International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

Structural, Morpological and Optical Properties of Hetarolite- $Znmn_2o_4$ Nano Particle by Hydrothermal Method

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Abstract: ***Hetarolite-$ZnMn_2O_4$ nanoparticles were synthesized by hydrothermal/solvothermal method using Mn $(CH_3COO)_2{\cdot}4H_2O$ and $Zn(CH_3COO)_2.2H_2O$ as precursors and Oleic acid as surfactant at synthesis temperature of 180ºC for 48hr. The synthesized product was characterized by X-ray Powder Diffraction (PXRD), Field Emission Scanning Electron Microscopy (FE-SEM), and Energy Dispersive X-ray analysis (EDAX), High Resolution Transmission Electron Microscopy (HR-TEM), Selected Area Electron Diffraction (SAED). UV-vis-NIR absorption and Fourier Transform Infrared Spectroscopy (FTIR) are also reported for the material. The XRD analysis reveals that $ZnMn_2O_4$ nanoparticles exhibit tetragonal structure. The functional group of $ZnMn_2O_4$ as confirmed from FTIR spectral study. The Uv-vis-NIR absorption spectrum of the synthesized nanoparticles was used discuss about the optical property of the sample. The role of Oleic acid in controlling the size and morphology of the final products is discussed. The chemical composition was confirmed by EDX analysis and confirmed the presence of Mn, Zn and O in the sample***

Keywords: Solvothermal, Surfactant, Nanoparticles, Tetragonal

1. Introduction

Today, nanotechnology (NT) is operating in various fields of science via its operation for materials and devices using different techniques at nanometer scale. Nanoparticles are a part of nanomaterials that are defined as a single particles 1–100 nm in diameter[1]. Nanometer-sized materials have recently attracted a considerable amount of attention due to their unique electrical, physical, chemical, and magnetic properties, these materials behave differently from bulk materials. Hetarolite $ZnMn_2O_4$ is one of the most attractive compounds of the AB_2O_4 series because of its low oxidation potential and low material cost[1]. Various nanostructures of Hetarolite $ZnMn_2O_4$ with different morphologies such as, nanorods/nanowires, mesoporous/hollow spheres, nanofibers and other structures have been synthesized by different routes, such as sol-gel process, thermal decomposition, co-precipitation, microwave synthesis, and hydrothermal process etc[2].**Pei Fan Teh** supported a work on $ZnMn_2O_4$ powders (nanofibers, nanorods, nanowebs) by facile electrospining technique by a simple variation of sintering profile and its can be used for anodes in lithium ion battery application[3]. **Zhang et al** prepared one –dimensional $ZnMn_2O_4$ nano rod viahydrothermal method using metal acetate as precusor at 140ºC for 12h[4].The formation of $ZnMn_2O_4$ hollow microspheres by $ZnMn_2O_4$nanosized building blocks, demonstrated by **L. Zhou et al** each building blocks of $ZnMn_2O_4$ provides the benefits of nanometer sized assembly ensures better structural stability &cyclability as an anodic material for lithium –ion-batteries.

In this work, we report the solvothermal methods for the synthesis of Hetarolite - $ZnMn_2O_4$ nanoparticle using ethanol as solvent and metal acetates as solute. Oleic acid (OA) is a commonly used surfactant to stabilize the metal oxide nanoparticles with strong chemical bond between the carboxylic acid and the amorphous Zinc manganese oxide nanoparticles. For this report, we studied oleic acid as the surface of the $ZnMn_2O_4$ to control the particle size, to prevent the nanoparticles from aggregation.

2. Experimental

2.1 Sample preparation:

The synthesis of - $ZnMn_2O_4$nanoparticles was carried out via a solvothermal treatment method. In a typical procedure, 3mmol of Mn $(CH_3COO)_2.4H_2O$ and1.5mmol of Zn $(CH_3COO)_2.2H_2O$ were dissolved in 80 ml of absolute ethanol after stirring for 30min, 0.2g of oleic acid was added, to form a homogeneous solution. The obtained solution was transferred into a 150 ml Teflon- lined stainless steel autoclave sealed and maintained at 180ºC for 48 h. The autoclave was cooled to room temperature naturally, and the resulting brown precipitated powder was separated by centrifugation, washed with anhydrous ethanol several times, dried in a vacuum at 80ºC for 24 h, collected for characterization.

