



**SPECTRAL, SEM, HRTEM, DIELECTRIC AND OTHER
STUDIES OF MANGANESE SULFIDE NANOPARTICLES
PREPARED BY SOLUTION METHOD WITH
BOTTOM-UP APPROACH**

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Abstract:

Nanoparticles have superior properties compared to microparticles and in nanomaterials the properties like mechanical strength, thermal stability, catalytic activity, electrical conductivity, magnetic properties, optical properties, etc are modified. In this work, nanoparticles of manganese sulfide (MnS) are prepared by solution method. MnS occurs in three forms viz., α -MnS, β -MnS and γ -MnS and it has the potential use in short wavelength optoelectronic devices, photo-catalysis, solar cells, single electron transistors etc. The nanoparticles of MnS were synthesized by solution method using a microwave oven. The synthesized MnS nanoparticles were subjected to various studies like XRD studies, FTIR studies, EDS studies, HRTEM studies, UV-visible spectral studies, SEM studies, photoluminescence studies, TG/DTA studies and dielectric studies and the obtained results are discussed.

Key Words: MnS, Microwave, Solution method, Nanoscience, XRD, FTIR, SEM, Photoluminescence, EDS, Dielectric Constant, HRTEM & FTIR

1. Introduction:

A nanometer (nm) is one thousand millionth of a meter. People are interested in the nanoscale because at this scale physical and chemical properties of materials differ significantly from those at a larger scale. Materials containing manganese are interesting because of their applications in many areas of modern technology [1]. Among them, manganese sulfide (MnS) has been the main subject of recent researches due to its magneto-optical properties [2, 3]. MnS is a wide band gap ($E_g \approx 3.1$ -3.7 eV) VIIB-VIA semiconductor that has a potential use in short wavelength optoelectronic devices such as in solar selective coatings, solar cells, sensors, photoconductors, optical mass memories [4-6] as well as like a blue green light emitter [7]. MnS is known to crystallize into three polymorphic forms: the rock salt type structure (α -MnS) which is the most common form. By low temperature growth techniques, MnS crystallizes into two metastable forms: zinc-blende (β -MnS) or wurtzite (γ -MnS) structure. These two tetrahedrally coordinated phases can transform into the stable octahedrally coordinated form at high temperatures ranging from 100 to 400 °C [8-14]. As a P-type semiconductor with wide band energy and varied crystal structures, MnS owns the promising optoelectronic properties and it has great potential applications in optoelectronic devices [15-17]. Moreover, MnS is an important diluted magnetic semiconductor, the outstanding magneto-optical properties of MnS has been extensively studied [18, 19]. In the present work, the preparation of undoped manganese sulfide nanopowders by microwave assisted solution method is reported and the various characterization studies like powder XRD, SEM, HRTEM, FTIR, UV-visible studies, EDAX, photoluminescence, thermal studies and dielectric studies of the prepared sample were carried out.

2. Preparation of MnS Nanoparticles:

Commercially available AR grade chemicals such as manganese acetate and thiourea were taken in 1:1 molar ratio and the required quantities were dissolved in the double distilled water in a 100 ml borosil beaker. The solution was stirred well using a hot plate magnetic stirrer for about 1 hour. The pH value of the solution was altered to 12 using sodium hydroxide solution. Then the solution was heated for about 30 minutes using a microwave oven and the temperature was maintained at 80 °C. L-tartaric acid was used to control the size of the particles. After heating, the solution was cooled to room temperature to get the precipitate of MnS. When thiourea is dissolved in water, it decomposes to give H_2S and H_2S dissociates to release S^{2-} . When manganese acetate is dissolved in water, it dissociates to release Mn^{2+} . Then these ions are combined to form MnS. The formed nanoparticles of MnS were filtered and washed using clean water and acetone.

