



Synthesis, Characterisation and Studies of Nanosized γ -Fe₂O₃

KEYWORDS

Govindgarh ,molluscans, gastropods.

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ABSTRACT Materials Chemistry is integrating by finding new routes for the synthesis of materials at nano dimension. Microwave method is a simple energy efficient technique for the synthesis of materials at nano dimension. In the present work, nanosized γ -Fe₂O₃ prepared by thermal decomposition of ferrous hydroxide precursor employing polyvinyl alcohol as a fuel. The structure of as synthesised γ -Fe₂O₃ is characterised by X-ray diffraction (XRD), bonding by Fourier transfer infrared (FTIR), morphology by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Frequency dependent dielectric study and d c conductivity of the γ -Fe₂O₃ is well studied. Crystallite sizes and density measurement of the sample is under taken. The crystallite sizes were calculated using X-ray line broadening and density measurements were under taken by various methods. TEM study shows that, particles are in the range of 50-60 nm. XRD pattern shows the formation cubic phase γ -Fe₂O₃, irregular shaped particles and small nano rods with compact arrangement in SEM and TEM images. FTIR study proves the formation of metal-oxide (Fe-O) in prepared γ -Fe₂O₃ sample. Dielectric constant and electrical study is undertaken for electrical and dielectric behaviour of the sample.

1. Introduction

Ferrite materials at nano dimension has gained much technological importance and these materials have attracted considerable interest as they exhibit materials properties that differ strongly from those of the bulk phases. γ -Fe₂O₃ phase is crystalline magnetic materials which is having spinel structure and finds commercially applications [1-3]. It is widely used medium for magnetic recording of continuous audio signal and discrete digital signals in longitudinal mode of operation. A thrust for higher density of data storage in case of digital recording has forced researchers to improve upon the magnetic property.

Magnetic iron oxide has attracted technological interest due to its magnetic and catalytic properties. The interest of researchers has increased due to the observation that, the properties are strongly dependent on the size of particles with dramatic changes when nanometric sizes are acquired [4, 5]. Development of new synthetic routes for preparation of nanostructured γ -Fe₂O₃ enhances the synthetic nanoscience. Various synthetic methods are reported in the literature; among this, microwave method finds much importance because of its simplicity, energy efficient and less time consuming [6-8].

In our earlier studies [9, 10], we have successfully prepared the ultrafine gamma ferric oxide nanoparticles from iron oxalate precursor and polymer fuel. Present work reports the synthesis of γ -Fe₂O₃ nanoparticle using ferric hydroxide precursor employing microwave route. Polyvinyl alcohol (PVA) is used as a fuel for the conversion of ferric hydroxide in to γ -Fe₂O₃ nanoparticles. Polyvinyl alcohol is a good surfactant and dispersant, hence the precursor will be well dispersed in the molton PVA which is needed for the initiation of combustion process. After partial burning, microwave heat treatment is given for the complete conversion of precursor in to gamma ferric oxide particles. The prepared sample is well characterised for its structure by X-ray diffraction (XRD), morphology by Scanning Electron Microscope (SEM) & Transmission Electron Microscope (TEM), bonding by Fourier Transform Infrared study (FT-IR) techniques. Thermal study, electrical study and magnetic study of the prepared sample is undertaken.

2.0. Experimental

2.1. Materials and Methods

Ferrous ammonium sulphate, hydrochloric acid, concentrated nitric acid and ammonia chemicals are used in the present study were of AR grade. Polyvinyl alcohol of molecular weight 125,000 was obtained commercially is used as fuel. Microwave method is adopted for the synthesis of γ -Fe₂O₃ nanoparticles

2.2. Preparation of ferric hydroxide precursor

About 0.8 gm of ferrous ammonium sulphate was dissolved in 50 ml of water, containing 10 ml of dilute hydrochloric acid (1:1). About 1-2 ml of concentrated nitric acid was added to the solution and boiled gently when the solution turned yellow. 200 ml of water was then added and boiled again. To the boiling solution, 1:1 ammonia solution was added in a slow stream until it was present in slight excess. Boiling was continued for one minute and then the precipitate was allowed to settle down. The supernatant liquid should be colorless. The clear supernatant liquid was decanted through a Whatman No.41 filter paper. The precipitate was thoroughly washed with hot 1% ammonium nitrate solution until the solution filtrate was free from chloride ions and then dried at 120 °C in a hot air oven [11].

