ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

Microstructural Characteriztion of Trimanganese Tetra Oxide (Mn_3O_4) Nanoparticle by Solvothermal Method and Its Dielectric Studies

S.Vijaya Lakshmi *, S.Pauline and V.Maria Vinosel
Department of physics, Loyola College, Chennai, India

Abstracts

Mn_3O_4nanoparticles were prepared by a solvothermal method using Mn $(CH_3COO)_2{\cdot}4H_2O$ as precursor and Oleic acid as surfactant at synthesis temperature of 160ºC. The particles have been characterized by X-ray Diffraction (XRD) analysis, Fourier Transform Infrared (FTIR) Spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Microscopy (HRTEM), and Energy Dispersive X-ray (EDX) analysis techniques. The XRD pattern showed that the Mn_3O_4 microsphere exhibit tetragonal hausmannite structure. Formation of Mn_3O_4compound was confirmed from FTIR studies. Mn_3O_4 microsphere prepared at 160ºC resulted in microsphere, nanoflower and flower –like nano rod structures. The manipulated size and shape were observed for various reaction times. The chemical composition was obtained by EDX analysis and confirmed the presence of Mn and O in the sample. The Selected Area Electron Diffraction (SAED) patterns revealed that the nanocrystals are polycrystalline in nature. Dielectric constant and AC conductivity of the nanomaterial at different temperatures were studied with respect to frequency.

Keyword: Solvothermal, Oleic acid, Manganese Acetate, SAED, Conductivity.

Introduction

Nanotechnology is a group of emerging technologies in which the design, characterization, production & application of materials, devices and systems, by controlling shape and size to nanometer scale [1, 2]. Over the past few decades, the 3d transition metal oxides have attracted enormous interest due to their potential applications in various fields ranging from catalysis, energy storage & magnetic data storage to drug delivery and biomedical imaging [3]. The properties of transition metal oxide nanoparticles are different from those of the bulk materials in many areas such as optical, magnetic, thermal and electrical properties [4-6].

On the other hand Hausmannite Mn_3O_4 is one of the most stable oxides of manganese, and it has a variety of important applications such as electrochemical materials, high density magnetic storage medium, catalyst, ion-exchange and molecular adsorption etc [6-8]. Nanometer-sized Mn_3O_4 powders, with remarkably increased surface area and different morphologies, are expected to display better performance in all aspects of the above-mentioned applications. Various nanostructures of Mn_3O_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 [9,10]. However, the preparation of nanostructures of manganese oxide single phase has always been a challenge due to multivalent states of manganese ions [11].

In the last decade, different shape and size of Mn_3O_4nanoparticles have been synthesized via various techniques. For example, **Chen et al**.[12] reported a work on Mn_3O_4 powders (nanoparticles, nanorods and nanofractals) by controlling the dripping speed of NaOH solution at200ºC.The dripping speed of the NaOH solution played an important role in the formation of Mn_3O_4 nanostructure shapes. **Hao et al.** [13] Synthesized octahedral Mn_3O_4 nanoparticles in simple synthetic approach by using metallic salt and PEG-6000 as the precursor and reducing agent. **Du et al**.[14] synthesized three-dimensional Mn_3O_4nanostructures by a soft chemical templating process using block co-polymer as the structure – directing agent at 400ºCfor 5hr.**Fan et al.** [15] recently reported Mn_3O_4 nanofibers by electrospining a solution of poly methyl methacrylate and manganese acetate and obtained a low electrochemical capacity from the Mn_3O_4 nanofiber anode. **Yang et al**. [16] synthesized Mn_3O_4 by a microwave assisted solution – based method at 80ºC using Mn $(CH_3COOH)_2$ and $(CH_2)_6N_4$ (Hexamethylene tetra mine) as the precursors. A good quality phase pure spherical/cubic

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

shape nano powders of $Mn_3O_4$with size ranging from 10-50nm were formed instantly at 50°C by **Apte et al**.

Herein, in this work, we evaluate the solvothermal methods for the synthesis of Mn_3O_4microsphere using ethanol as solvent and metal acetate 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 manganese oxide nanoparticles. For this report, we studied oleic acid as the surface of the $Mn_3O_4$to control the particle size, to prevent the nanoparticles from aggregation.

Experimental

Materials:

Manganese acetate Mn $(CH_3COO)_2 .4H_2O$, Oleic acid and absolute ethanol were purchased from Merck Company. All chemicals of analytical grade were used without further purification. Deionized water was used throughout the experiments.

