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Low temperature synthesis of spherical zinc sulphide nano particles doped with Mn²⁺

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ABSTRACT

Spherical Zinc sulphide nanoparticles with good photoluminescence have been successfully fabricated using a simple chemical precipitation method doped with Mn²⁺ at low temperature. An emission peak at around 590nm confirms the presence of Mn²⁺. TEM picture reveals the formation of spherical nano particles. This low cost fabrication process for spherical Zinc sulphide nanoparticles with good photoluminescence can be applied to opto-electronic devices. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Synthesis;
Zinc sulphide;
Photoluminescence.

INTRODUCTION

Luminescent II-VI semiconductor nanocrystals like CdS, ZnS, ZnSe etc have attracted a lot of attention in the past two decades due to their unique properties and potential applications in nonlinear optics^[1], electronic devices^[2] and biotechnology^[3]. In addition to their fundamental interest, doped semiconductor nanoparticles have tremendous potential for use in light emitting applications. ZnS doped with manganese (orange red emission at around 590nm)^[4], copper (green emission at around 510nm)^[5] and silver (blue emission at around 440nm)^[6] have potential application in field emission devices (FED)^[7]. Doped semiconductor nanoparticles ZnS:Mn⁺ is used as phosphors and also in thin film electroluminescence devices^[8]. Considerable efforts have been made towards the preparation of doped ZnS nano. Various synthesis methods have already been reported. Organometallic method of syn-

thesis Mn doped ZnS nanoparticles has been described by^[9, 10]. Synthesized nanoparticles of ZnS: Mn²⁺ in methanol by using sodium polyphosphate as the capping agent^[11]. In this article, we describe an easy, simple and low cost chemical precipitation method for the synthesis of ZnS: Mn²⁺ spherical nanoparticles at low temperature.

EXPERIMENTAL DETAILS

Materials used in the present synthesis are Zn (CH₃COO)₂ (as zinc source), Na₂S (as sulphur source), Mn (CH₃COO)₂ (as manganese source), ethanol and deionized water. Zn(CH₃COO)₂, Na₂S, and Mn(CH₃COO)₂ were obtained from E Merck, Ranbaxy Fine Chemicals Ltd., and LOBA Chemie, respectively and were used without any further purification. Here, 50 ml of 1M zinc acetate, 10 ml of 0.1M manganese acetate and 50 ml of 1M sodium sulphide solutions were

Full Paper

prepared in deionized water and were mixed using magnetic stirrer at 75°C. During stirring 50 ml of ethanol was also added to the solution. The process of heating and stirring was continued for two hours. After that the solution was cooled at room temperature. Then the colloidal sample was filtered out, washed with distilled water and ethanol for removing the additional impurities formed during the process. The filtrate was dried in hot air oven and set for various characterizations, viz XRD for crystallinity and particle size, TEM for morphology and particle size, FTIR spectroscopy and PL for optical properties.

XRD spectra are recorded by Philips X-pert pro diffraction, (Model- PW 1830) with CuK α (0.154 nm) radiation. TEM pictures are taken by JEM 100CXII, JEOL Japan at accelerating voltage of 100 KV, FTIR spectra are recorded by Perkin Elmer Spectrum RXI FTIR System, photoluminescence spectra are recorded by Hitachi F-2500 Fluorescence spectrometer.

DISCUSSION AND RESULTS

XRD study

Figure 1(a) and Figure 1(b) show the XRD patterns of the undoped ZnS particles and Mn²⁺ doped ZnS particles respectively. These patterns show diffraction peaks at $2\theta = 28.91^\circ$, 48.11° and 57.107° corresponding to the (111), (220) and (311) planes, respectively for cubic phase ZnS (JCPDS No.80-0020). The particle sizes of nanocrystalline ZnS is estimated