3. Results and Discussion:

3.1 Powder XRD Studies:

Powder X-ray diffraction (XRD) pattern of the as-synthesized sample was recorded by the X-ray diffractometer (Rigaku D/max-rB) with Cu K_α radiation ($\lambda=1.54178 \text{ \AA}$) at a scanning rate of 6 °C/min in the 2 θ range of 20–80°. The recorded XRD pattern of the manganese sulphide nanoparticles is shown in the figure 1. All the diffraction peaks on the pattern were indexed to the cubic unit cell. The Deby-Scherrer's formula

($D=0.9 \lambda/\beta \cos \theta$) was used to find the grain size of the sample [20]. The average size of the nanoparticles of the MnS was found to be 11.25 nm. The recorded powder XRD pattern of MnS nanoparticles is observed to be in good agreement with the pure rock-salt (α - MnS phase) with preferential orientation in the (200) plane (JCPDS No: 88 -2223).

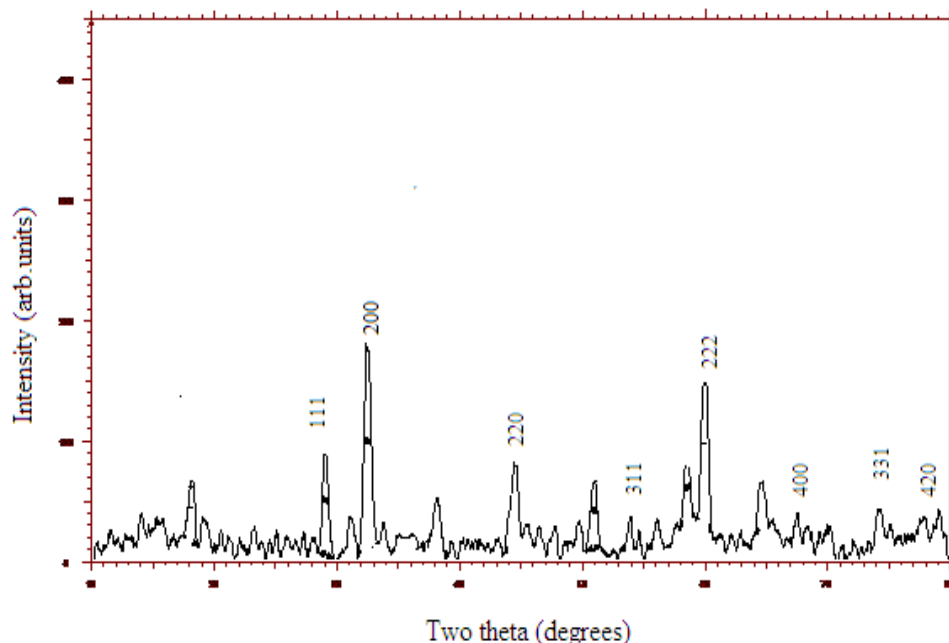


Figure 1: Powder XRD pattern of MnS nanoparticles

3.2 SEM, HRTEM and SAED Studies:

The scanning electron microscopic (SEM) image was taken for the nano powdered sample prepared by the present microwave-assisted solution method using Scanning Electron Microscope Model Hitachi SEM S 2400 device. Figure 2 shows the SEM image of MnS nanoparticles and it is observed from the figure that most of the particles of the sample are spherical in shape and slightly agglomerated. The high resolution transmission electron micrograph (HRTEM) for the sample is taken using TEM, Model JEM 100 CX II and HRTEM Model JOEL-J2000 operating at 200 kV and the HRTEM image of the sample is shown in the figure 3. The grains are observed to be nearly same and all are in nearly spherical in shape, as observed in the SEM and HRTEM images. From the particle size distribution in the images, it is observed that the size of particles is varies from 10 to 20 nm. Figure 3 indicates that the nanoparticles are nearly spherical and slightly elongated and it confirms the possibility of different crystallographic planes of different atomic density. These images also provide evidence for the formation of larger aggregates (supra-aggregates) of nanoparticles. These supra-aggregates are likely to be the stable form of these nanoparticle suspensions. Figure 4 shows the selected area electron diffraction (SAED) pattern of MnS nanoparticles. Since the nanoparticles tend to lower the surface energy, the agglomeration of nanoparticles are observed to be spherical shape. The high crystallinity of the powder leads to its corresponding well-pronounced Debye-Scherrer diffraction rings in the SAED pattern that can be assigned to the reflections (1 1 1), (2 0 0), (2 2 0), (222) and (3 1 1) of cubic phase of MnS.