Sample preparation:

The synthesis of Mn_3O_4 microsphere was carried out via a solvothermal treatment method. In a typical procedure, 0.85mmol of Mn $(CH_3COO)_2.4H_2O$ was dissolved in 60 ml of absolute ethanol after stirring for 30min, 0.43mmol of oleic acid was added, to form a homogeneous solution. The obtained solution was transferred into a 100 ml Teflon- lined stainless steel autoclave sealed and maintained at 160ºC for 24 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 15 h, collected for characterization.

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.

Result and discussion

Powder X-ray diffraction:

Fig.1, shows the X-ray Diffraction(XRD) results of the synthesized product at 160ºC for 24h.The planes corresponding to (101), (112), (200), (103), (211), (202), (220), (105), (312), (303),(321),(224),(400) are in good agreement with the standard value of tetragonal hausmannite Mn_3O_4 structure (JCPDS.NO-24-0734) with a lattice constant a=b=5.766Å,c=9.341Å and V=310.55 with a small difference in peak intensities. No additional peaks of other phases have been detected, indicating high purity and good crystalline of the Mn_3O_4 products. Mn_3O_4 is well-known to have the normal spinel structure in which the Mn^{2+} ions occupy the tetrahedral sites while the Mn^{3+}ions occupy the octahedral sites. Mn_3O_4 also has a stable tetrahedral structure in which the oxygen octahedron is tetragonally distorted due to the Jahn-Teller effect on Mn^{3+} ions.XRD analysis results are used to evaluate crystallite size of the obtained samples. The crystal size of the Mn_3O_4 Nanoparticles was determined by the X-ray line broadening method using the Debby-Scherrer equation,

$$D=K\lambda/\beta COS\theta.$$

Where D, is the crystal size in nanometers. λ is the wave length of the radiation (1.54056Å for CuKα radiation), K is a shape constant equal to 0.94. β is the peak width at half-maximum intensity and θ is the peak position. The crystallite size obtained from the preferentially oriented peak of (211) plane was found to be 48.5nm. The estimated average crystallite size is given in table 1

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

Sample	Phase	Crystal system	Standard lattice parameter	Observed lattice parameter	Particle size (nm)
As-prepared	Mn_3O_4	Tetragonal	a=5.762Å;c=9.469Å and V=314.20	a=5.766Å;c=9.341 and V=310.55	48.5nm

Table.1, Lattice constant and particle size of Mn_3O_4

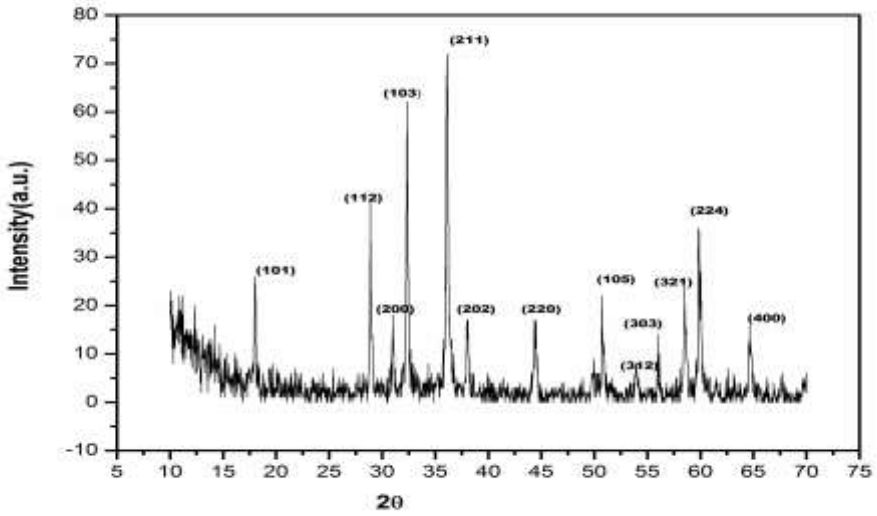


Fig.1, XRD pattern of Mn_3O_4

FTIR analysis:

In order to know the chemical bonds present in the Mn_3O_4 (Oleic acid as surfactants) compound, the sample was characterized by FTIR within the wave length range 400-4000cm^{-1}. Fig.2, display the spectrum of Mn_3O_4. In the range of 1000-400cm^{-1}, the two broad absorption bands at727,739 , 639 and 523cm^{-1} are associated with the coupling mode between Mn-O stretching mode of tetrahedral and octahedral sites, as expected from a normal spinel structure. The third band, located at a wave number around 447cm^{-1} can be attributed to the vibration of manganese species (Mn^{3+}) at an octahedral site. More over the band between3500cm^{-1} and 2200cm^{-1} is due to the O-H stretch of the carboxylic acid group of oleic acid. A strong adsorption at 949 and 1069 cm^{-1} arises from C-O single bond stretching .this results revealed that Oleic acid were chemisorbed on to the Mn_3O_4nanoparticles as a carboxylate. Thus the FTIR –Spectrum further confirms that the octahedrons are composed of Mn_3O_4

