Structural, Optical and Thermal Studies on Zinc Sulfide Nanorods and Manganese Sulfide nanoparticles

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Abstract—Nano sized ZnS and MnS_2 were synthesized through a simple wet chemical route. In this Synthesis metal sulfides were used as the starting material and allowed to react with the transition metal source at 60°C for 75 minutes. The products were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Photoluminescence spectra (PL), Raman Spectra, Thermogravimetry analysis Differential thermal analysis (TGA/DTA) and Fourier Transform Infrared Spectroscopy (FT-IR). The crystalline structure of ZnS and MnS_2 were confirmed by XRD pattern.

Key words - Zinc sulfide nanorod, Manganese Sulfide nanoparticle, Raman Spectroscopy, TGA/DTA, SEM and XRD.

I. INTRODUCTION

In the past decade, a great deal of attention had been invested in the synthesis and characterization of varying nanomaterials and quantum dots. Nanomaterials are defined as small materials with size varied from 1-100nm [1]. Zinc sulfide (ZnS) is a (II–VI) semiconductor material which finds application in electroluminescence, optoelectronic devices, photo catalysis, solar cell, IR window, Cathode-Ray Tubes (CRT) and Field Emission Displays (FED)[2]. Semiconductor nanomaterials exhibit size-dependent electronic band gap energies [3]. Semiconductor metal sulfide (like ZnS, MnS_2) nanoparticles have been extensively investigated due to their unique properties and potential application in diverse areas such as photo catalysis, solar cells, display panels and new devices like single electron transistors and so on [4–9]. Manganese sulfide (MnS_2) has a wide band gap energy of Eg (T=0) ~ 3.7 eV. MnS_2 occurs in three forms namely: the stable green α- MnS with rock-salt-type structure, and two pink meta stable tetrahedral structures, β-MnS_2 (sphalerite type) and □-MnS_2 (wurtzite type) [10]. Many methods have been introduced to synthesise nanomaterials such as colloidal chemical method, microwave irradiation hydrothermal synthesis, ultrasonic irradiation, and so on. Among them, the colloidal chemical method is proven to be powerful one. Crystal structure, size and shape-controlled nanoparticle and many metastable materials can be formed in colloidal chemical method at low temperature [11-14].

II. EXPERIMENTAL

1.1 Chemicals:

Zinc acetate (or) Zinc ethanoate [minimum assay 99.5%)], Manganese (II) sulphate, monohydrate [minimum assay 99.0], sodium sulfide [minimum assay 32.0-38.0%], are purchased from Merck chemicals Ltd.

1.2 Synthesis of Zinc sulfide (ZnS) and Manganese sulfide (MnS_2) nanoparticles:

The nanocrystalline ZnS and MnS_2 samples were prepared by wet chemical methods. Zinc acetate (Zn $(CH_3COO)_2$. H_2O) and manganese sulphate monohydrate ($MnSO_4.H_2O$) and 50ml of 0.1N sodium sulfide (Na_2S) are taken in a beaker. The above mixture was heated and stirred for 3 hours at 75°C. A precipitate was obtained and has been allowed to cool to room temperature. To remove the impurities the precipitate was washed several times with absolute ethanol and double distilled water. The final product was filtered and dried in a hot-air-oven at 60°C.

Characterization:

The products were characterized by powder X-ray technique using SEFERT diffractometer, equipped with a curved graphite mono chromate using Cu Kα radiation (□-1.54 nm) operating at 45 KV and 40mA at a scan rate of 5°/min. The synthesized products were investigated at a magnification of 5 to 30,000X and secondary electron resolution of 3.0 NM (30Kv, WD8mm) SEM JELOL –JSM-6390 JAPAN and UV-Visible spectra were recorded by using ELICO-BL-198 spectrophotometer at

room temperature. Thermo gravimetric analysis was carried out with a PERKIN ELMER PYRIS 1/DIAMOND by using Pt crucible at various temperatures up to 1000°C. Raman and Photoluminescence spectrum were recorded using 514.5nm detector and CCD by using HORIBA spectrophotometer.

