the valence band and will be trapped on a longer time scale [20]. The emission spectra of ZnS:Mn$^{2+}$ (Figure 3) show that the interaction between ZnS and Mn$^{2+}$ resulted in two emissions peaks at 450 (minor) and 600 nm (major). The minor peak at 450 nm (blue emission) can be attributed to the hole trapping and recombination with electrons by defect states (zinc or sulphur vacancies) in ZnS. The orange emission at 600 nm for nanoparticles can be attributed to $^4T_1 \rightarrow ^6A_1$ transitions of Mn$^{2+}$ ions. For the process denoted by A, two possible routes for this emission are possible. For A1, an excited electron in the conduction band can relax to the vacancy level and then to the $^6T_1$ level of Mn$^{2+}$ non-radiatively, followed by radiative transition to the ground
state (4A1) and recombination with a hole trapped in the ground state. The radiative transition is accompanied by emission of orange photons at 600 nm. Since the orange emission at 600 nm is more intense than the blue (violet) emission at 450 nm, this suggests that non-radiative relaxation to the 4T1 level of Mn2+ was faster than hole capture and recombination with electrons by defects states of ZnS. For A2, an excited electron in the conduction band can first relaxes non-radiatively to the 4T1 level of Mn2+ and finally to the 6A1 level emitting orange photons in the process.

**Figure 4(c):** The emission peak of nano-sized ZnS:Mn2+ was observed to be red shifted by 10 nm from that of the bulk spectrum. So far, there have been many reports about the origin of this red shift in the emission. Cruz et al. [21] reported that the red shift might be caused by a large density of surface states in the nanoparticles, or by strong electron-phonon coupling in the nanoparticles. They also report that it might be possible that the size-dependent crystal field effect is responsible for this red shift. Li et al. [22] reported that the red shift may come from the quantum confinement effect in nanoparticles which leads to a change of the crystal field surrounding the Mn2+ ions. Shionoya and Yen [23] reported that when a metal ion occupies a certain position in a crystal, the crystal field strength that affects the ion increases as the space containing the ion becomes smaller. Therefore for increases in the field, the transition energy between the 4T1 and 6A1 levels of Mn2+ is predicted to decrease (shift to longer wavelengths). From these reports it can be seen that a change in the crystal field will most likely cause a red shift in the emission of nanoparticles. The quantum confinement effect (that arises from the very small particle sizes) will change the crystal field. From XRD data it can also be seen that the bulk sample is much more crystalline than the nano samples. It can therefore be concluded that a change in the crystal field would cause a change in the parabola offset in the configurational coordinate diagram. The offset is given by ΔQ = Q0 − Q', where Q0 is the equilibrium distance of the excited state, Q' is the equilibrium distance of the ground state and ΔQ is the parabola offset. The configurational coordinate diagram also describes the Stokes' shift (difference in absorption and emission energy) [23]. When there is a displacement between the potential wells of the ground and excited states, there will be a difference in the Stokes' shift. The parabola offset will therefore also increase. In figure 4(c) the configurational coordinate model for Mn2+ [8],[24] is used. The same process as in figure 4(a) occurs, but the difference between the emission of the bulk and nanoparticles is shown. The insert (ii) in Figure 4 shows the emission spectra for bulk and nanoparticles of ZnS:Mn2+. For bulk particles there is only a slight offset in the parabola of the excited state. An electron relaxes non-radiatively from the conduction band to the 4T1 state. This electron then relaxes non-radiatively to the bottom of the 4T1 state. The excess energy will be released in the form of heat to the lattice. The electron will then recombine with a trapped hole in the ground state (6A1) and emission of orange photons at 590 nm takes place. In the case of nanoparticles the parabola offset is greater than that of bulk particles. The same process of electron relaxation and recombination will occur, but in this case emission at 600 nm takes place.

4. Conclusion

ZnS:Mn2+ nanoparticles were synthesized using the chemical precipitation method. The structure and particle morphology were analyzed by using XRD, TEM and SEM. The average particles size was found to be 3 ± 1 nm. The band gap of ZnS nanoparticles was determined as 4.1 eV and it was blue shifted from that of bulk ZnS (3.6 eV). For the Mn2+ doped samples two PL peaks were observed at 450 nm and at 600 nm. The 450 nm peak corresponds to excitonic emission of ZnS and the 600 nm peak corresponds to the characteristic 4T1 → 6A1 transition of Mn2+ ions. These transitions were explained in terms of Tanabe-Sugano diagrams for the d5 level and the Ligand field theory. The blue shift in the excitation spectra of nano sized ZnS can be explained according to the energy dispersion diagram for bulk and nano semiconductors, while the red shift in the emission spectra can be explained according to the configurational coordinate model of Mn2+.

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**REFERENCES**

Figure 4: Schematic diagram of the proposed luminescent mechanism of ZnS and ZnS:Mn