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

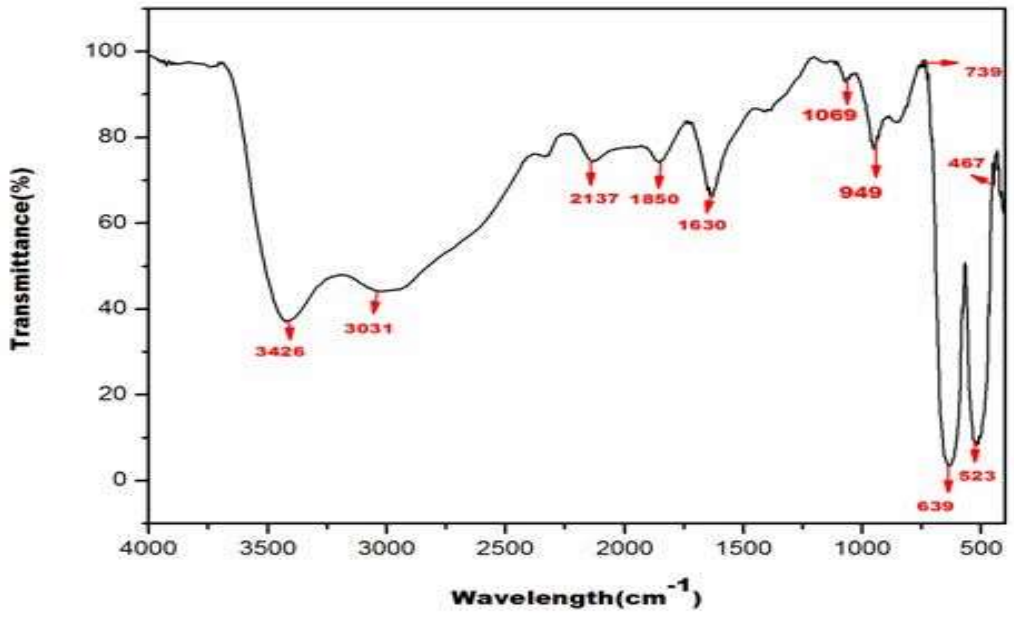


Fig.2, FTIR spectrum of Mn_3O_4.

SEM analysis:

In the experiments, typical Mn_3O_4microspheres are shown in fig.3. The morphology and structure of the products should be affected by the synthesis temperature and reaction time. SEM image of the as-prepared products at 160ºC with different solvothermal treatment time were shown in fig.3.After the 1st reaction time of 20 h, the material has spherical flower (Fig.3a) with in homogeneous size distribution ranging from 1µm to several micrometers, which indicates that the microsphere is formed due to aggregation of small nanocrystallites. When the reaction time is increased up to 22h, the image shows the break open of more number of flowers(Fig.3b) in them .Further prolonging the reaction time to 24h, the entire image shows break opened flowers with multirods(Fig3c),were each flowers is made up of many thin nano rods with thickness of 10~15