III. RESULTS AND DISCUSSION:

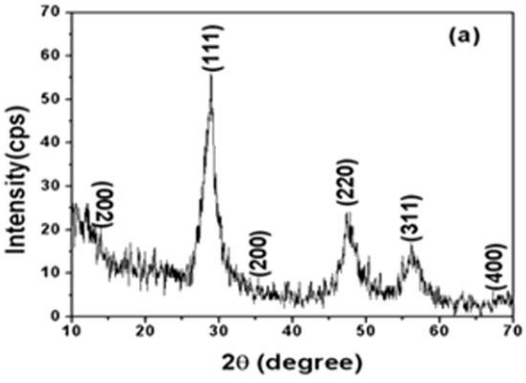
3.1 X-Rays Diffraction Studies:

The grain size was calculated from the full-width at half-maximum (FWHM) of the most intense diffraction peaks using Debye-scherrer formula:

$$D = 0.9\lambda / \beta\cos\theta$$

Where,
λ-Wavelength of X-ray (1.54 Å in this case),
β-Width half maximum of the diffraction peak (radians),
θ- Diffraction angle of the peak on the 2θ scale [15].

ZnS shows [Fig- (1a)] fairly broad peak suggesting the nanocrystalline nature. From the JCPDS No 05-0566, the three strong peaks appeared at angles (2 θ of 28.7°, 47.7° and 56.6° are corresponding to (111), (220) and (311) planes which confirms the cubic crystalline structure. The size of the nano rods were calculated using Debye –Scherrer formula using (111) reflection of the XRD pattern and average particle size estimated was 107nm. Fig (1b) shows the XRD of MnS_2. The JCPDS No 25-0549 indicates that the XRD peaks appeared in 2θ of values 25.87°, 32.44°, 36.01°and 38.03° correspond to (111), (012), (112) and (022) planes respectively. It confirms the cubic crystalline structure of MnS_2. The size of the nano particles and Nanorods was calculated using Debye –Scherrer formula using (112) reflection of the XRD pattern and average particle size was 54.58nm.



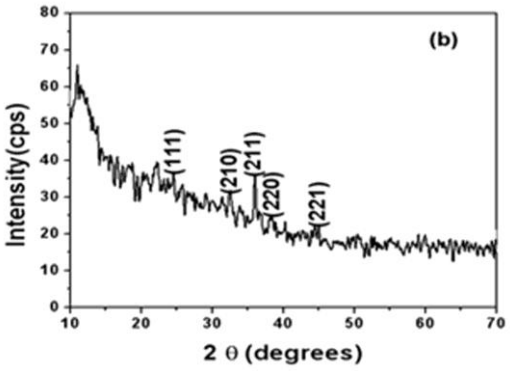


Fig (1) XRD patterns of the nanostructures (a) ZnS nanorod and (b) MnS_2 nanopaticles.

3.2 Infrared Spectroscopy:

The FT-IR spectrum of the ZnS and MnS_2 nanoparticles in the frequency range of 300-4000 cm-1, reveals the various vibrations involved in the molecules. Fig (2a) shows the FT-IR peaks of ZnS nanoparticles, which can be assigned to S-S group in the molecules. The characteristic absorptions are due to S-S stretching. The absorption peak of ZnS nanoparticles appears as a weak band in the region of 2877cm^{-1}, 3014 cm^{-1}, 3459cm^{-1}. The Metal peaks appear as a weak band in the region of 877.65cm^{-1}. Fig (2b) shows the FT-IR spectra of MnS_2 nanoparticles in which the absorption bands are at 1737cm^{-1} and 1553cm^{-1}. The M-S stretching is confirmed by the peaks at 3459cm^{-1}, 3014cm^{-1} and 2877cm^{-1}.