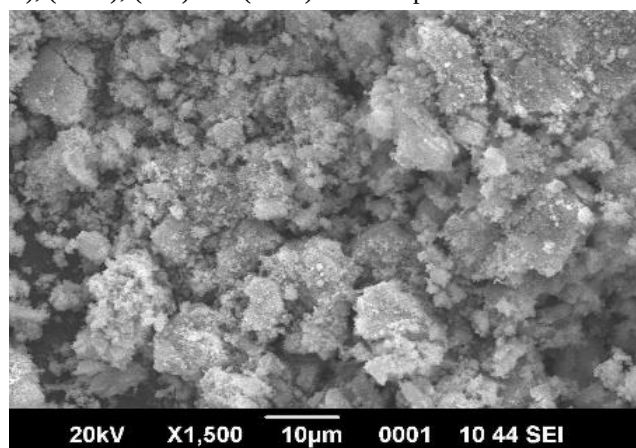


Figure 2: SEM image for MnS nanoparticles

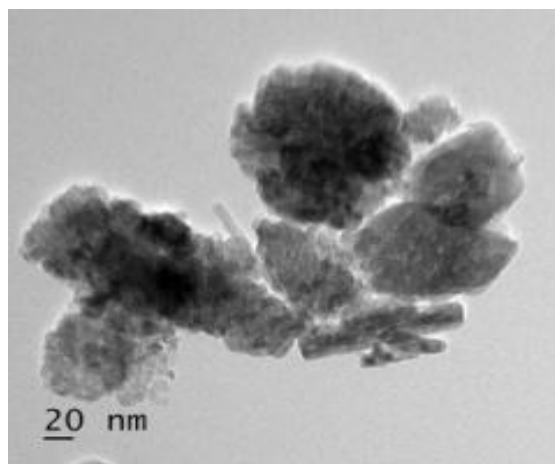


Figure 3: HRTEM image of MnS nanoparticles

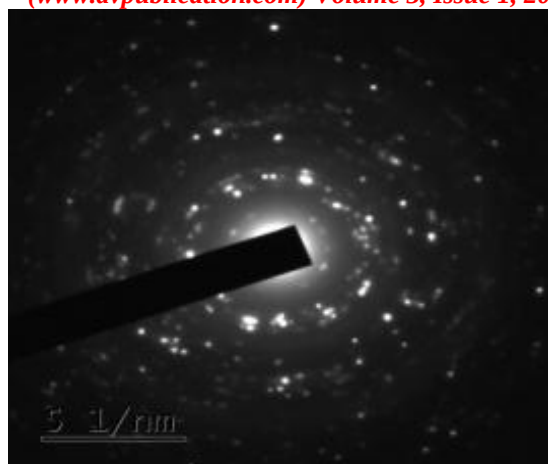


Figure 4: SAED pattern of MnS nanoparticles

3.3 FT-IR Studies:

The presence of functional groups of the as-prepared MnS nanoparticles synthesized by the present microwave-assisted solution method are analyzed using FT-IR spectroscopy. The infrared spectrum of the sample is recorded in the range $400\text{--}4000\text{ cm}^{-1}$ on a Shimadzu 8400S FT-IR spectrometer. The powder sample is finely dispersed in KBr using an agate mortar and grounded well. The finely dispersed material is then pressed in the form of circular disc of nearly 10 mm diameter and 0.5 mm thickness at a pressure of 250 MPa. The pellet is then dried with IR light before the FT-IR spectrum has been recorded. The FT-IR spectrum of the nanoparticles of MnS is shown in Fig. 5. The broad absorption band located around 3450 cm^{-1} corresponds to the O-H stretching vibration of residual water and hydroxyl groups, while the absorption bands at 1566 cm^{-1} and 1412 cm^{-1} are due to the scissor bending mode of associated water. The band at 1097 cm^{-1} can be attributed to C-O stretching vibration.

