



SYNTHESIS AND ELECTROLUMINESCENCE STUDY OF MANGNESE DOPED ZINC SULPHIDE NANOPARTICLES

Anju Singh^{1*} and H. L. Vishwakarma²

^{1*}*Department of Applied Physics, Rungta College of Engg. & Tech., KohkaKurud Road, Bhilai (C.G.), INDIA*

²*Department of Physics, Surguja University, Ambikapur (C.G), INDIA*

Abstract

Manganese doped zinc sulphide (ZnS: Mn) nanoparticles were synthesized by a simple chemical precipitation method in the presence of mercaptoethanol as a capping agent at room temperature. X-Ray Diffraction (XRD) result indicated that prepared ZnS: Mn nanoparticles have zinc-blende structure. It has been seen that the growth orientation of the prepared ZnS: Mn nanoparticles were (111), (220) and (311). The crystallite size has been estimated from the broadening of the first diffraction peak using Debye-Scherrer formula. The crystallite size has been found to decrease from 1.54 nm to 0.91 nm with increasing the capping agent concentration from 0.005M to 0.025M. The optical absorption studies showed that the absorption edge shifts towards blue region as the capping agent concentration is increased. The absorption edge was found at shorter wavelength with decreasing particle size. As the capping agent concentration increased, the optical band gap was found to increase, which was calculated using the absorption edge. It was found that as the capping agent concentration is increased, there is reduction in particle size. Electroluminescence (EL) studies showed that emission of light is possible at very small threshold voltage and increases rapidly with increasing applied voltage. It was observed that smaller ZnS: Mn nanoparticles give higher electroluminescence brightness, starting at lower threshold voltage. The brightness was also affected by increasing the frequency of AC signal.

Keywords: *Electroluminescence, nanoparticles, absorption edge, mercaptoethanol.*

1. Introduction

ZnS is a direct transition semiconductor with the widest energy band gap among the group II-VI compound materials. The most striking feature of ZnS nanocrystallites is that their chemical and physical properties differ dramatically from those of bulk solids. ZnS is a semiconducting material, which has a wide band gap material of 3.70 eV [1, 2]. Among these, luminescent semiconducting nanocrystals, also termed as nanophosphors, were paid much attention particularly for their life time shortening and enhanced emission efficiencies [3, 4]. Bhargava *et al.* first reported luminescent properties of Mn doped ZnS nanocrystals prepared by a chemical process at room temperature, which initiated investigation on this topic [5, 6]. Depending on the capping molecules present on the ZnS: Mn, particles passivate surfaces. ZnS doped with Mn²⁺ nanoparticles are having high quantum efficiency and luminescence intensity [7]. The band structure of the semiconductor changes with decreasing in particle size.

Zinc sulphide doped with manganese (ZnS: Mn²⁺) shows interesting luminescence properties for application as phosphors [8]. In 1994 Bhargava *et al.* reported that the luminescence efficiency increases with decreasing particle size and life time of Mn²⁺ emission was shortened from



milliseconds to nanoseconds due to quantum confinement effect. This result has led to a new class of luminescent material finding applications in displays, sensors, lasers etc. As far as display is concerned the resolution depends greatly on the size of the pixel and improves with a reduction in the size of the pixel that is in turn determined by the size of the phosphor particles.

Zinc sulphide is an important semiconductor and has many optoelectronic applications including solar cells, photodiodes, light emitting diodes, nonlinear optics and heterogenous photocatalysis. In the present study we have synthesized ZnS nanoparticles with varying concentration of capping agent using chemical precipitation technique. The particles are characterized using XRD.

2. Experimental Work

2.1: Preparation of Mn doped ZnS nanoparticles

All the reactants and solvents used in this study were analytical grade and used without any further purification. The synthesis was carried out in water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at room temperature and under ambient conditions. In the present investigation, chemical route synthesis technique has been adopted. Nanoparticles of ZnS are synthesized in aqueous medium through chemical precipitation technique starting from analar grade zinc salt and sodium sulphide, and using mercaptoethanol as capping agent. The nanoparticles are separated from the reaction medium by centrifugation at 3500 rpm and finally air dried. Different samples were prepared by changing the capping agent concentration.

2.2: Characterization Technique

Absorption of the samples prepared with various concentrations of capping agent and dopant were studied. Perkin Elmer λ -12 spectrometer was used to obtain the absorption peak of ZnS nanoparticles. The lambda- 12 UV/ VIS spectrometer features in all reflecting optical system.