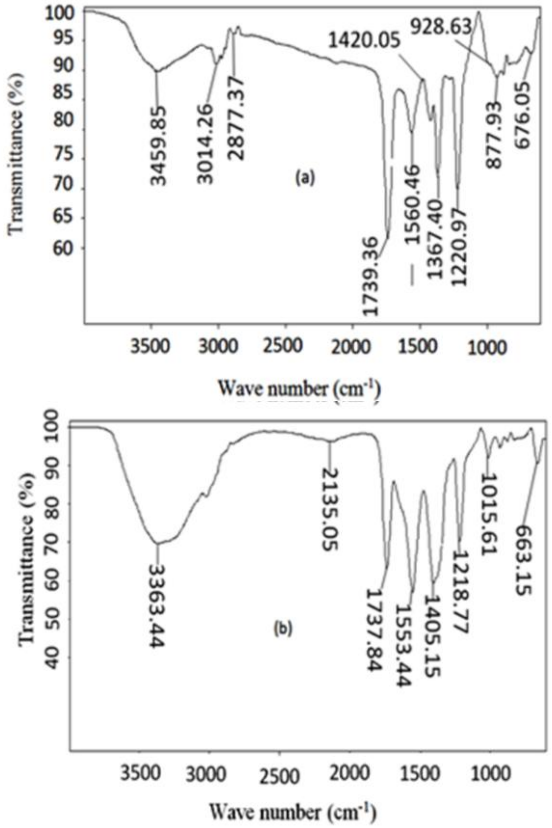


Fig (2) The FT-IR spectra of (a) ZnS nanorod and (b) MnS_2 nanoparticles.

3.3 UV-Visible Spectroscopy:

The UV-Visible absorption spectrum of ZnS and MnS_2 nanoparticles were measured and the band gap was calculated. Fig (3a) shows the absorption spectrum of ZnS nanoparticles dispersed in ethanol by sonication. An intense peak at 375.66 nm and one less intense peak at 271.66 nm were observed. Fig (4a) shows the band gap of ZnS nanorod was 2.6eV. Fig (3b) shows the absorption spectrum of the MnS_2 nanoparticle which is dispersed in ethanol by sonication. An intense peak centered around 321.51 nm and one less intense peak around 238.35 nm were observed. Fig(4b) shows the band gap of MnS_2 nanoparticles as 2.8 eV.

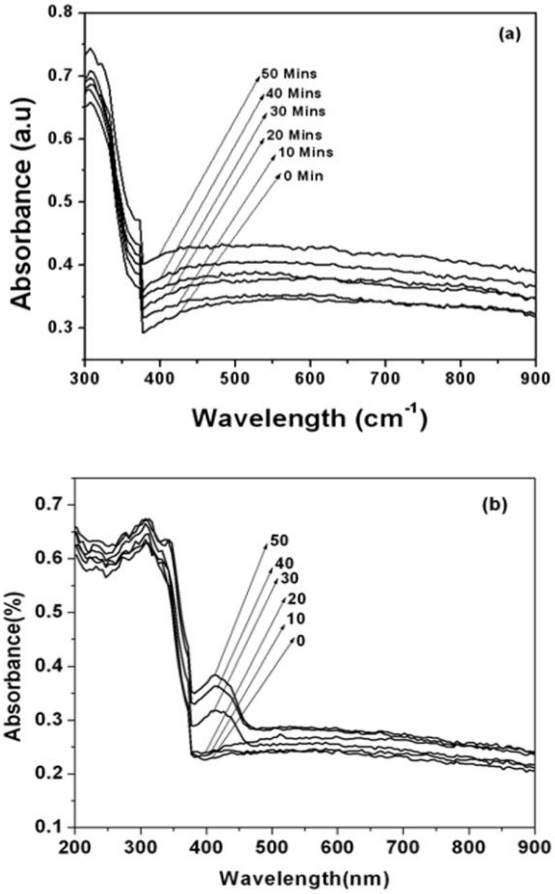
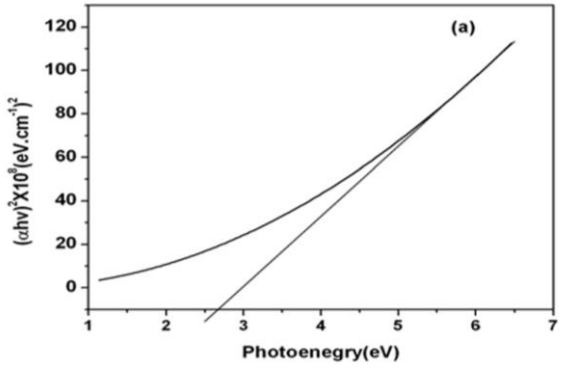


Fig (3)The UV-Visible spectrum of the nanorod and nanoparticles prepared in ethanol (a) ZnS nanorod and (b) MnS_2 nanoparticle.