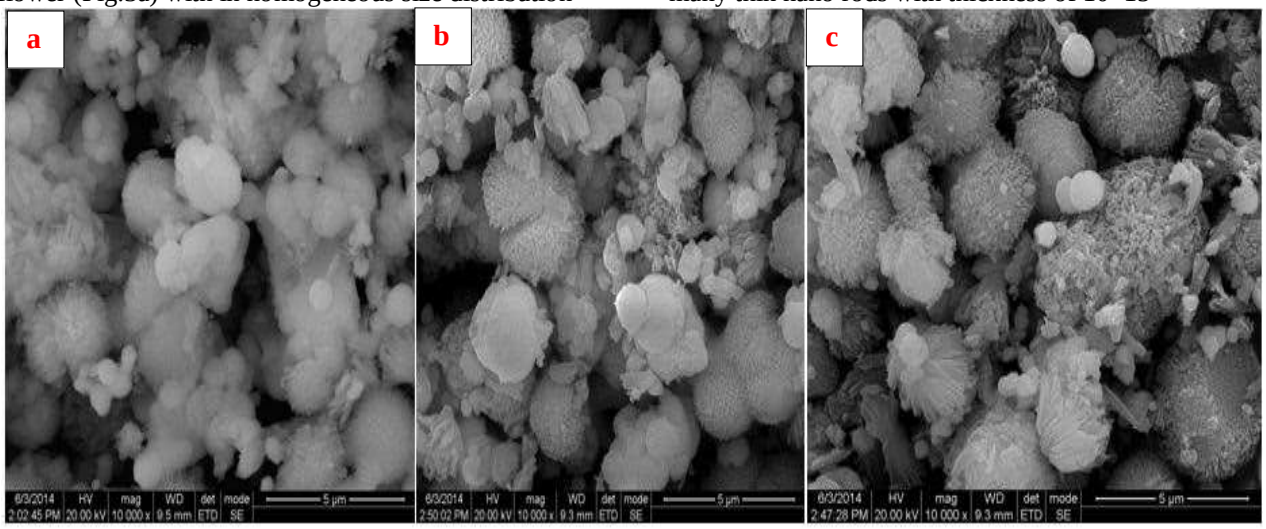


Fig.3, SEM image of the product obtained at 160ºc with different solvothermal treatment time a).20h, b).22h, c).24h.

Different magnification FESEM images of Mn_3O_4:

Fig.4 shows the morphological characterization of the as-synthesized products prepared by the solvothermal process. The typical FESEM images of the present Mn_3O_4 products with different magnification are shown in figs 4a &4b. It is

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

evident from lower magnification image that the Mn_3O_4 nanoparticle exhibits different sized spherical nanoflowers structure in a large- scale area with inhomogeneous size. And the size of the flower are marked in the image (Fig.4a).Fig.4b shows the higher magnification image of Mn_3O_4 nanoparticles

.

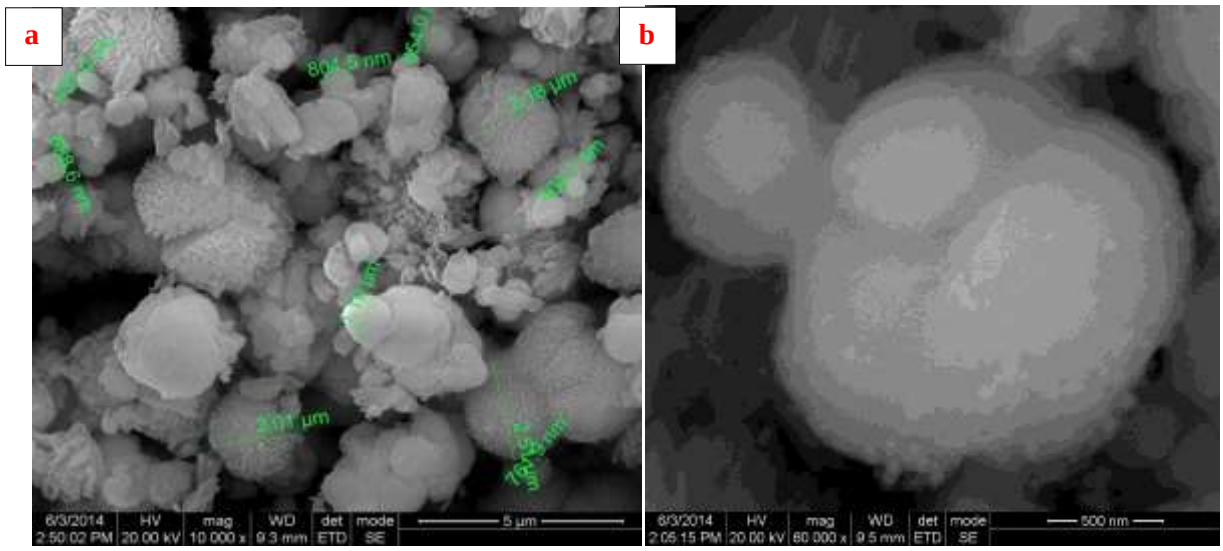


Fig.4, a) low –magnification& b) high-magnification FESEM image of Mn_3O_4.

Different amount of oleic acid:

The FE-SEM images of products with different amount of Oleic acid are show in fig.5, when the amount of Oleic acid was 0.43mmol, only spherical particle and spherical flower were obtained (fig.5a), Increasing the amount of the Oleic acid to 0.86mmol(fig.5b) ,these image revealed that the spherical shaped single flower could be formed. The image means, that Oleic acid as surfactant is playing an important role for determining the morphologies of the final products.

