Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S55-S58

ASIAN JOURNAL OF CHEMISTRY

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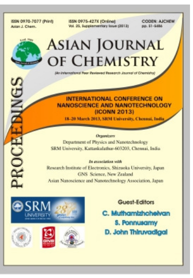

Synthesis and Characterization of Pure Metastable γ-Manganese Sulfide Microsphere at Low Temperature by Wet Chemical Technique†

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AJC-12791

In the present work, pure metastable γ-manganese sulfide (γ-MnS) microspheres have been synthesized in a controlled manner by varying the refluxing temperature of the solution using wet-chemical route. The γ-MnS particles has been synthesized by using manganese acetate [$Mn(CH_3COO)_2$] and thioacetamide (CH_3CSNH_2) in aqueous solution. The prepared γ-MnS microsphere has been characterized by X-ray diffraction, scanning electron microscope, UV-visible absorbance and photoluminescence. X-ray diffraction results show that as-prepared MnS microstructures exhibit tetrahedrally coordinated γ-MnS wurtzite structure. The average crystallite size and specific surface area have been calculated from the XRD data. The morphological changes of the prepared γ-MnS microspheres have been investigated. The EDAX analysis indicates the purity of as-prepared sample. UV-visible optical spectroscopy study has been carried out to determine the band gap energy of γ-MnS particles. The room temperature photoluminescence spectrum exhibits a blue emission peak at around 440 nm.

Key Words: γ-MnS, Wet-chemical method, Refluxing, Crystallite size, Morphology, Optical band gap, Emission band.

INTRODUCTION

The fabrication and characterization of crystalline semiconducting metal sulfides have an intense field of research due to their attractive properties and potential applications. Manganese chalcoginides (sulfides, selenides and tellurides) are the magnetic materials and they have unique morphological, physical and chemical properties[1,2]. Manganese sulfide belongs to VIIB-VIA magnetic *p*-type semiconductors with optical band gap energy Eg of *ca.* 3.7 eV[3]. It is a dilute magnetic semiconductor, whose interest is related to their outstanding magneto-optical properties[4] that are of potential use in optoelectronic devices and buffer materials, solar selective coatings, anti reflection coating, solar cells, sensors, photoconductors, optical mass memories and spintronics applications.

MnS powders have three polymorphic forms[5]: The stable rock salt type α-MnS structure which is the most common form and two metastable tetrahedral β-MnS (sphalarite type) and γ-MnS (wurtzite type) structures. The β-phase and γ-phase MnS can be prepared at low temperature, but it will transform irreversibly to the octahedrally coordinated stable α-phase at 100-400 ºC.

Some works on MnS studies *e.g.*, MnS thin film crystals have been produced by chemical bath deposition technique[6-9], amorphous manganese sulfide thin films have been characterized by SILAR method[10], the α-MnS and γ-MnS particles have been synthesized by hydrothermal process[11-13] and synthesis of α-MnS crystals by solvothermal route[14].

In the present paper, we address the synthesis of wet-chemical route based γ-MnS microspheres at low temperature. This work is focused to study the influence of refluxing temperature during the preparation of γ-MnS particles. The synthesized micro particles have further been characterized by XRD, SEM, EDAX, UV-visible optical spectroscopy and photoluminescence properties. Only limited work has been done in this preparation method of γ-MnS powder particles.

EXPERIMENTAL

Manganese acetate [$Mn(CH_3COO)_2$], thioacetamide (CH_3CSNH_2), ammonium chloride (NH_4Cl), triethanolamine [$N(CH_2CH_2OH)_3$] and trisodium citrate ($C_6H_5Na_3O_7$). All chemicals used are of analytical grade purchased from Merck Chemicals, India and used as received without further purification. Deionized water is used for all the preparation process.

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†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

Preparation of MnS powders: Aqueous solutions of manganese acetate has been used as manganese source and thioacetamide as sulphur source. The triethanolamine and trisodium citrate as capping agents for preparing γ-MnS particles. A typical synthesis has been performed as follows: 20 mL of (1.0 M) manganese acetate and 2 mL of triethanolamine were dissolved in 100 mL of deionized water. This solution has been stirred for few minutes. Under the continuous stirring, 20 mL of ammonia was added drop-wise, the solution became clear and homogenous. After 0.5 h, 0. 4mL trisodium citrate was mixed in, followed by addition of 20 mL of (1.0 M) thioacetamide solution. The pH of solution is measured to be *ca.* 8.5. The ammonia is added drop by drop to get pH 10.5 and the final solution is stirred for 2 h. All the above process has been done at the room temperature. The solution is refluxed at different temperature for 3 h. At the end of reaction, the precipitate has been centrifuged for 5 min and washed several times with deionized water. The final product has been dried at 70 ºC for 10 h. The above process with refluxing temperature at 55 ºC and 65 ºC yields two samples namely MnS-S1 and MnS-S2 respectively.