2.2 Sample Characterization

The structures of the precursor and final products were characterized by powder x-ray diffraction. The Powder X-ray Diffraction pattern was recorded on RICH SEIFERT X-ray powder diffractometer with a monochromatic nickel filtered CuKα (λ=1.5406Å) radiation. The morphology and size of the resultant products were characterized by JEOLJSM6310 Field-Emission Scanning Electron Microscope (FE-SEM) operated at 15 kV and Energy Dispersive X-ray spectrometer (EDX)High-Resolution Transmission Electron Microscope (HRTEM) images and Selective Area Electron Diffraction (SAED) pattern were characterized using JEOL JEM-2100 microscope operated at 200kv. In the preparation of samples for TEM observation, the materials were first dispersed in

ethanol using an ultrasonic bath for 10 min and then dropped onto a copper grid, which was dried in air at room temperature and kept in vacuum before TEM observation. The Fourier Transforms Infrared (FTIR) spectra were recorded at 20ºC using 'Perkin Elmer' model. The specimens were pressed into small disks using a spectroscopically pure KBr matrix. The spectra were recorded using a KBr beam splitter in the mid IR region (4000-400cm^{-1}). HIOKI 3532-50 LCR HITESTER meter was used to take the dielectric measurements with respect to frequency at different temperatures.

3. Result and Discussion

3.1 XRD

The crystalline structure and phase purity of the obtained product were determined by XRD as shown in fig.1, reveals that all the diffraction peaks can be exclusively indexed as the tetragonal phase structured $ZnMn_2O_4$ with a lattice constant of a=b=5.762 Å, c=9.470Å and space group of $I4_1/amd$, which is in good agreement with the standard data (JCPDS.No:24-1133) No other crystalline phases are observed .The strong and sharp reflection peaks suggest that the as- Prepared nanoparticles were well crystallized .The crystallite size was estimated using Scherer formula,

$$D = \frac{K\lambda}{\beta COS\theta}$$

Where D is the crystallite size, K is the shape factor, λ the X-ray wave length, θ the Bragg's angle in radians, and β the full width at half maximum in radians. The crystallite size obtained from the preferentially oriented peak of (211) plane was found to be 24nm.

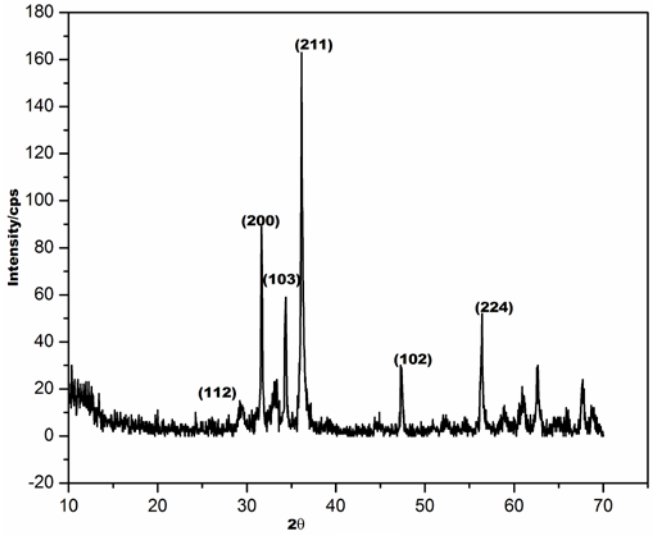


Figure 1: XRD pattern of $ZnMn_2O_4$

3.2 FTIR

FTIR analysis which was recorded in the range of 400-4000Cm^{-1}and shown in fig.2. In the region from 700 to 500cm-1, two absorption peaks were observed at 667.9 and 556.9cm-^{1}, which may be associated to M-O (M=Zn,Mn) and M-O-M bond respectively. The weak band at 1114.2 cm^{-1}, which can be attributed to Mn-O-H vibration of ethanol molecules on the surface of the Hetarolite ($ZnMn_2O_4$) particles. More over the band between3800cm^{-1} and 2200cm^{-1} is due to the O-H stretch of the carboxylic acid group of oleic acid. The Weak shoulder at 1616cm^{-1}can be assigned to the C=C stretching mode for oleic acid. A strong adsorption at 1330.2 and 1407.25cm^{-1} arises from C-O single bond stretching .These results revealed that Oleic acid were chemisorbed on to the Hetarolite -$ZnMn_2O_4$nanoparticles as a carboxylate