All the samples were characterized at IUC Indore. The morphologies and sizes of the mercaptoethanol capped ZnS: Mn was determined by X- ray diffraction studies with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). XRD data were collected over the range $5^\circ - 75^\circ$ at room temperature. X- ray diffraction patterns have been obtained by Bruker D8 Advance X- Ray diffractometer. The particle size was calculated using Debye- Scherrer Formula.

The EL brightness was measured by photomultiplier tube (PMT) operated at high voltage and output fed to a pico-ammeter. For the EL studies, a particular frequency is set in the audio generator and voltage applied to the EL cell was increased from 0 to 700 volts and corresponding current and EL brightness were recorded. The EL was studied at various frequencies for ZnS nanoparticles with different Mn concentrations.

2.3: Preparation of Electroluminescence cell

The Electroluminescence cell was prepared using triple layer structure. Nanoparticles emission layer was sandwiched between two electrodes. The transparent electrode has been prepared by depositing of thin film of Indium Tin Oxide (ITO) on clean glass substrate. This ITO coated glass behaves as an electrode. The surface resistivity of this electrode is $70\text{-}100 \Omega/\text{sq}$ and $L \times W \times \text{thickness}$ is about $75 \text{ mm} \times 25 \text{ mm} \times 1.1 \text{ mm}$. Then a mica sheet having window of $2 \times 2 \text{ mm}$ was placed on the conducting glass plate so that window is on the film of ZnS sample. An Aluminium foil strip was placed tightly over this window so as to have good contact with ZnS nanoparticle film and there is no air gap. The aluminium strip acts as second electrode (area 1 cm^2 and thickness $\sim 100 \text{ \AA}$). The layer of

nanoparticle should be uniform and thin. Alternating voltage of various frequencies was applied and EL brightness (B) at different voltages (V) was measured with the help of photomultiplier tube and corresponding current was also recorded.

3. Results & Discussion:

3.1: Optical Property

Absorption spectra of ZnS nanoparticles at various concentrations of capping agent as well as for doped ZnS have been studied in the present investigation. The samples were prepared with capping agent concentration of 0.005 M, 0.01M, 0.015M, 0.02M, and 0.025 M respectively. It is clear from the spectra (**Fig.1**) that there is practically uniform absorption in the visible range (800nm – 390nm). The absorption increases suddenly in the visible range. Sudden increase in absorption occurred at 240nm, 235 nm, 230nm, 225nm, and 220nm respectively. The absorption edge was found at shorter wavelength with decreasing particle size. As the capping agent concentration increases the optical band gap is found to increase which was calculated using the absorption edge. It was observed that no optical absorption occurs at surface states and therefore these do not affect the absorption.

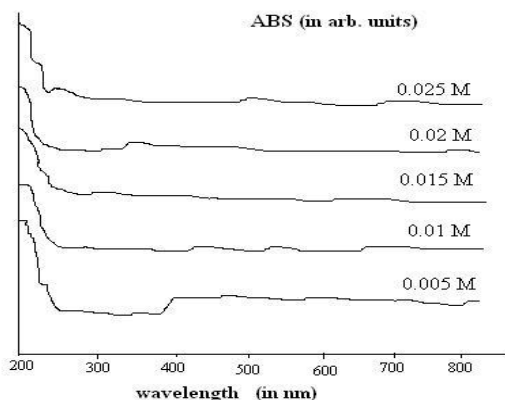


Fig. 1 Absorption spectra of ZnS nanoparticles at various concentration of capping agent

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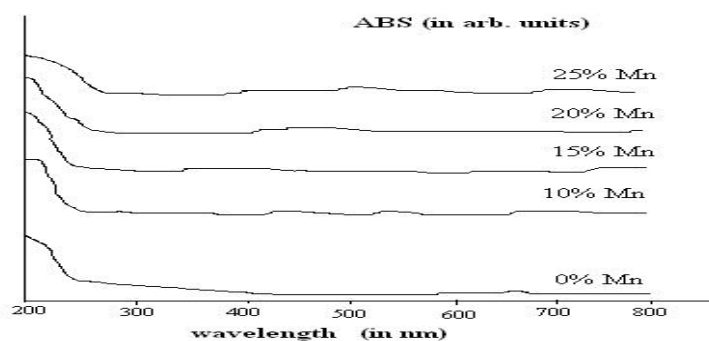


Fig. Absorption spectra of ZnS Mn nanoparticles

Fig.2: Absorption spectra of ZnS: Mn nanoparticles.