2.3. Preparation of γ -Fe₂O₃

The prepared ferric hydroxide precursor is mixed with polyvinyl alcohol in the weight ratio 1:5 [12] and ground well using pestle and mortar. The resultant mixture was transferred into a crucible and ignited in an electrical oven. The dispersed phase ignited with the evolution of large volume of gases. Here, PVA reacts with the precursor; a partially decomposed product was obtained after the complete evolution of gases. The temperature of the process does not exceed 300°C at any time. Chemical and physical characterisation of the partially decomposed products did not give any confirmable phases. The possible reason for a partially decomposed product formed may be attributed to the low temperature of the reaction giving rise to the insufficient energy needed for complete conversion. Hence, the sample is treated in a microwave oven to get the desired product. This partially decomposed product was placed in a domestic microwave oven having frequency 2.45GHz for about 15 minutes at 90% The solid burns by producing golden yellow colour light due to the presence of iron metal in the precursor and leaving behind a brown coloured γ -Fe₂O₃ sample.

2.4. Density measurement

2.4.1. Density evaluation from X-ray data

The X-ray densities of the samples have been computed from the values of lattice parameters using the formula [13, 14].

$$d := 8 \frac{M}{Na^3}$$

Where 8 represents the number of molecules in a unit cell of a spinal lattice

M = Molecular weight of the sample N = Avogadro's number

a = Lattice parameter of the sample

The lattice constant for the cubic was calculated using the equation

$$d = \frac{a}{(h^2+k^2+l^2)^{1/2}}$$

2.4.2. Tap density

The as prepared g-Fe₂O₃ was crushed in agate mortar using a pestle and mortar. A known amount of this powder was filled into a graduated cylinder of 25ml capacity. The cylinder was tapped until the powder level remains unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density [15].

2.4.3. Powder density

The powder densities were measured using Archimedes principle [20] with a pycnometer and xylene as a liquid medium. The pycnometer of volume 25ml was used. The following weights were taken and used in the density calculation.

$$\rho_{\text{sample}} = \frac{(w_2 - w_1) \rho_{\text{sol}}}{(w_4 - w_3) + (w_2 - w_1)}$$

Weight of the bottle = W₁g, Weight of the bottle + Substance = W₂g, Weight of the bottle + Substance + Xylene = W₃g, Weight of the bottle + Xylene = W₄g, Density of Xylene = ρ_{sol}, Density of sample = ρ_{sample}

2.4.4. Crystallite size from X-ray data

Detailed knowledge of crystallite size, shape and strain in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid-state reaction. X-ray line broadening analysis provides a method of finding bulk average size of coherently diffracting domains and r.m.s strain. The average crystallite size (D) from X-ray line broadening has been calculated using the Scherrer equation [16, 17]. The instrumental broadening was corrected using quartz as an internal standard.

$$D = \frac{0.9\lambda}{\beta_{1/2} \cos\theta}$$

Where λ is the wavelength of the X-ray beam, β_{1/2} is the angular width at the half-maximum intensity and θ is the Bragg angle

2.5. Characterisation

The X-ray diffraction patterns were obtained employing a Geol JDX-8p spectrometer using CuK_α radiation. The X-rays generator was operated at 30kV and 20mA. The scanning range, 2θ/q was selected. The scanning speed = 1°min⁻¹ were employed for precise lattice parameter determination. High purity silicon powder was used as an internal standard. The shape, size and distribution of the powder, as prepared tin oxide sample, microstructure of the sample have examined using a Leica-440 Cambridge Stereoscan, scanning electron

microscope image. The SEM was operated at 20kV. The sample were made conducting by the sputtering of gold using a Polaron DC "sputtering unit" operated at 1.4kV and 18-20mA. The TEM images were obtained by Technia-20 Philips transmission electron microscope operated at 190KeV. The infrared spectra of the oxide sample were recorded on a Perkin-Elmer FTIR spectrophotometer [Model 1000] in the range 300 cm⁻¹ to 4000cm⁻¹. Dielectric measurements were taken on a HP-4192A impedance analyser for samples prepared in the pellet form of 1cm of diameter and 1cm in thickness. The g-Fe₂O₃ is pressed in the form of circular pellets of 1cm diameter and 1cm thickness. The dc conductivity measurements of g-Fe₂O₃ is made using the conducting silver paste as electrodes on both sides and is carried out by Keithly 2010 electrometer using two probe method. The vibrating sample magnetometer is well suited for measuring hysteresis loops, initial magnetization curves and remanent magnetization curves.