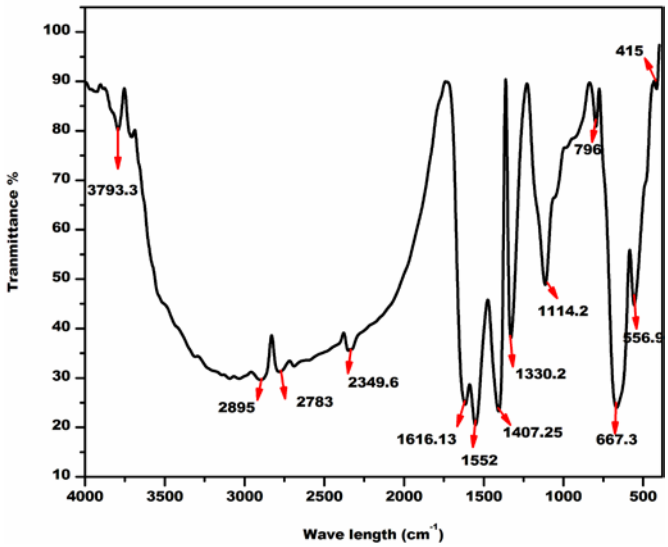
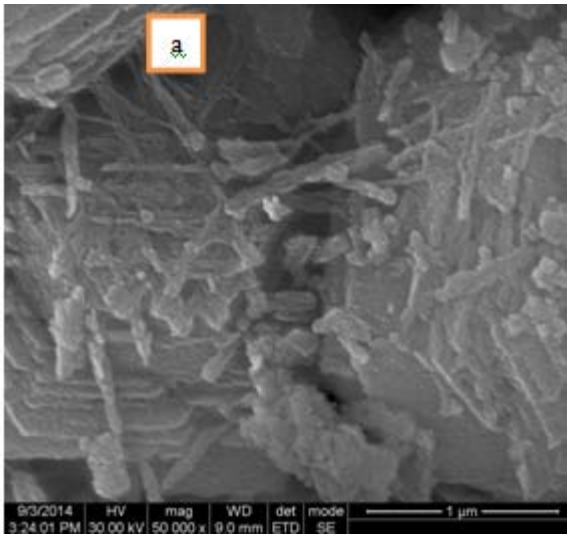
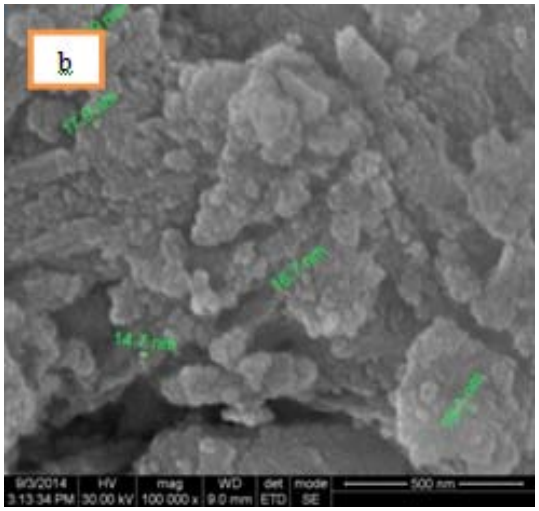


Figure 2: FTIR spectrum of $ZnMn_2O_4$

3.3 SEM

The morphology and nanostructural details of the as prepared the Hetarolite -$ZnMn_2O_4$nanoparticles were investigated by SEM. Fig3(a), shows a low magnification SEM image of the as-obtained product. It may clearly be found that the as-obtained product possesses nanofiber like rod structure .Further ,high magnification SEM image reveals that almost spherical shape like nanofiber is assembled from numerousnanoparticle and the size of the product is about 18nm as shown in fig3(b). The composition of obtained nanoparticles was then analyzed by Energy-dispersive X-ray (EDX) spectroscopy as shown in fig3(c).It was found that the product was composed of the following elements Mn , Zn and O. No other peak related with any impurity has been found in the EDX, which demonstrates that, the Hetarolite -$ZnMn_2O_4$ are composed only with Mn, Zn and O.