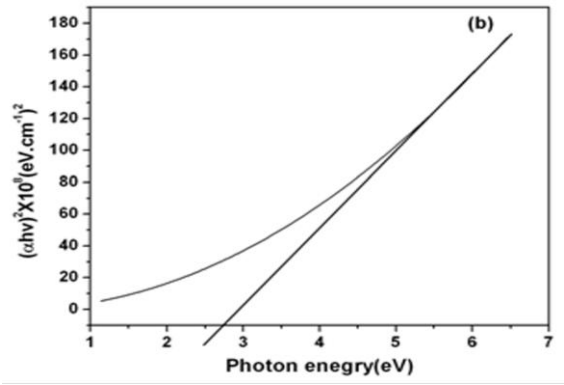


Fig (4) Photon-enegry graph of the prepared nanostructures (a) ZnS nanorods and (b) MnS_2 nanoparticles.

3.4 Micro Raman Spectroscopy:

In the present work, a systematic study has been conducted on the effect of finite size by using Raman spectra of particles sized in the nanometer range of ZnS and MnS_2. The spectra were obtained using 514nm excitation from the Ar^+ion laser. Fig (5a) shows the Raman scattering performed at room temperature to investigate the crystal quality and vibration properties of ZnS nanoparticles. Wurtzite ZnS belongs to the C^4_{6V} space group, with two formula units per primitive cell [16]. Fig (5b) shows the Raman spectrum of MnS_2 with three strong bands at 153.4, 219.1 and 472.2 cm^{-1} and weak bands at 433.4 cm^- and 660.7 cm^{-1}. From the above discussion it is established that MnS_2 has antiferromaganetic structure. The Raman spectrum is believed to correspond to the MnS_2-Hauerites [17].

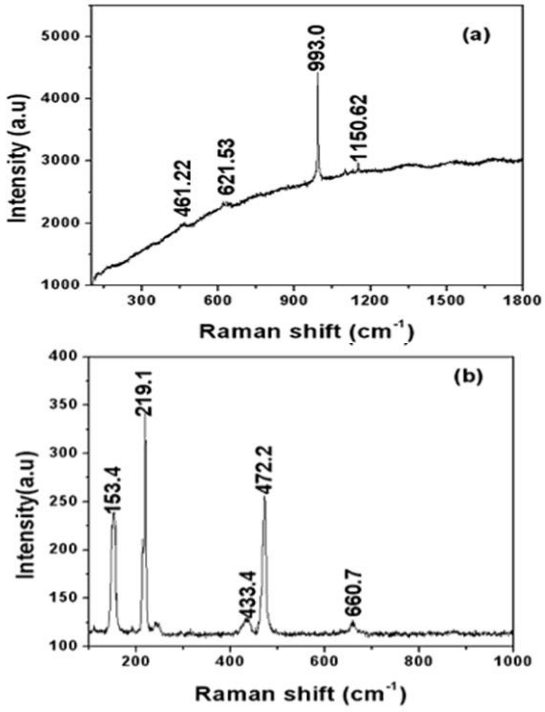


Fig (5) The Raman spectrum of the nanostructures (a) ZnS Nanorod and (b) MnS_2 nanopaticles.

3.5 Micro Photoluminescence:

In Fig (6a) the strong PL intensity was observed for ZnS nanorods. The broad and intense peak at 428.49 nm (2.5eV) is a typical luminescence of undoped ZnS resulting from the transition of electrons from shallow near the conduction band to sulfur vacancies present near the valence band. Fig (6b) shows a PL spectrum of the synthesized MnS_2 nanoparticles with an excitation of 273 nm. It consists of one strong narrow emission at 422.02 nm (2.81 eV), which is similar to the band gap of the bulk counterpart [18].