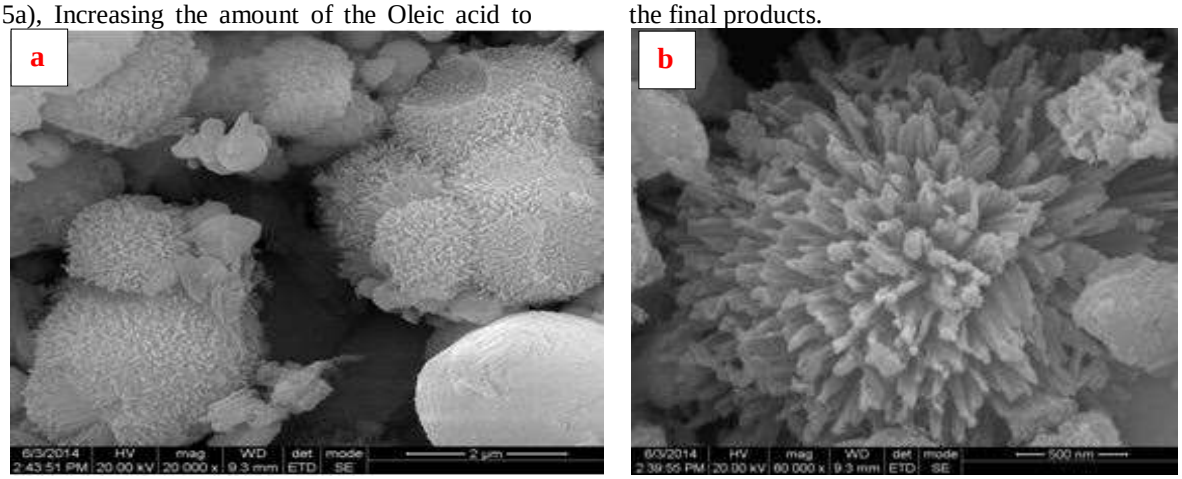


Fig.5, FE-SEM image of Mn_3O_4 with different amount of oleic acid a) 0.43mmol, b) 0.86mmol.

Energy-Dispersive X-Ray Spectroscopy (EDX):

The composition of obtained nanoparticles was then analyzed by Energy-dispersive X-ray (EDX) spectroscopy as shown in fig.6. It was found that the product was composed of the following elements Mn and O. No other peak related with any impurity has been found in the EDX, which demonstrates that, the Mn_3O_4 microspheres are composed only with Mn and O.

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

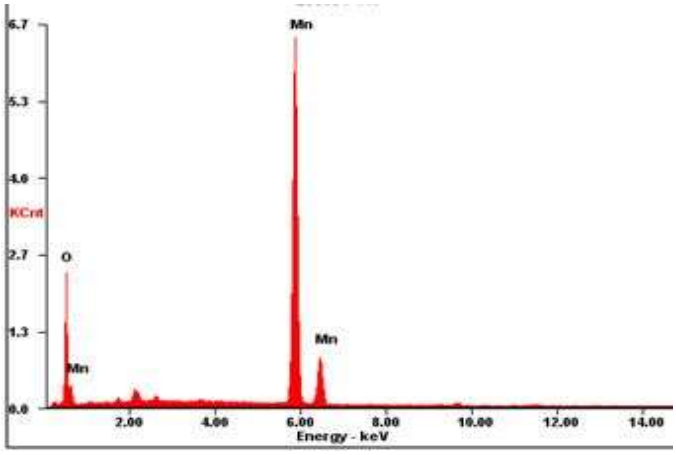
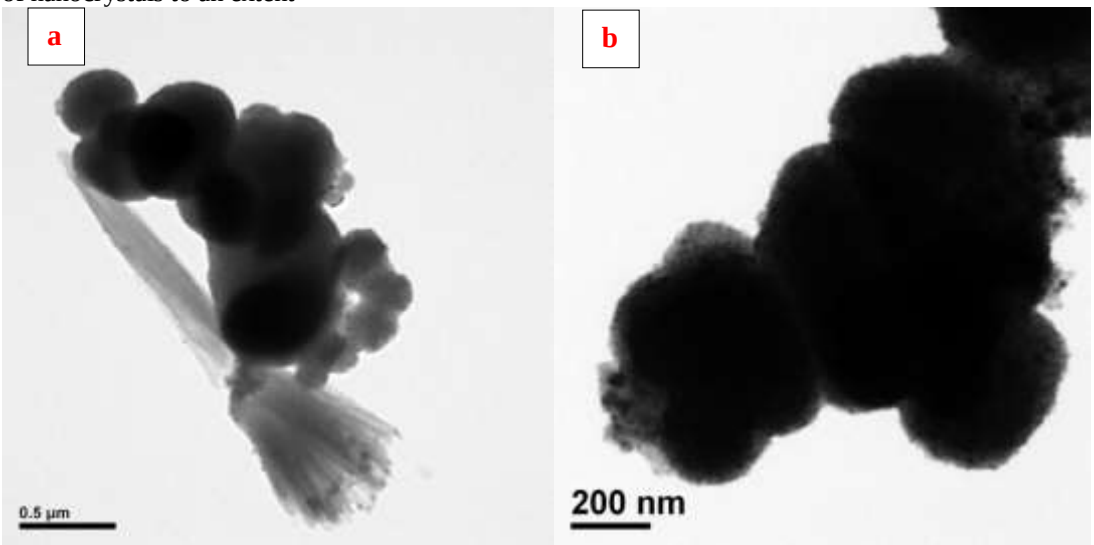