3.2: Structural studies

typical X-ray diffractograms (XRD) of nanocrystalline ZnS and ZnS doped with Mn^{2+} are shown in **Fig.3** and **Fig.4**. XRD study reveals that ZnS nanoparticles have zinc-blende crystal structure. For all the samples three peaks are observed corresponding to diffraction from (111), (220) and (311) planes. Due to the size effect, the XRD peaks tend to broaden and their width increases as the size of the crystal decreases. The crystallite size has been estimated from the broadening of the first diffraction peak using Debye –Scherrer formula. The finite three- dimension crystal lattice diffracts X- rays in manner analogous to the reflection of visible light from a ruled grating. When the particle size is of the order of the wavelength of incident beam, the diffracted beam becomes diffused. The width of the X-ray diffraction line is able to give the crystallite size. The relation between crystallite size and diffracted ray line broadening was given by Scherrer [9] which is shown in equation (1).

$$D = \frac{K\lambda}{\beta \cdot \cos\theta} \quad (1)$$

Where K is a constant which depends on the crystalline shape and diffractometer setup, λ is the wavelength of monochromatic radiation, β is full width half maxima (FWHM) in radians, θ is Bragg's angle. The value of K and λ are equipment parameters and the value of β and θ can be obtained from the diffraction pattern.

Three different peaks are obtained at 2θ values of 29° , 47° and 57.5° for all the samples. This shows that the sample has zinc blende structure and the peaks corresponding to diffraction at (111), (220) and (311) planes respectively [10].

Lattice parameter 'a' can be determined using equation (2), substituting the value of $\sin^2\theta$ and corresponding h, k and l.

$$a = \frac{\lambda}{2 \sin\theta} \sqrt{h^2 + k^2 + l^2} \quad (2)$$

The lattice parameter has been computed as 5.33 \AA , which is close to the standard value of ZnS – zinc blend structure (5.42 \AA).

The crystallite size has been found to decrease from 1.54 nm to 0.91 nm with increasing the capping agent concentration from 0.005M to 0.025M.

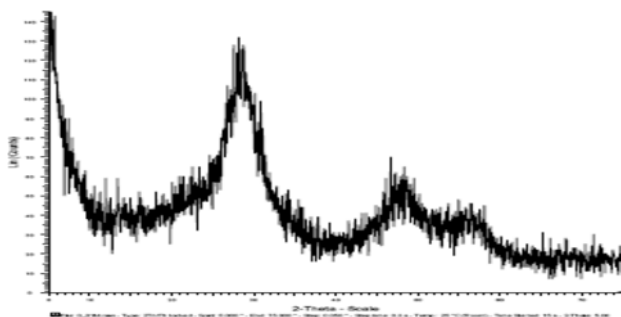


Fig.3: XRD patterns of undoped ZnS nanoparticles.

From the XRD patterns of undoped and doped ZnS nanocrystals it is observed that the presence of Mn increases the broadening of peaks. The broadening of peaks in Mn doped samples is indicative of small crystallite size.

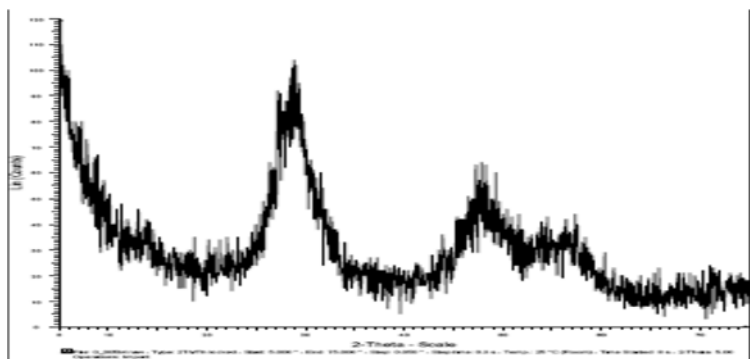


Fig.4: XRD pattern of ZnS: Mn nanoparticles.

3.3: Electroluminescence Studies:

The Electroluminescence (EL) was observed in all the samples of different concentration of ZnS: Mn and their brightness have been recorded at various frequencies. Some other characteristics have been also studied.