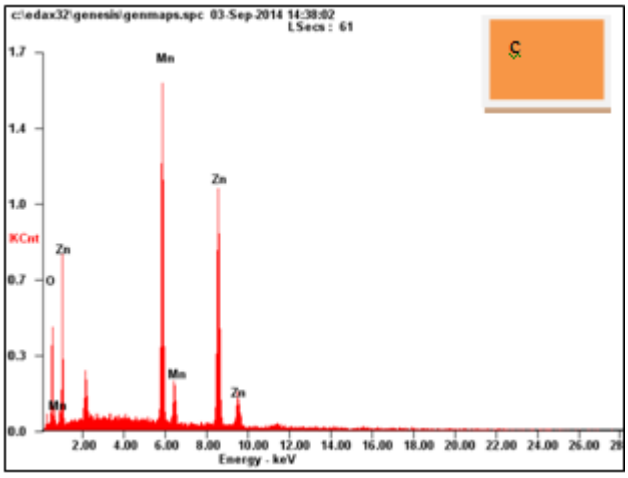
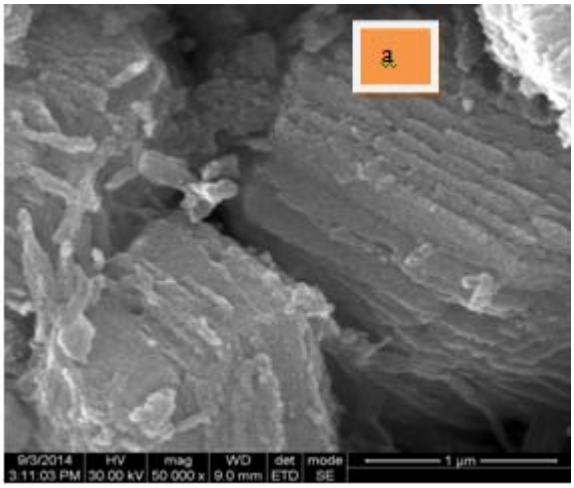
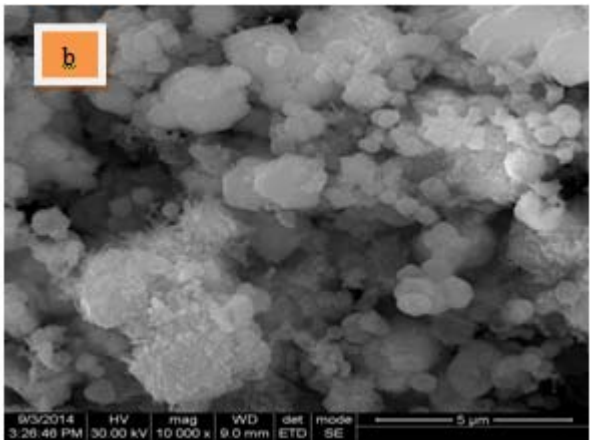


Figure 3: a) low –magnification b) high- magnification c)EDX of FESEM image of $ZnMn_2O_4$

On Keeping the same reaction conditions the amount of oleic acid is changed to investigate the effect of oleic acid on the morphology of the obtained materials ,and the experimental results are shown in fig.4.0.2 g of oleic acid(fig.4a) is used in the hydrothermal system, the particle of the obtained material is nanofiber like rod structure . Increasing the amount of oleic acid(fig.4b) to o.3g the particle of the obtained materials is irregular spherical morphology is hardly observed .Onthe other hand again increasing the amount of oleic acid(fig.4c) to 0.4 g ,the particle size becomes large and some microspheres crack to some extent.