Characterization of samples: The crystal structure of the obtained γ-MnS powder is examined by X-ray diffraction (XRD) using a Shimadzu XRD6000 diffractometer. The morphology of the samples is observed by SEM which is performed on a JEOL JSM-6390LV scanning electron microscope. The chemical analysis using EDAX has been performed by the EDAX spectrometer attached to the scanning electron microscope. Optical Absorption spectra of as-prepared samples are recorded with an UV scanning spectrophotometer (JASCO V-570) in the range 300-500 nm. The photoluminescence measurements have been carried out using a HORIBA JOBIN YVON Fluorolog at the excitation wavelength of 350 nm.

RESULTS AND DISCUSSION

Fig. 1 represents the X-ray diffraction pattern of the synthesized γ-MnS particles as a function of two different refluxing temperatures. The d-spacing values of MnS-S1 and MnS-S2 samples corresponding to the diffraction peaks are compared with the standard data (JCPDS, powder diffraction file No. 40-1289)[7] and found to be in good agreement with the wurtzite phase pure metastable γ-MnS. The sharp peaks of the XRD pattern indicate that the synthesized γ-MnS particles are well crystalline in nature[11-18]. The lattice constants have been calculated as a = b = 3.986, c = 6.3713 for MnS-S1 and a = b = 3.9408, c = 6.3937 for MnS-S2 which are agreed well with standard JCPDS data. In addition, the broadening of XRD peaks which in turn to leads particles in small size[19]. From the XRD data, the broadening of the XRD peaks gradually decreases with increasing refluxing temperature which has been shown in Table-1. The average crystallite sizes were calculated from the Debye-Scherrer formula:

$$D_{avg} = k\lambda/\beta \cos \theta$$

where, k denotes the Scherrer constant (k = 0.90), λ = 1.5406 Å is the wavelength of the incident radiation, β is the FWHM height of the diffraction peak at angle θ[15]. The average crystallite sizes have been calculated as 4.26, 4.70 and 6.13 nm for