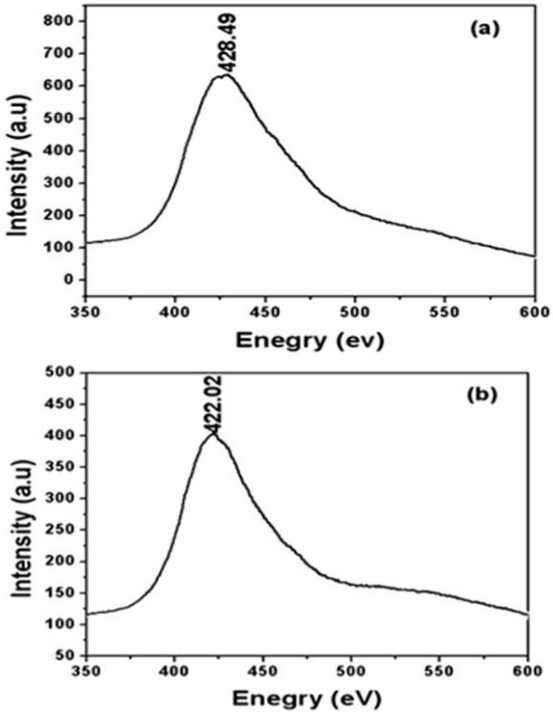
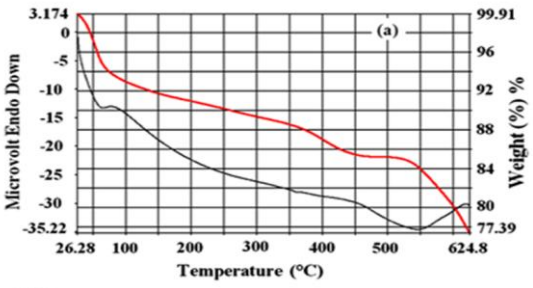


Fig (6) The PL of the prepared nanostructures (a) ZnS nanorods and (b) MnS_2 nanoparticles.

3.6 Thermogravimetry and Differential thermal analysis:

Figure (7a) shows TGA/DTA graph of ZnS nanorods. The TGA curve indicates the two stages of weight loss approximately at 80-90°C and a rapid weight loss in the region 455-500°C leaving 79.3% residue. Fig (7b) shows TGA/DTA curve of MnS_2 compound which undergoes three stage rapid weight loss approximately 56% at 220-250°C, second stage approximately 61.5% at 400-420°C and a rapid weight loss approximately 78% around 570-610°C.



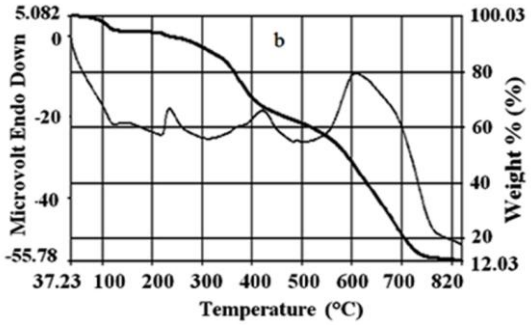


Fig (7) The TGA/DTA of the prepared nanostructures (a) ZnS nanorods and (b) MnS_2 nanoparticles.

3.7 Scanning Electron Microscopy:

The size and morphology of the prepared products were characterized by scanning electron microscopy (SEM). From the fig (8) nano rods of ZnS , and the same was characterized by low – magnification SEM. The product is synthesized by wet chemical method, in the absence of the surfactant at 75°C for 3 hrs. Hence, it is proved that the large amount of ZnS crystals are in rod shape with the range of 1.7µm and 2.2µm and can be synthesized using wet chemical approach. Fig (9) shows SEM image of the MnS_2 in water. The MnS_2 nanoparticles are approximately mono dispersive spheres with an average diameter of approximately 3-5µm.