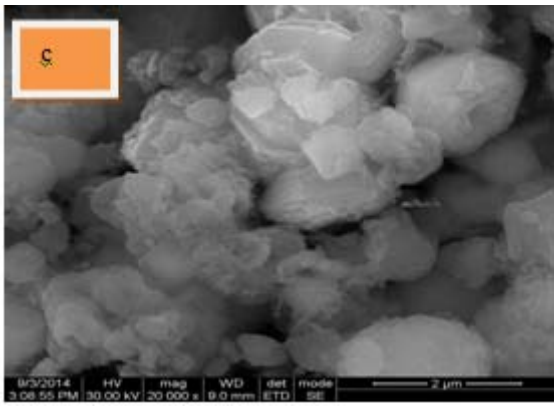
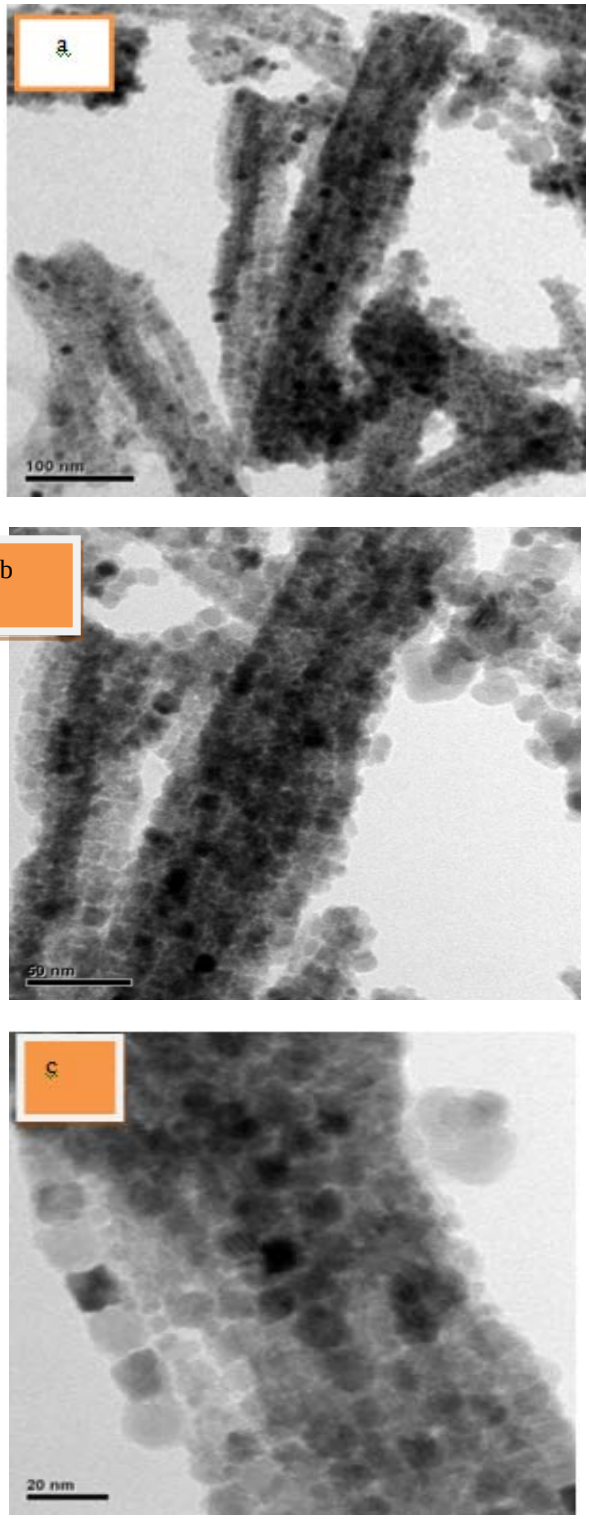


Figure 4: FE-SEM image of$ZnMn_2O_4$ with different amount of oleic acid a) 0.2mmol, b) 0.3mmol.c)0.4mmol

3.4 TEM

The figure.5, illustrate typical HRTEM image for the as prepared Hetarolite -$ZnMn_2O_4$ nanoparticles. It has observed that the nanocrystal exhibits morphology of nanorods. In addition in a solution –phase synthesis, impurities or capping agents can change the orde of free energies of different factes through their interaction with the crystal surface .this alternationmay significantly affect the relative growth rates of different facets. The SAED pattern shows the Hetarolite-

$ZnMn_2O_4$ nanocrystals were polycrystalline in nature. The lattice spacings of 3.8Å, 3.2Å corresponds to the indexed peaks (211) and (200) from the XRD spectrum**.**



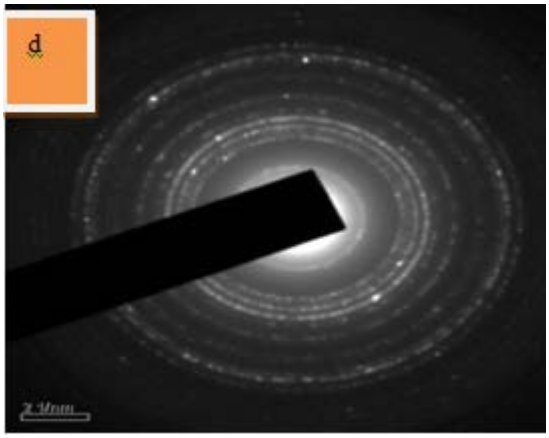


Figure 5: a, b, c) low –magnification ,high-magnification d)SAED of HRTEM image of $ZnMn_2O_4$