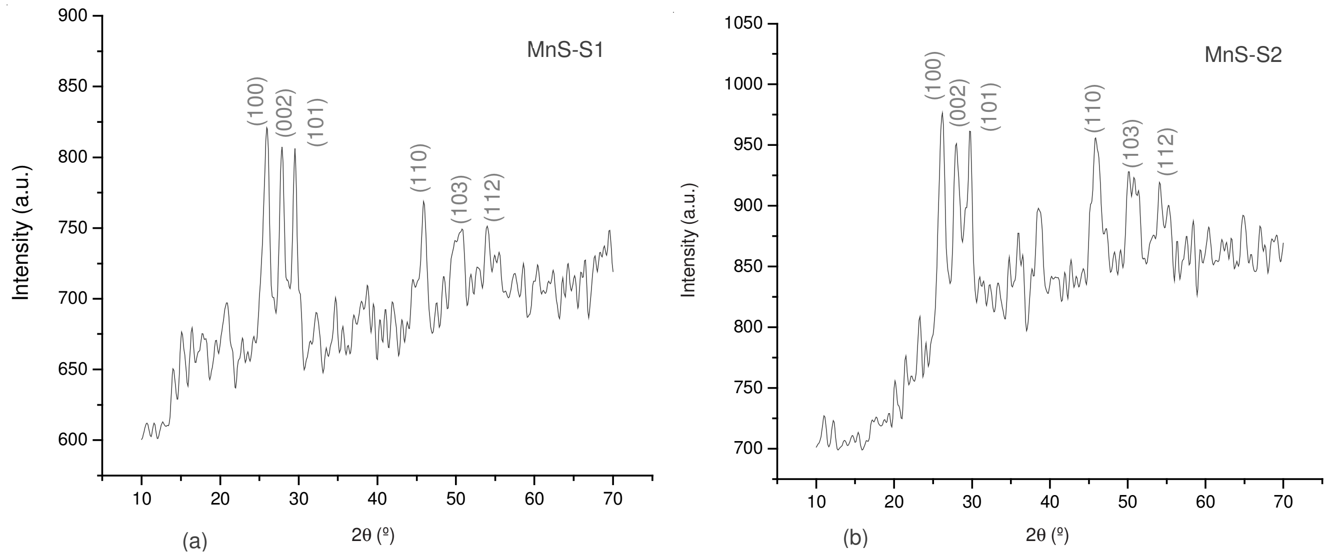

Fig. 1. X-ray diffraction patterns of γ-MnS particles for (a) MnS-S1 (b) MnS-S2

TABLE-1
AVERAGE CRYSTALLITE SIZE (D) AND SPECIFIC SURFACE AREA (SSA) OF γ-MnS PARTICLES

Sample ID	k	λ (nm)	2θ	θ	β in radians	cos θ	D (nm)	SSA (m^2/g)
MnS-S1	0.94	0.15406	25.8000	12.90	0.0348889	0.97479	4.26	353.15
MnS-S1	0.94	0.15406	28.0000	14.00	0.0317488	0.97033	4.70	319.89
MnS-S1	0.94	0.15406	29.6000	14.80	0.0244222	0.96686	6.13	245.19
MnS-S2	0.94	0.15406	26.1019	13.05	0.0183306	0.97420	8.11	185.43
MnS-S2	0.94	0.15406	27.9000	13.95	0.0144928	0.97054	10.30	146.06
MnS-S2	0.94	0.15406	29.6000	14.80	0.0179817	0.96686	8.33	180.53

the sample MnS-S1 and 8.11, 10.3 and 8.33 nm for the sample MnS-S2. The specific surface area of the samples has been calculated as:

$$S = 6 \times 10^3/\rho D \ m^2/g$$

where, S is the specific surface area (m^2/g), ρ is the density of MnS (3.99 g/cm^3) and D is the average crystallite size. The specific surface area is increased as the particle size becomes small (Table-1). It is shown that the increase in XRD peak width, decreases average crystallite size and increases specific surface area[16].

The chemical purity and stoichiometry of the γ-MnS particles have been examined by energy dispersive X-ray analysis. The EDAX spectrum shown in Fig. 2 exhibits the presence of only manganese and sulphur, suggesting the particles are indeed made up of Mn and S. The inset shows the ratio of Mn and S ion concentration. The spectrum is devoid of any other metal ion which indicates the purity of the prepared samples.

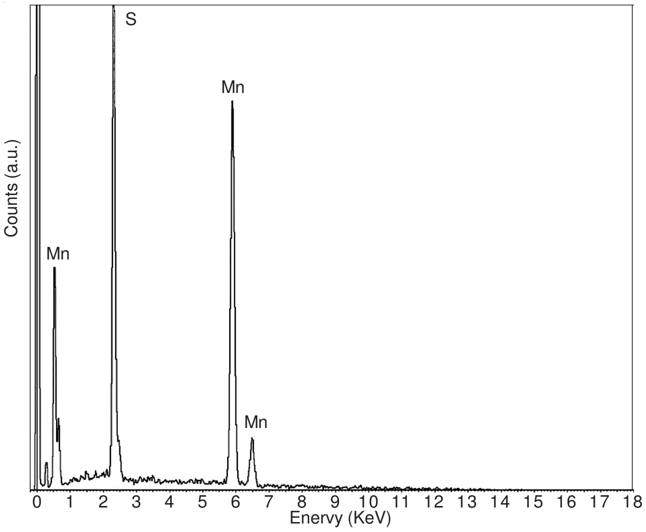

Fig. 2. EDAX Spectrum of γ-MnS particles

The morphology of the synthesized γ-MnS particles have been examined by SEM imaging at different magnifications and shown in Fig. 3. The SEM images reveal the perfectly solid spherical shape of γ-MnS particles. Fig. 3(a) shows the growth of MnS-S1 with smooth spherical surface and the particle size estimated from the SEM images is 400-1000 nm. Fig. 3(b) shows the SEM image of MnS-S2 that is micro sized spherical rough surface and approximated particle size of 1 to 5 µm. By increasing the refluxing temperature, the nucleation rate of the particles decreases rapidly. XRD and SEM analysis are in perfect agreement with each other.