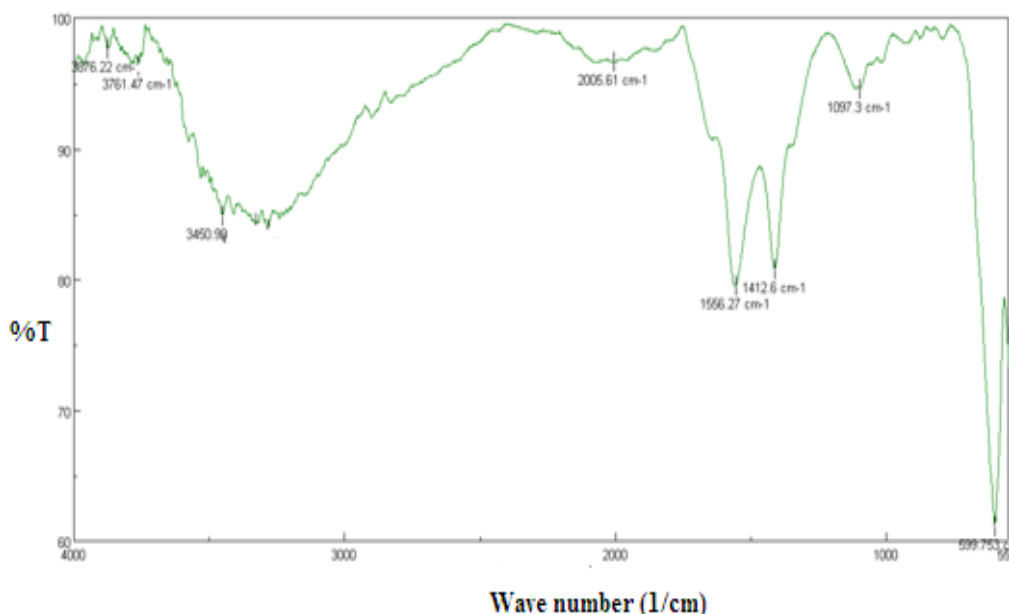


Figure 5: FTIR spectrum of MnS nanoparticles

3.4 Photoluminescence Studies:

In photo excitation process, the electrons are excited to the conduction band and they eventually fall back down to the valence band. As they fall down, the energy is converted back into a luminescent photons and the light is emitted from the material. Thus the energy of the emitted photon is a direct measure of the band gap energy. In this process a lower wavelength radiation is converted into higher wavelength visible radiation [21]. The recorded photoluminescence spectrum of MnS nano crystal is shown in the Fig.6. The spectrum consists of one strong emission centered at 380 nm [22] and a weak peak located at around 490 nm. The former corresponds to the near band edge emission of MnS and the latter one at 490 nm should be attributed to the higher level transition of MnS from the surface states.