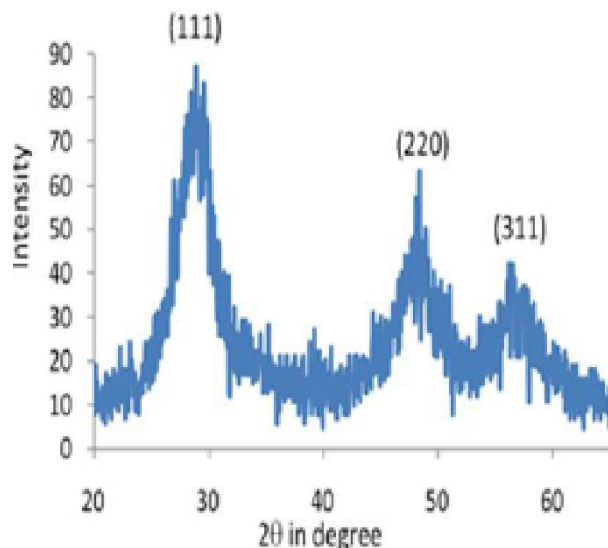


Figure 1(a) : XRD of undoped ZnS particles

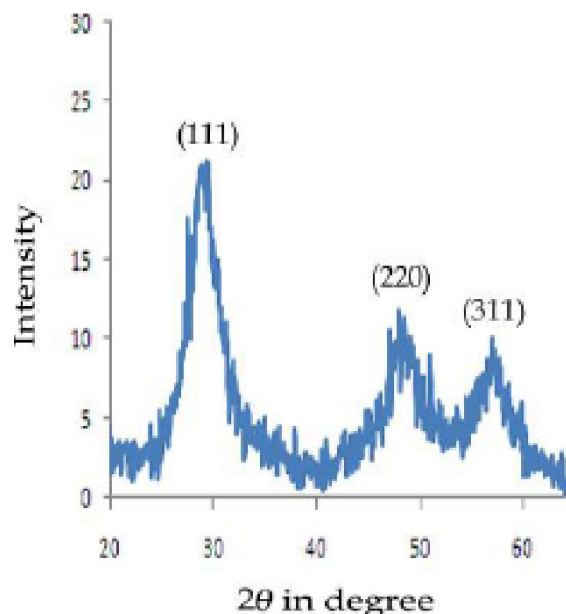


Figure 1(b) : XRD of doped ZnS particles

by using Debye-Sherrer formula:

$$t = K\lambda/\beta\cos\theta \quad (1)$$

where, K is a constant of value 0.9, λ is wavelength of X-ray used, which is CuK α radiation and is equal to 0.154 nm and β is Full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane. Broadening of the peak indicates the nanocrystalline nature of the material. The crystallite size is calculated from the FWHM diffraction peak (111) as 2.59 nm for ZnS nanoparticles doped with Mn²⁺.

TEM study

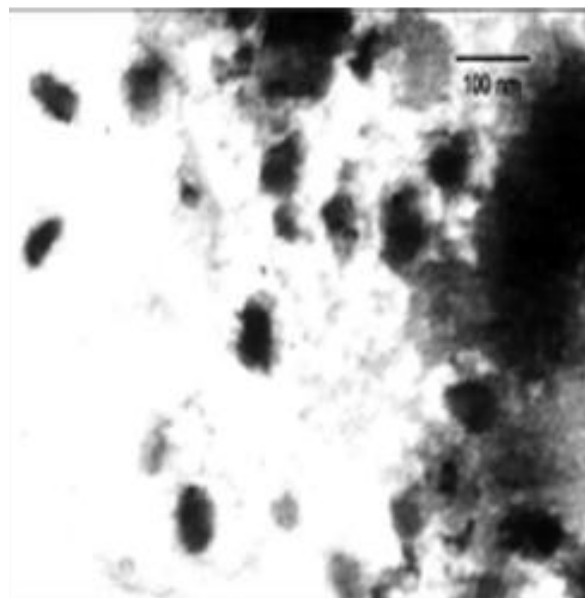


Figure 2(a) : Morphology of undoped particles

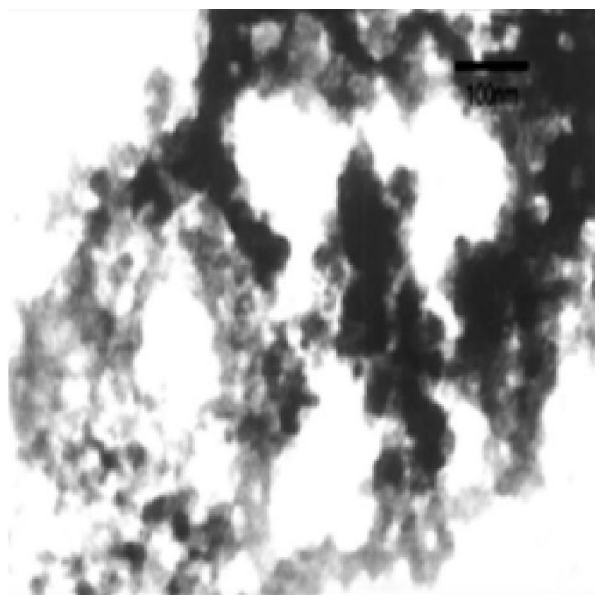


Figure 2(b) : Morpholog of doped particles

Figure 2(a) and Figure 2(b) show the morphology of the undoped ZnS and doped (ZnS: Mn²⁺) nanoparticles respectively. From the micrographs it is clear that ZnS grains are not uniformly distributed. Also, the grain sizes are not same. The average grain size estimated from the histograms of frequency of occurrence versus particles size is found to be 28 nm for undoped ZnS and 15nm for doped ZnS. It is however to be noted that the average grain size determined by TEM are comparatively larger than the particle size measured by XRD. This larger value of grain sizes may be due to the agglomeration of grains^[12].