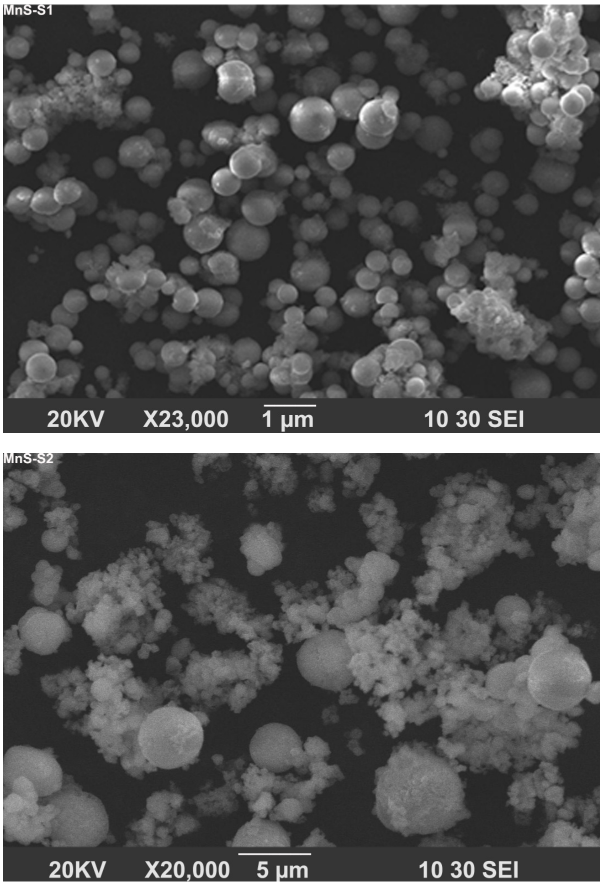

Fig. 3. SEM images of γ-MnS microsphere particles at different magnifications

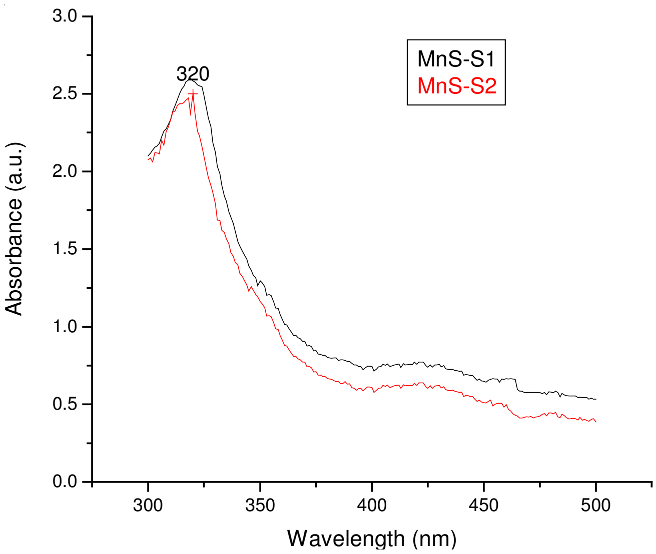

Fig. 4. UV-visible absorption spectrum of γ-MnS particles

Fig. 4 shows the UV-visible absorption spectrum of γ-MnS particles at room temperature. The samples are ultrasonically dispersed in absolute ethanol. From the absorption spectrum, the cutoff wavelength is observed at 320 nm for both samples. The band gap energy of γ-MnS particles has been calculated as:

$$\text{Band gap energy } (E_g) = h^*C/\lambda$$

where, h = Planks constant, C = Speed of light and λ = Cut off wavelength. The energy band gap of as-prepared γ-MnS is found to be 3.88 eV at 320 nm wavelength, which is slightly blue shifted from the bulk value of 326 nm (3.8 eV)[14,17].

Fig. 5 presents a room temperature photoluminescence spectrum of as-prepared γ-MnS particles which has been obtained with an excitation wavelength of 350 nm. The photoluminescence spectrum shows the efficient emission of blue light with peak at 438 and 440 nm for the prepared samples which corresponds to the direct recombination between electrons in the conduction band and holes in the valence band[20,21].

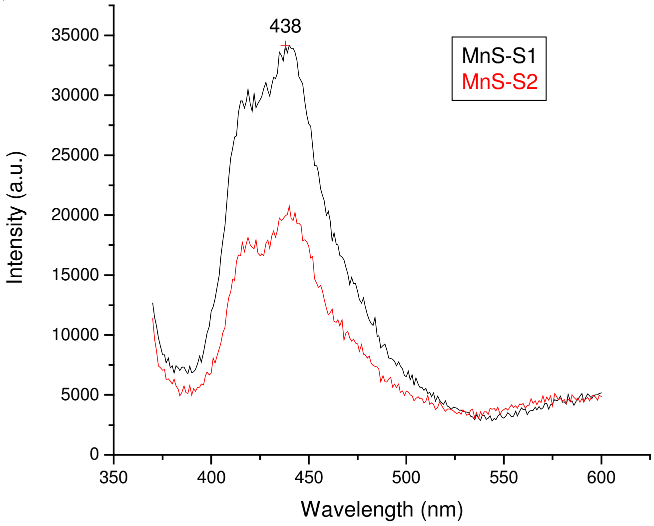

Fig. 5. Photoluminiscence spectrum of as-prepared γ-MnS particles

Conclusion

In summary, we have successfully prepared metastable γ-MnS microspheres *via* a wet chemical synthesis route at low temperature. This method offers to produce a large quantity of γ-MnS with low cost. The crystallite size, lattice parameters and specific surface area of as-prepared samples have been determined by using XRD data. The XRD results show that the increase in XRD peak width, decreases average crystallite size and increases specific surface area. SEM indicated the spherical shape morphology of γ-MnS microparticles. EDAX spectrum shows the good stoichiometric ratio. The optical band gap energy of as-prepared sample is 3.88 eV, which is higher than the bulk. The γ-MnS microspheres emit stoke-shifted blue light at 440 nm. The optimum refluxing temperature for minimum size is found to be 55 ºC.

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