Fig.6, EDX spectrum of Mn_3O_4

HRTEM Analysis:

The figure.7, illustrate typical HRTEM images for the as prepared hausmannite nanoparticles. It has been observed that a pseudo spherical morphology is exhibited by the nanocrystals. In different ranges multi spoke wise structure has been arising from the central zone. In addition in a solution-phase synthesis, impurities or capping agents can change the orde of free energies of different facets, through their interaction with the crystal surface. This alternation may significantly affect the relative growth rates of different facets. As a result, the facet with flower growth rate will be exposed more on the nanocrystals surface. The dimension of the nanostructure observed in the micro graph does not facilitate to give the size range. Since the range has been wide spread it invalidates us for the estimation of size.

The SAED pattern shows the hausmannite nanocrystals were polycrystalline in nature. The lattice spacing of 3.2Å, 2.9Å, 2.2Å, 1.88Å, and 1.52Å corresponds to the indexed peaks (112), (103), (211), (105), (321) from the XRD spectrum. The growth of the (211) nanocrystals plane depends on the availability of Mn^{3+} in which the density of Mn^{3+} in the (211) surfaces is higher in the natural growth direction. The addition of capping agents (oleic acid) impedes the growth of nanocrystals to an extent



ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

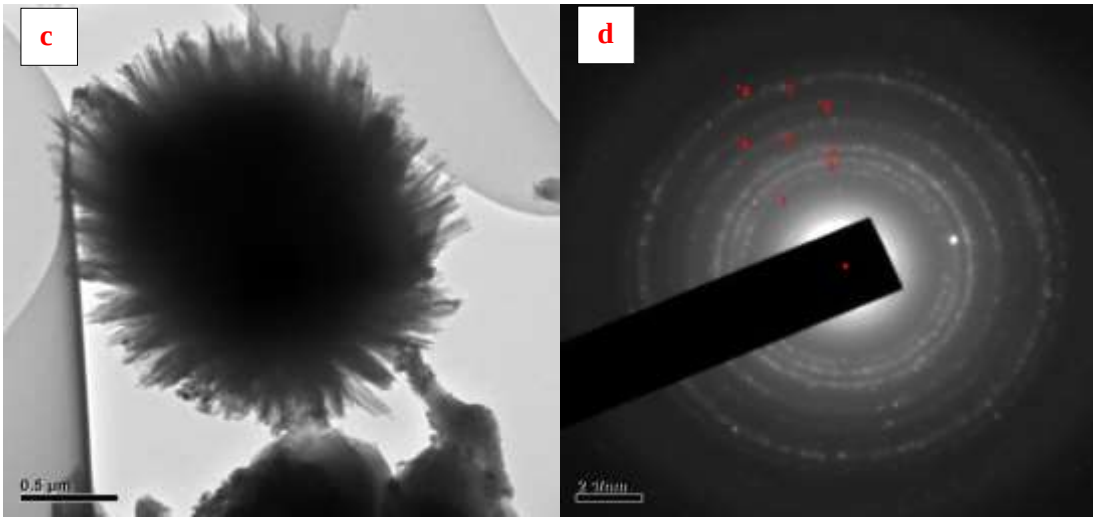


Fig.7, (a-c) HRTEM images of Mn_3O_4 with different magnification, d) SAED pattern of Mn_3O_4

Dielectric property:

Fig. 8 shows the variation of dielectric constant (ε_r) with respect to frequency for the nanomaterial at various temperatures of 353K ,373K,423K,473K,523K,573K,623K and 673 K. Using the expression, the dielectric Constant (ε_r) of the nano sample was calculated. Where C is the capacitance, d is the thickness; A is the surface area of the sample and ε_0 is the absolute permittivity of free space (8.854×10^{-12} F/m).