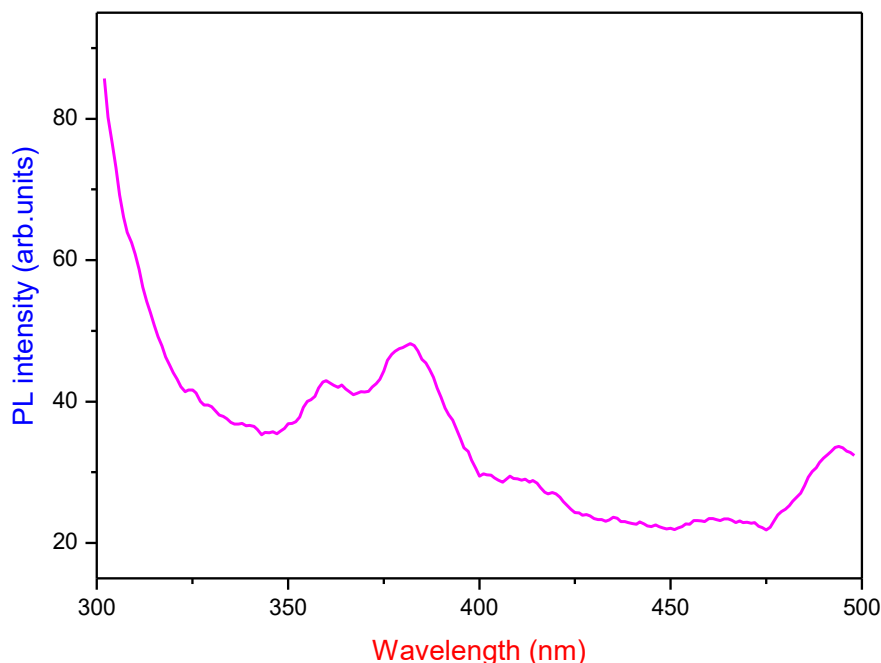


Figure 6: Photoluminescence spectrum of MnS nanoparticles

3.5 UV-Visible Studies:

The UV-visible spectroscopy is used to study about absorbance, transmittance, reflectance, optical band gap and other linear optical constants. The ultraviolet-visible spectrum of the sample has been recorded in the absorption mode in the region 190-1100 nm using a Varian Cary 5E UV-Vis-NIR spectrophotometer and the spectrum is given in the figure 7. The absorption of the sample in the visible is low compared to that in UV region and the spectrum has large absorption at 360 nm and this value is found to be in good agreement with the reported value [23].

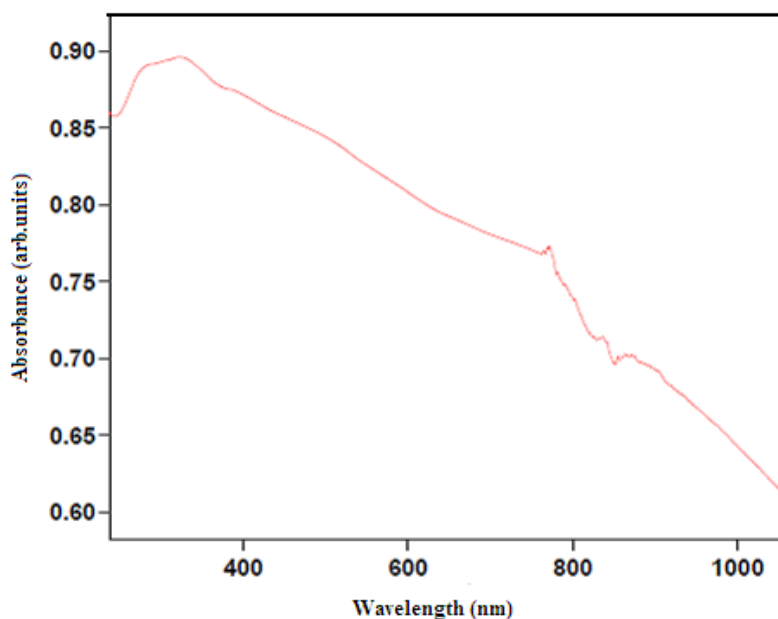


Figure 7: UV-visible absorption spectrum of MnS particles

3.6 TG-DTA Studies:

The thermal stability of the sample can be analysed by TG/DTA studies and the recorded TG/DTA curves of the sample are shown in the figure 8. The TG curve shows a three-step decomposition process. The first step is observed below 100 °C with around 5 wt% weight loss which is due to the removal of absorbed water. During the second step up to 200 °C, there is a further weight loss of about 10 wt% and this is due the

complete removal of water. The third step of decomposition above 200 °C is due to emission of gaseous particles from the sample and in this case the DTA curve shows the broad exothermic peak. Initial sample of MnS taken for this experiment was 11.221 mg and the residual sample left after 700 °C is about 9 mg. Hence, TG/DTA studies show that MnS sample has high melting point.

