

Studies on the Synthesis and Characterization of Nano Phosphors for Field Emission Devices

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Abstract: Nano phosphors were synthesized by chemical precipitation method with mercaptoethanol as the capping agent. Manganese doped ZnS nano phosphors (ZnS: Mn) with varying concentration of capping agent as well as of Mn²⁺ were synthesized at room temperature. The optical absorption studies show that the absorption edge shifts towards blue region as the capping agent concentration is increased indicating that the effective band gap energy increase with decreasing particle size while with the change in doping concentration no variation was observed in the absorption spectra. The nano phosphors obtained were characterized by XRD. It was found that as the capping agent concentration is increased, there is reduction in particle size.

Keywords: Nano phosphors, characterization, Luminescence, Optical properties.

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 nanocrystals 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 nano phosphors, 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 nano phosphors 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⁺ nano phosphors 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⁺) show 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 heterogeneous photo catalysis. In the present study we have synthesized ZnS nano phosphors with varying

concentration of capping agent using chemical precipitation technique. The particles are characterized using XRD.

2. Experimental Method

- 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. Nano phosphors 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 nano phosphors 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. Special care has to be taken to maintain the same physical condition during the synthesis of the samples.
- 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 nano phosphors. 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^o - 75^o 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 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]

$$D = \frac{K\lambda}{\beta \cdot \cos\theta}$$

- 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.
- Figure shows the X- ray diffraction pattern prepared with different mercaptoethanol concentrations. 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.

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

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

3. Results and Discussions

- Absorption spectra of ZnS nano phosphors 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).

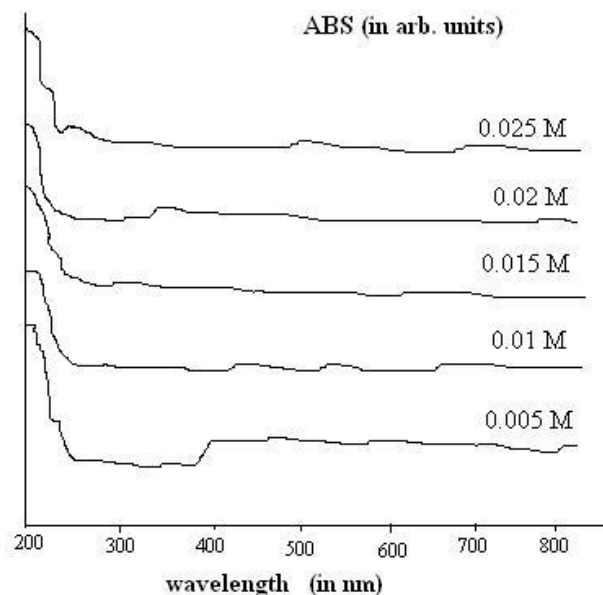


Figure 1: Absorption spectra of ZnS nano particles at various concentration of capping agent

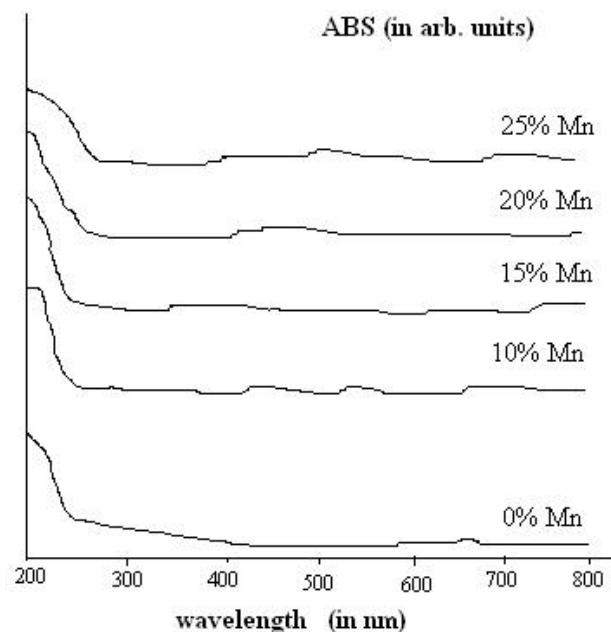


Figure 2: Absorption spectra of ZnS Mn nano particles

Figure 1 Absorption spectra of ZnS at various concentration of capping agent and ZnS:Mn at various concentration of doping materials.

- 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 is observed that no optical absorption occurs at surface states and therefore these do not affect the absorption spectra.
- A typical X-ray diffractogram (XRD) of nanocrystalline ZnS doped with Mn²⁺ is shown in fig.2. XRD study reveals that ZnS nano phosphors have zinc-blende crystal structure. For all the samples three peaks are observed corresponding to diffraction from (111), (220) and (311) planes.

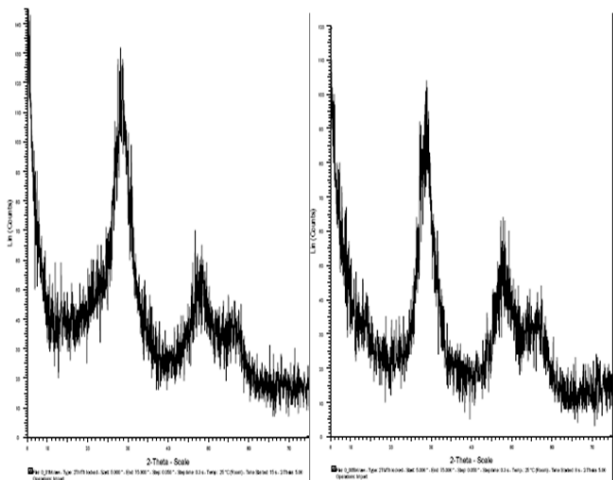


Figure 3: X-Ray Diffraction study of Mn²⁺ doped ZnS nanocrystalline

- 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 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.
- From the XRD patterns of undoped and doped ZnS nano phosphors 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.

4. Conclusions

- 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 blende structure for ZnS crystals. The lattice parameter has been obtained as 5.24 Å⁰ 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.

5. Future Scope

Phosphors are a luminescent material that emits light when it gets excited. The ideal phosphors have smaller size, high luminescence intensity, good color, purity and well dispersion. ZnS doped with Mn²⁺ show interesting luminescent properties for application as phosphors. The efficiency of luminescence of phosphors increases with decreasing particle size, so luminescent materials such as ZnS used as display devices, sensors, lasers etc.

6. Acknowledgment

This work has been partially supported by IUC, Indore (M.P.). The authors are thankful to the management of Rungta College of Engineering and Technology, Bhilai (C.G.) and KITE, Raipur for providing financial assistance and research facility to carry out research work.

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