3.5 UV-VISIBLE SPECTROSCOPY:

UV-Visible absorption, and band gap spectra for Hetarolite - $ZnMn_2O_4$nanoparticles are shown in Figure .6. The spectrum shows the band edge- absorption peak which is found to be at 233nm. In UV-Vis, high energy electromagnetic radiation in the wavelength range of 100-700nm is utilized to promote electrons to higher energy orbital's. From the UV spectra, it is clear that he absorbance decreases with increase in wavelength. This decrease in the absorption indicates the presence of optical band gap in the material. The relation between absorption coefficients (α) and the incident photon energy (hυ) is given by the equation,

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^n$$

Where A is a constant .E_g is the band gap of the material and the exponent 'n 'depends on the type of transition n=1/2,2.3/2&3 corresponding to allowed direct, allowed indirect respectively talking n=1/2, we have calculated the direct energy band gap from the $(\alpha h\upsilon)^{1/n}$ vs hυ plots(fig).using this method , the estimated band gaps of the sample is found to be 1.54eV

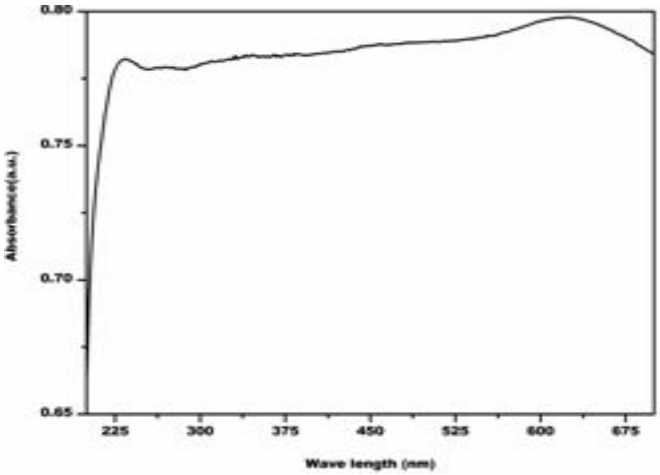


Figure 6: UV-Vis spectrum and $(\alpha h\upsilon)^2$vs hυ graph

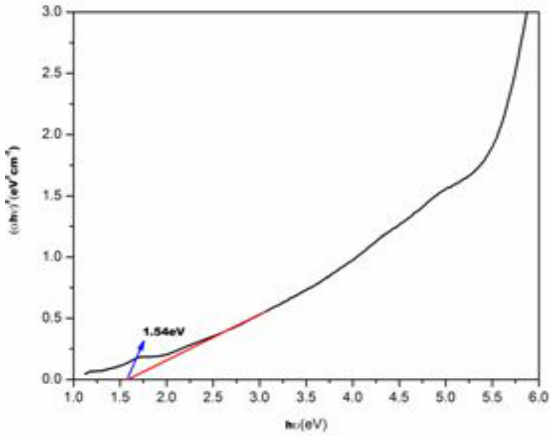


Figure 6: UV-Vis spectrum and $(\alpha h\upsilon)^2$vs hυ graph

4. Conclusion

This study demonstrates the fact that manganese acetate and zinc acetate are a proper precursor for the formation of Hetarolite -$ZnMn_2O_4$ nanoparticles. The XRD pattern confirms that the Hetarolite -$ZnMn_2O_4$is formed in the tetragonal spinel structure. FTIR spectrum reveals that the sample prepared has the finger print of Hetarolite -$ZnMn_2O_4$nanoparticles. The major stretching and bending vibrational frequencies have been identified. Hetarolite -$ZnMn_2O_4$nanoparticles were prepared by hydrothermal method using different magnification and different amount of surfactant. Oleic acid was used as a surfactant in the formation of Hetarolite -$ZnMn_2O_4$. FESEM images confirm the formation of nano-fiber like rod structures. The results of HRTEM and SEAD corroborate very well with that of FESEM and XRD results respectively

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