3.0. Results and discussion

3.1. X-ray diffraction

Figure-1 shows indexed XRD pattern of microwave derived g-Fe₂O₃. The pattern shows large number of peaks confirms the formation of cubic phase g-Fe₂O₃. The d-spacing values of the sample matches well with standard 4-755 JCPDS file. Unit cell parameters were obtained by least-square refinement of the powder XRD data. This study reveals that the sample is monophasic g-Fe₂O₃ with cubic spinal structure having nanosized particles. The values in the parenthesis indicate miller indices

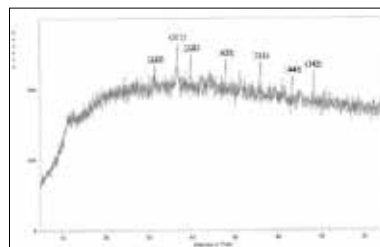


Figure-1: XRD pattern of g-Fe₂O₃

3.2. Crystallite size and density

The crystallite size of the g-Fe₂O₃ sample is calculated from XRD data is 45.6 nm. The size obtained is dependent on solid-state transformation reaction, which generally adopts the habit of its precursor. Thus, the conversion of iron hydroxide precursor into g-Fe₂O₃ is considered to be topotactic in nature, indicating that the synthesis of precursor with very small particle sizes would be required for obtaining nanosized g-Fe₂O₃ sample. The densities of the sample calculated from XRD data, tap density and powder density is 4982 kg/m³, 5089 kg/m³ and 3550 kg/m³ respectively. The sample shows approximately same density may be attributed to their average shape which might have similar surface area.

3.3. Scanning Electron Microscopy (SEM)

Figure-2 shows SEM image of g-Fe₂O₃. This image shows the irregular shaped particles are arranged in agglomeration. Most of the particles are spherical and joined together. Joints between fine particles of g-Fe₂O₃ with non-chain structure is also observed.

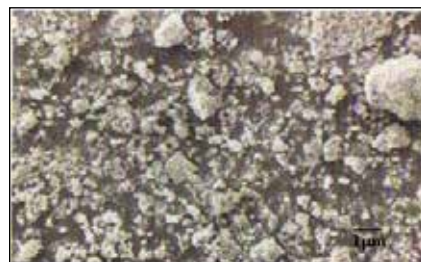


Figure-2 shows SEM image of g-Fe₂O₃

3.4. Transmission electron microscopy (TEM)

The nanocrystalline nature of the microwave derived g-Fe₂O₃ is further confirmed by the transmission electron micrograph and electron diffraction (ED) pattern. Transmission electron microscopy studies of the microwave derived g-Fe₂O₃ provide information on the microstructure, the particle size and distribution in the sample. The bright field TEM micrographs, their corresponding ED patterns for the prepared g-Fe₂O₃ sample is shown in Figure 3(a-b). The bright field TEM micrograph represents the basic powder morphology where the smallest visible ultrafine particles might be identified with the crystallites or their aggregates. From this figures, it is cleared that particle-sizes are in the nano range. The electron diffraction (ED) patterns confirm the polycrystalline nature of the samples.

Figure 3(a): TEM micrograph of g-Fe₂O₃



Figure 3(b): ED pattern of the prepared g-Fe₂O₃



3.5. Infrared studies

The aim of infrared study is to ascertain the metal-oxygen (M-O) bond and nature of the synthesised g-Fe₂O₃ sample. Metal oxides generally give absorption bands below 1000cm⁻¹ arising from inter-atomic vibrations [18]. Figure 4 shows FTIR spectrum of as prepared g-Fe₂O₃ sample. The sample shows the absorption in the region 3210, 1095, 545, 510 and 455cm⁻¹. The peak 3210cm⁻¹ corresponds to water of absorption and the peak at 1095cm⁻¹ due to the presence of some overtones. The peaks at 545, 510 and 455 cm⁻¹ corresponds to metal-oxygen (Fe-O) vibrational modes of the spinel compound. This conform the formation of g-Fe₂O₃.

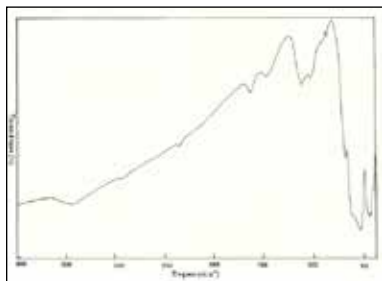


Figure 4: FT-IR of g-Fe₂O₃ sample

3.6. Thermal Study

Figure 5 shows the DTA trace under static air atmosphere for prepared g-Fe₂O₃ sample. A strong endothermic peak at 98°C corresponds to the loss of adsorbed water molecule. The weak exothermic peak at 270°C corresponds to phase transition of g-Fe₂O₃ i.e tetragonal to cubic crystal system. This step is followed by the presence of sharp exothermic peak at 420°C for the g @ a transition. The XRD pattern of the g-Fe₂O₃ sample isothermally heated at 420 °C resembles a-Fe₂O₃. The phase changes of a-Fe₂O₃ is observed in the sample by the presence of weak exothermic and endothermic peak.