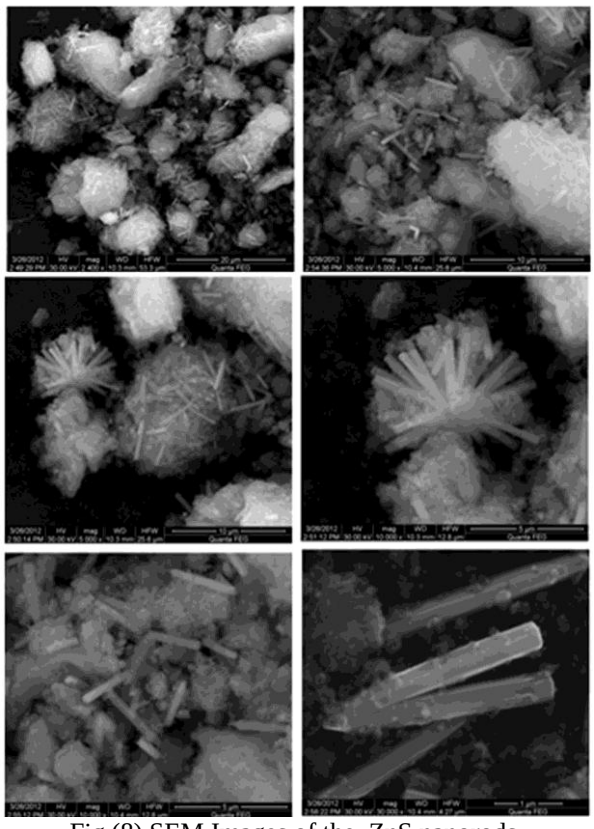


Fig (8) SEM Images of the ZnS nanorods.

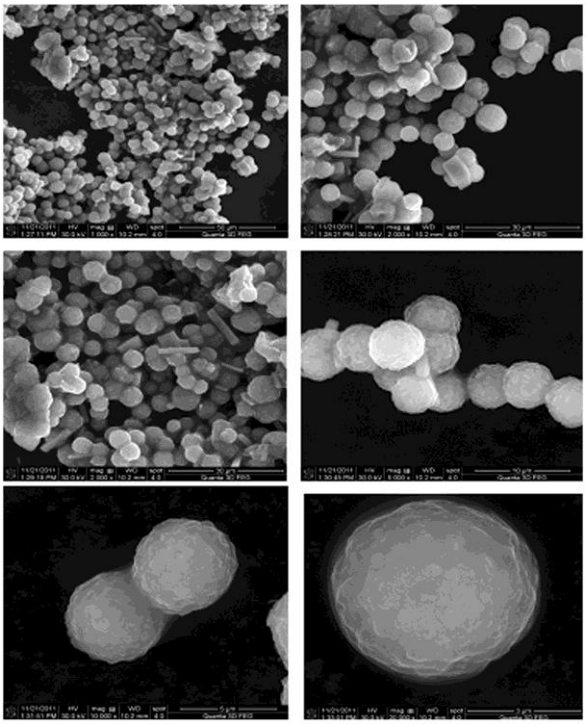


Fig (9) SEM image of the MnS_2 nanoparticles.

CONCULSION

The synthesis of ZnS nanorods and MnS_2 nanoparticles can be achieved by wet chemical route in a single step process. The XRD measurement of crystalline phase determines the structure of ZnS and MnS_2. The FTIR has confirmed the formation of metal sulfide nanoparticles in the range of $2135.05^{-1}cm^{-1}$ to $3363.44cm^{-1}$. The bulk band gap of ZnS- 2.66eV and that of MnS_2-2.74eV were calculated from the UV-VIS measurement. Raman study determined the strength of metal-sulfur bond in ZnS as $993.0cm^{-1}$. The Raman frequency range of MnS_2 is 153.4, 219.1 and 472.2 cm^{-1}. Band gap of nanoparticles is evident by the calculation, using Photoluminescence and UV-Visible measurement. The TGA/DTA results determine the weight loss and removal of water and organic solvent.

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