3.3.1: Voltage – Brightness characteristics

The EL studies on nanocrystalline powder samples have shown that the light emission starts at certain threshold voltage and then usually increases rapidly with increasing voltage (**Fig. 5& Fig.6**). It is found that for smaller nanocrystals, threshold voltage is lower and EL brightness (B) increases rapidly with voltage. The relationship between applied voltage (V) and current is found to be linear indicating ohmic nature. In general, higher brightness is obtained at higher frequencies. By increasing nanocrystalline loading, EL starts at lower threshold voltages and higher intensity is observed. From the EL investigations of nanocrystalline powder, it is seen that $\log B$ vs. $1/V^{1/2}$ curve is a straight line with negative slope. This indicates that EL is produced by acceleration-collision mechanism. Low energy states are also populated by electrical excitation that cannot be populated by optical process. Therefore EL emission is obtained at photon energies much less than the band gap of the material. The investigations have revealed that the EL efficiency can be increased by reducing the size of semiconductor crystals to nanometer range. The device performance is improved, if the nanoparticles are embedded in polymer matrix.

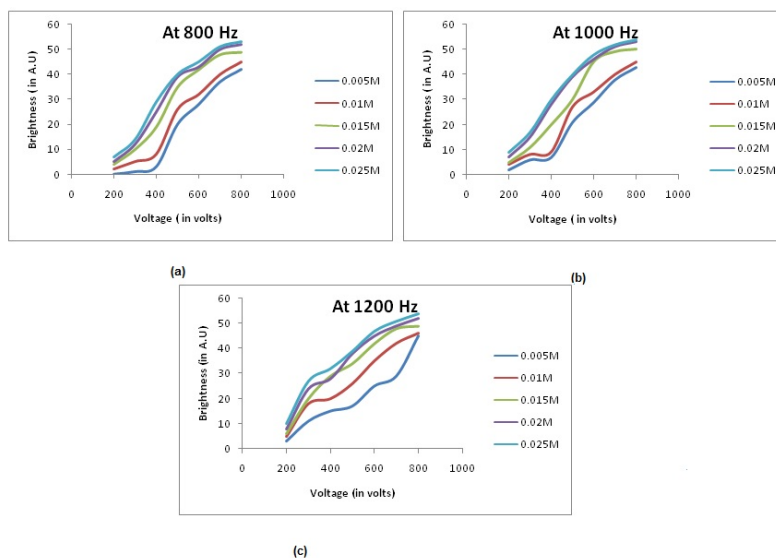


Fig.5: Voltage – Brightness characteristics of ZnS nanoparticles at different concentration of capping agent.

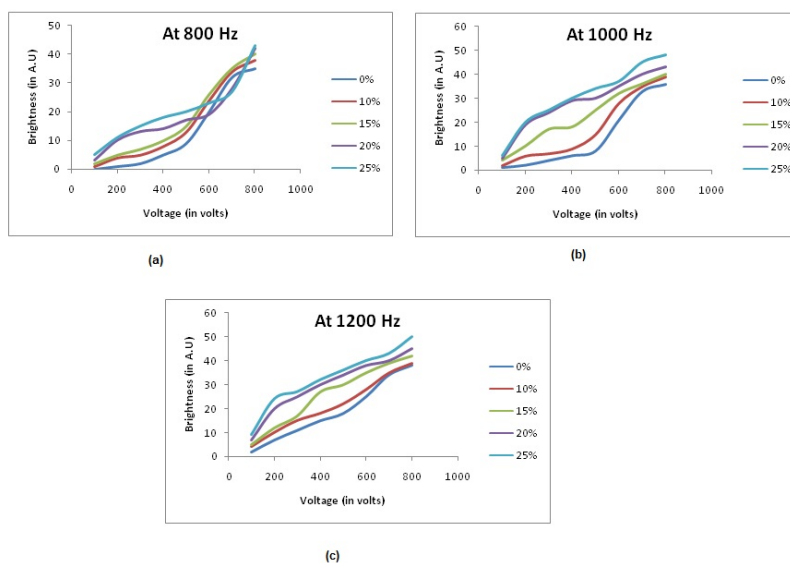


Fig.6: Voltage –Brightness characteristics of ZnS nanoparticles at different concentration of Mn.

3.3.2: Current – Voltage characteristics

The dependence of EL brightness on applied voltage nanoparticles with varied concentration of Mn is presented in **Fig.7** & **Fig.8**. It is noted that at lower voltages the increase in brightness is comparatively slow, which becomes quite fast at higher voltages. Also it is observed that light emission starts at a threshold voltage for different samples [11]. The threshold voltage reduces with increasing concentration of Mn content in ZnS nanoparticles. The threshold voltage as well as maximum EL brightness depends on the frequency of AC. The reason may be that as voltage is increased, more electrons and holes are injected into the emission layer and their subsequent recombination results in higher EL brightness. At high enough applied voltages, electrons tunnel from

interface states into conduction band of the active layer. They are subsequently accelerated by the high electric field and the impacts excite the activator ions. As a result, the threshold voltage is related primarily to electron tunneling, which is induced by electric field. The voltage variations of EL brightness are in agreement with excitation- collision mechanism and formation of Mott- Schottky barrier.