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$

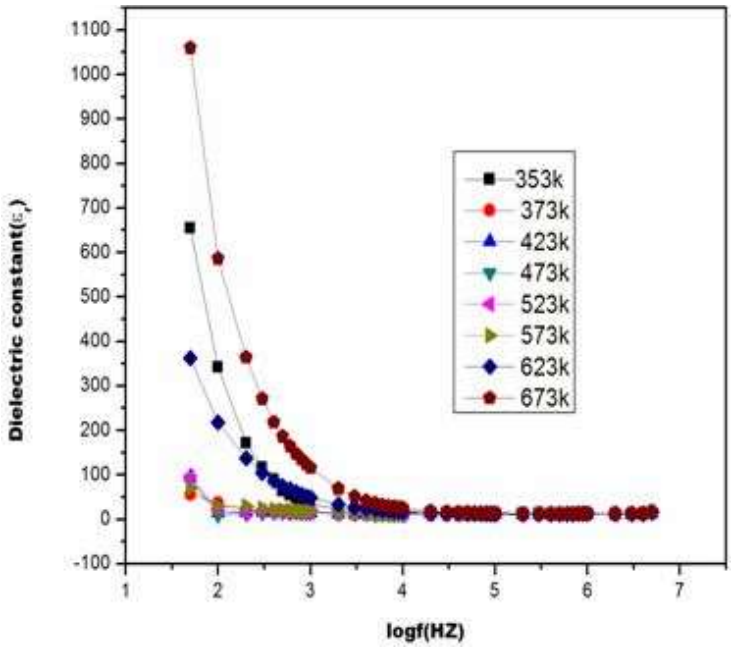


Fig.8, Frequency dependence of dielectric constant at various temperatures of Mn_3O_4.

From the graph, it is seen clearly that the dielectric constant has high values in the low frequency regions for the nano material. This is due to the existence of various types of polarization mechanisms like electronic, ionic, orientation and space charge polarization .This may lead to large values of dielectric constant at low frequencies. Due to the application of an electric field the space charges are moved and dipole moments are created. This is called as space charge polarization. In addition to this, these dipole moments are rotated by the field applied resulting in rotation polarization which is also contributing to the

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

high values. Whenever there is an increase in the temperature, more dipoles are created and the value increases. In the high frequency region, before the field reversal occur the charge carriers may have started to move and dielectric constant falls to a small value.

A. C. Conductivity Studies

The A.C conductivity of the sample can be determined by using the relation

$$\sigma_{a.c} = 2\pi\varepsilon_0\varepsilon_r f \tan\delta .$$

Where ε_0 is permittivity in free space, ε_r is dielectric constant, and f is the frequency and tan δ is the loss factor. The a.c. electrical conductivity of the nanomaterial as a function of frequency and temperature is shown in Fig.9. There is a small increase in the electrical conductivity of the nano material at the low frequency region, for an increase in frequency. This pattern is the same for all temperatures. But, at high frequencies especially in the MHz region, there is an abrupt increase in the conductivity and it is enormous at high temperatures. The high ac conductivity at high temperatures could be attributed to small polaron hopping. The increase in conductivity with temperature may be explained based on the assumption that within the bulk, the oxygen vacancies due to the loss of oxygen are usually created during increase in temperature and the charge compensation, which would leave behind free electrons. In metal oxides, electrical conduction occurs through strong coupling between phonons and electrons with the creation of polarons.

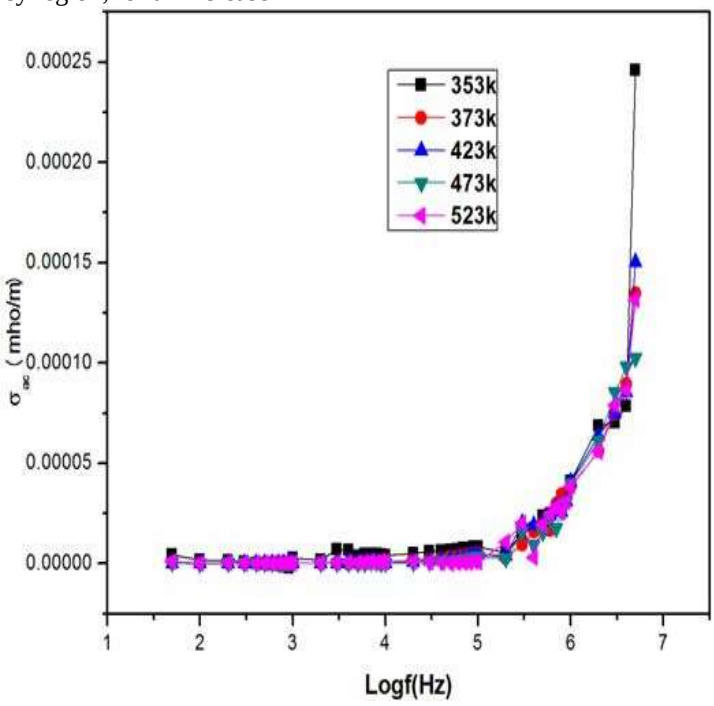


Fig.9, Frequency dependence of AC conductivity at different temperature of Mn_3O_4