Photoluminescence (PL) study

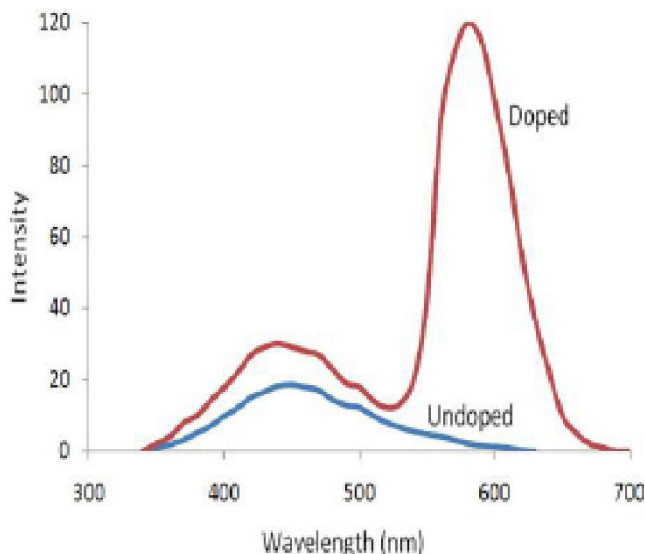


Figure 3 : PL spectra of undoped and ZnS:Mn doped samples

Photoluminescence (PL) spectra of undoped (ZnS) and doped (ZnS: Mn²⁺) nanoparticles were carried out at room temperature with excitation wavelength 280nm and are shown in Figure 3. Emission spectra showed a small broad peak at 447.5nm which is comparable with the other group^[13]. Photoluminescence in this region is due to the presence of sulphur vacancies in the lattice, as previously found for ZnS colloids^[14-16]. On doping zinc sulphide with manganese, the PL spectra revealed orange red emission peak at around 585nm with one weak peak at 443.5nm. Mn²⁺ based emission has also been observed by other workers in the photoluminescence of doped ZnS: Mn²⁺ nanoparticles at about 585nm^[9, 14, 17] and 588nm^[18-19]. The emission at around 443.5nm is typical luminescence of undoped ZnS resulting from the transition of electrons from shallow states near the conduction band to sulphur vacancies present near the valance band^[20].

FTIR Study

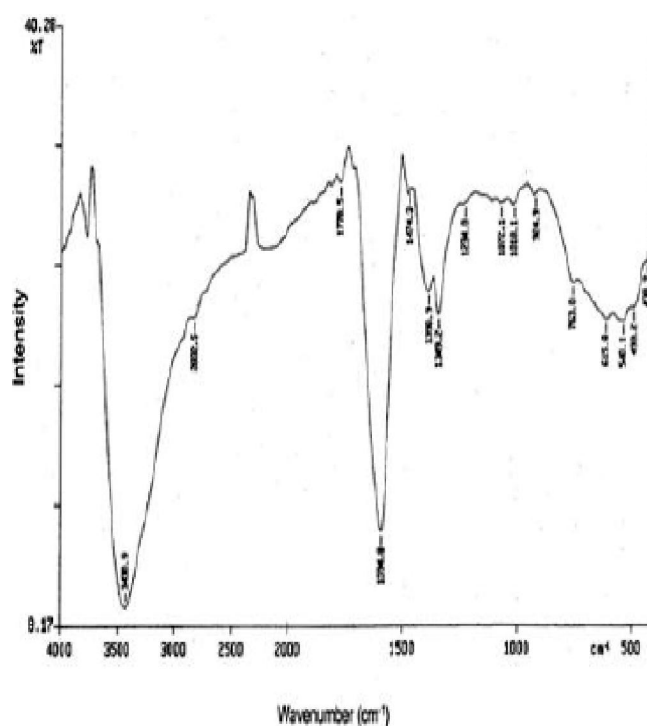


Figure 4 : FTIR spectrum of ZnS:Mn doped sample

IR Spectra of doped ZnS nanoparticles is shown in Figure 4. IR peaks are assigned to the sample at room temperature.

Our measurement of the spectrum of powder sample yields the bands, which are in good agreement with the reported values. The band at 3430.9cm⁻¹ cor-

Full Paper

responds to valance vibrations of the occluded water. Bands around 900-1474 cm⁻¹ are due to oxygen stretching and banding frequency. Weak additional band was observed at 924.9 cm⁻¹. This mode indicates the presence of resonance interaction between vibrational modes of sulphide ions in the crystal^[14]. The peak at 615.8.4cm⁻¹ is assigned to ZnS band (i.e. corresponding to sulphides), whereas the presence of peak at 540.1cm⁻¹ represents either manganese-oxygen or sulfur-oxygen interaction. Again the bands around 493.2cm⁻¹ and 439.2cm⁻¹ are assigned to the Mn-O band which confirms the presence of manganese.

CONCLUSION

Undoped and doped ZnS spherical nanoparticles have been successfully synthesized by a simple chemical precipitation method at low temperature. X-ray diffraction studies revealed that the synthesis particles have cubic zinblende structure. ZnS spherical nanoparticles with emission represent good candidates for use in optoelectronic devices.

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