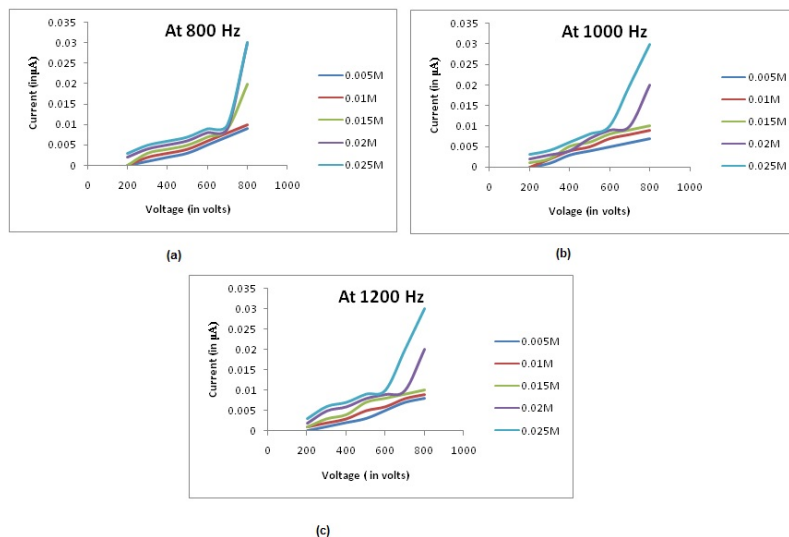


Fig.7: Voltage – Current curve of ZnS nanoparticles at different concentration of capping agent.

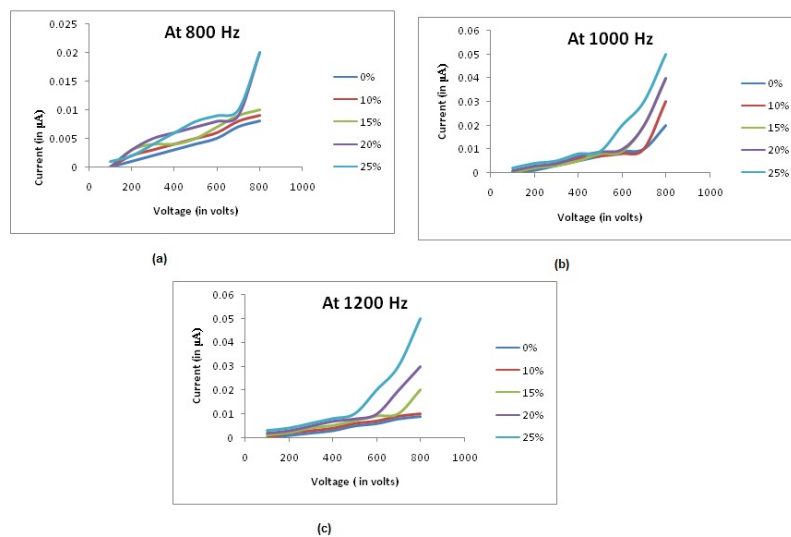


Fig.8: Voltage – Current curve of ZnS nanoparticles at different concentration of Mn.



4. Conclusion

Optical excitation of electrons across the band gap is strongly allowed transition, producing an abrupt increase in absorptivity at the wavelength corresponding to the gap energy. The studies have revealed that capping agent restricts the growth of crystals and by increasing its concentration; the small crystals can be obtained. Optical absorption studies show that the absorption edge shifts towards blue region as the capping agent concentration is increased indicating that effective band gap energy increases with decreasing particle size. XRD study reveals the zinc blend structure for ZnS crystals. The lattice parameter has been obtained as 5.33 \AA , which is approximately same as for bulk. The crystalline size computed from the XRD peaks comes out to be of the order of few nanometers. Maximum EL brightness is observed for a particular concentration of ZnS:Mn. The minimum voltage (threshold voltage) required to obtain EL has been 14 volts, which can further be reduced by proper doping. This observation is sufficient for the utilization of these nanoparticles in fabricating of EL devices.

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