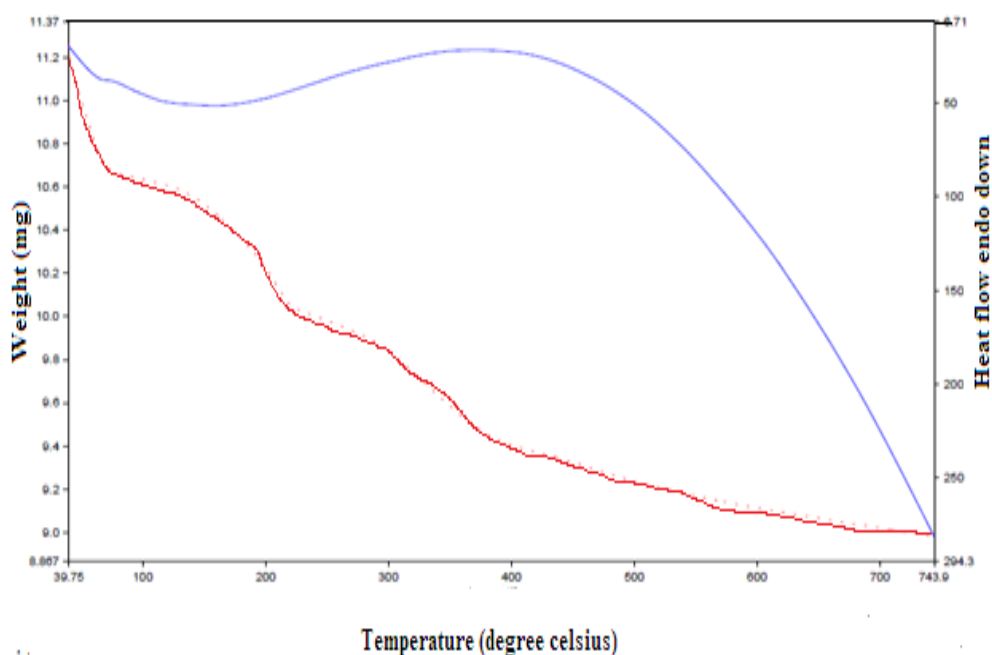


Figure 8: TG/DTA thermal curves for MnS nanoparticles

3.7 EDS Studies:

Energy dispersive spectroscopy (EDS or EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles [24]. EDAX spectrum of the sample has been recorded using a SEM and is shown in figure 9. The result confirms that the elements such as Mn and S are present in the sample.

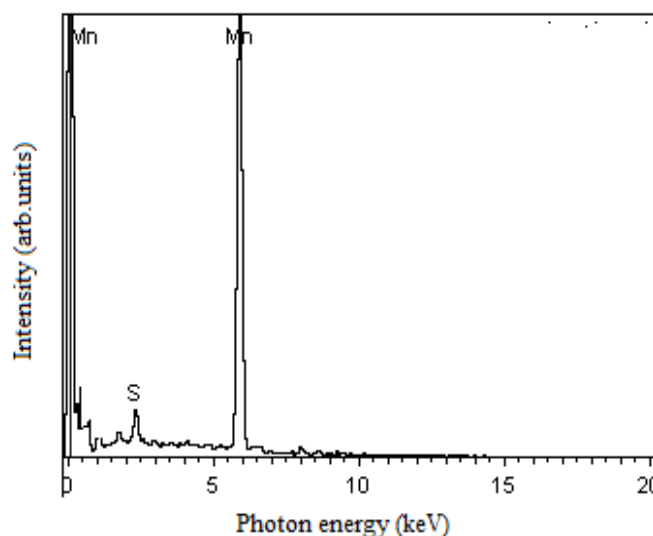


Figure 9: EDS spectrum of MnS nanoparticles

3.8 Dielectric Studies:

The important dielectric properties of the samples are dielectric constant and dielectric loss. The capacitance and dielectric loss factor ($\tan \delta$) measurements were carried out using the parallel plate capacitor method at various frequencies using an Agilent 4284A LCR meter at temperatures 29 and 60 °C.. Using the

values of capacitance without sample and with sample of the capacitor, the dielectric constant is calculated. The dielectric loss factor can be measured directly from the LCR meter. The variations of dielectric constant and dielectric loss with frequency and with temperature for the pelletized sample of MnS are displayed in figures 10 and 11. The results show that both dielectric constant and loss factor decrease with frequencies and increase with increase of temperature. The high value of dielectric constants for the sample in low frequency region is attributed to space charge polarization which depends on the purity and perfection of the sample. The increase of dielectric parameters with increase of temperature is due to change of polarization, expansion of the sample and production of crystal defects [25].