Conclusion

This study demonstrates the fact that manganese acetate is a proper precursor for the formation of Mn_3O_4 nanoparticles. The XRD pattern confirms that the tri manganese tetra oxide is formed in the tetragonal spinel structure. FTIR spectrum reveals that the sample prepared has the finger print of hausmannite Mn_3O_4. The major stretching and bending vibrational frequencies have been identified. Mn_3O_4 micro sphere like nanoflowers were prepared by solvothermal method using different reaction time and different amount of surfactant. Oleic acid was used as a surfactant in the formation of hausmannite Mn_3O_4. It was found that the amount of Oleic acid played vital role in the formation of micro sphere in solvothermal methods. Both SEM and FESEM images confirm the formation of microsphere like nano flowers. The results of HRTEM and SEAD corroborate very well with that of SEM and XRD results respectively. The dielectric constant decreases with increase of frequency. The a.c. conductivity is found high for higher frequencies at a given temperature.

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

References

1. *G.A. Mansoori, T.A.F. Soelaiman, Nanotechnology—an introduction for the standards community, J. ASTM Int. 2 (2005) 21.*
2. *G.A. Mansoori, Nanotechnology: the emerging cutting-edge technology, United Nations Tech. Monit. 53 (Special Issue) (2002).*
3. *A.R.Armstrong, P.G.Bruce, Nature381 (1996)499.*
4. *Z.Durmus-, H.Kavas, A.Baykal, M.S.Toprak, Cent.Eur.J.Chem.7 (3)(2009) 555.*
5. *M.C.Bernard, H.L.Goff, B.V.Thi, J.Electrochem.Soc.140 (1993)3065.*
6. *A.H.DeVries, L.Hozoi, R.Broer, Phys.Rev.B66 (2002)035108.*
7. *Y. Yamashita, K. Mukai, J. Yoshinobu, M. Lippmaa, T. Kinoshita, M. Kawasaki, Surf. Sci. 514 (2002) 54.*
8. *Y.C. Zhang, T. Qiao, X.Y. Hu, J. Solid State Chem. 177 (2004) 4093.*
9. *Y. Zhao, C.G. Li, F.F. Li, Z. Shi, S.H. Feng, One-step synthesis of highly water dispersible Mn_3O_4 nanocrystals, Dalton Transactions 40 (2011) 583–587.*
10. *Y.W. Tan, L.R. Meng, Q. Pengb, Y.D. Li, One-dimensional single-crystalline Mn_3O_4 nanostructures with tunable length and magnetic properties of Mn_3O_4 nanowires, Chemical Communications 47 (2011) 1172–1175.*
11. *W.Z. Wang, C.K. Xu, G.H. Wang, Y.K. Liu, C.L. Zheng, Preparation of smooth single-crystal Mn_3O_4 nanowires, Advanced Materials 14 (2002) 837–840.*
12. *C.S. Du, J. Yun, R.K. Dumas, X.Y. Yuan, K. Liu, N.D. Browning, N. Pan, Three-dimensionally intercrossing Mn_3O_4 nanowires, Acta Mater. 56 (2008) 3516–3522.*
13. *Z.W. Chen, J.K.L. Lai, C.H. Shek, Shape-controlled synthesis and nanostructure evolution of single-crystal Mn_3O_4 nanocrystals, Scripta Mater. 55 (2006)735–738.*
14. *X. Hao et al. Mild aqueous synthesis of octahedral Mn_3O_4 nanocrystals with varied oxidation states, Colloids and Surfaces A: Physicochem. Eng. Aspects 374 (2011) 42–47.*
15. *Fan, Q.; WhiHingham, M.S.Electrochem.solidstate let.2007, 10, A48.*
16. *L.X. Yang, Y.J. Zhu, H. Tong, W.W. Wang, G.F. Cheng, Low temperature synthesis of Mn_3O_4 polyhedral nanocrystals and magnetic study, J. Solid State Chem. 179 (2006) 1225–1229.*