It is strongly felt that the g-Fe₂O₃ sample shows a well-defined dehydration and a g @ a transition, is a suitable example for the case study for synthesis of g-Fe₂O₃.

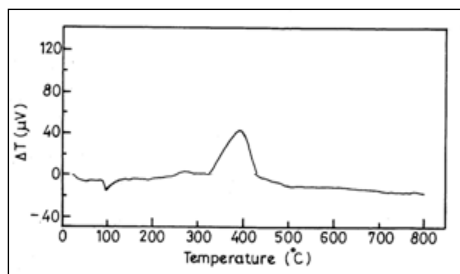


Figure: 5 DTA trace of g-Fe₂O₃

3.7. Electrical conductivity

Figure-6 shows the variation of electrical conductivity of as prepared g-Fe₂O₃ sample. The room temperature conductivity values are of 10⁻³S/cm. Initially, conductivity of the sample increases very slowly (near to constant values) with temperature up to 250°C, again increase up to 350°C. This is due to the loss of adsorbed water molecules then exponential increase in conductivity with increase in temperature is observed.

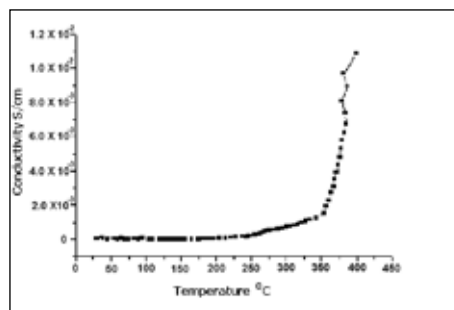


Figure 6: d.c conductivity of g-Fe₂O₃ sample

3.8. Dielectric behavior

Figure 7 shows The frequency variation of room temperature dielectric constant, e', for as prepared g-Fe₂O₃ sample from 0 Hz to 1GHz.

The dielectric properties of ferrites are dependent upon several factors, including the method of preparation, chemical composition, and grain structure or size. The sample shows a dielectric constant of 200 to 250 and there is a decreasing trend in the value as the frequency is increased which is the normal behaviour of ferrimagnetic materials. The e', value increases nonlinearly with respect to temperature and frequency. In the low temperature range in 30-70 °C the traces shows a peak in the e', value. The presence of the peaks are more pronounced for 10³ and 10⁴ Hz. Possible reasons for the occurrence of these peaks may be loss of adsorbed water molecules as it is known that dielectric relaxation may cause this type of behavior. At low frequencies and temperature the e', are no longer smooth lines but show some irregularities.

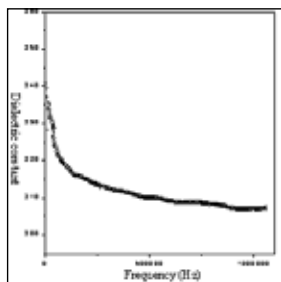


Figure 7: Dielectric constant of g-Fe₂O₃ sample

3.9. Vibrating sample magnetometer

Figure 8 shows the magnetic hysteresis curve for the g-Fe₂O₃ sample at room temperature. The value of saturation magnetisation, permanence magnetisation and coercivity are 11.36emu/g, 3.55emu/g and 214.88 Oe respectively. It can be seen that both of them have no specific saturation magnetisation and their coercivities approach 0Oe, indicating that the obtained MPs are super magnetic further more, they have strong magnetic induction than those obtained by other methods. The magnetic hysteresis loop of the sample demonstrates thmagnetic.

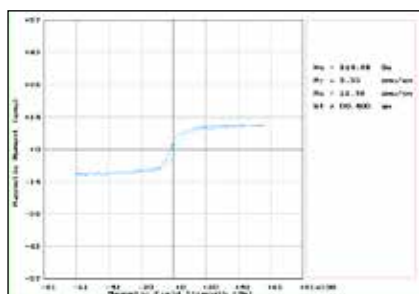


Figure 8: Magnetic hysteresis curve of g-Fe₂O₃ sample

4. Conclusions

The nanosized g-Fe₂O₃ is synthesized by microwave irradiation with precursor and polyvinyl alcohol as an efficient fuel. Because of its simplicity this method can adopt for the synthesis of other metal oxides at nano dimensions not only for laboratory preparation, this procedure may be extended for large-scale synthesis of nanoparticle. The calculated X-ray crystallite sizes and results of TEM image confirm the nanocrystalline nature of the prepared gamma iron oxide. The electrical studies shows, the electrical behavior of the sample may depending upon the number of Fe²⁺ and Fe³⁺ ions present in that sample. The observed coercive forces of the gamma iron oxide sample indicating that, it may be used in magnetic recording materials.

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