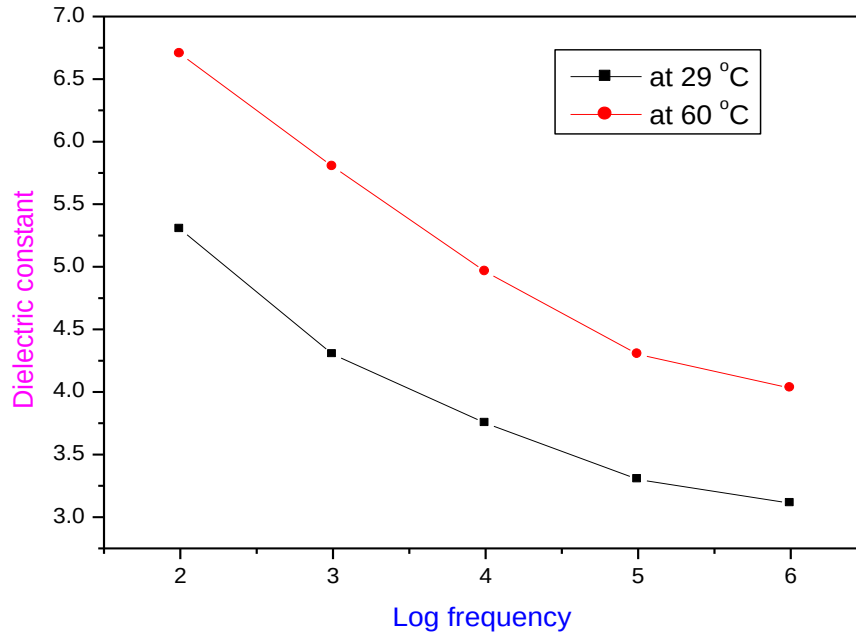


Figure 10: Frequency dependence of dielectric constant for the pelletized sample of MnS at temperatures 29 °C and 60 °C.

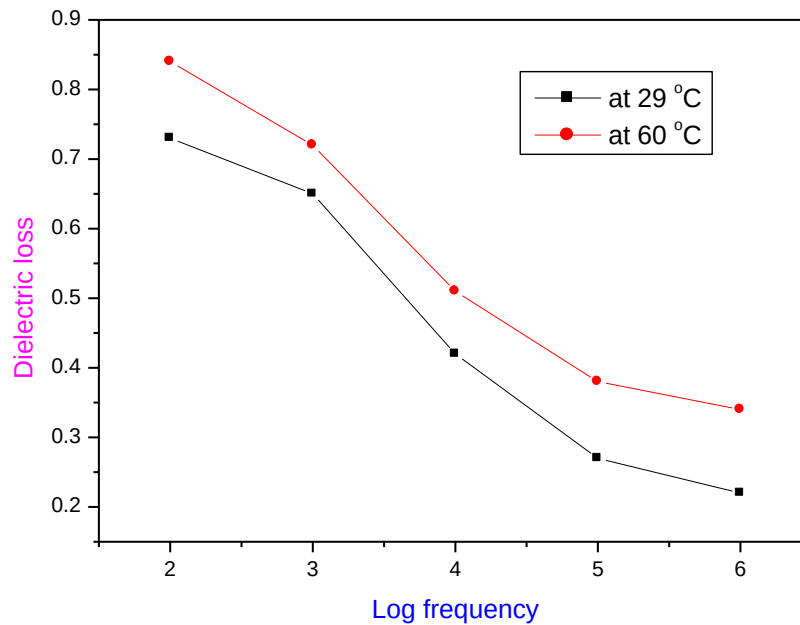


Figure 11: Frequency dependence of dielectric loss for the pelletized sample of MnS at temperatures 29 °C and 60 °C.

4. Conclusions:

Manganese sulfide nanoparicles were synthesized by microwave assisted solution method using manganese acetate and thiourea as the reactants and L-tartaric acid was used as the capping agent. Powder XRD pattern has shown slightly broad reflection peaks indicating the nanobehaviour of the sample. Most of the nanoparticles of MnS were observed to be spherical in shape and the particles are slightly agglomerated. The presence of functional groups such as OH, C-O have been identified by FTIR studies. UV-visible absorption study shows large absorption at about 360 nm for MnS sample. The TG/DTA studies show a three-step decomposition process in the sample and the PL emission spectrum of MnS sample indicates a strong emission centered around 380 nm. SEM and HRTEM studies are used to identify the morphology and size of the prepared MnS nanoparticles. The electrical properties of the pelletized sample of MnS was analysed by measuring dielectric constant and dielectric loss and the elements such as Mn and S were identified in the sample by EDS studies.

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