Chapter 6

Synthesis and Characterisation of Magnetic Iron Oxide Nanostructures

Nano magnetic oxides are promising candidates for high density magnetic storage and bio-medical applications. This chapter discusses the synthesis and studies on spherical and non-spherical (acicular) Iron Oxide (\(\gamma\text{Fe}_2\text{O}_3\)) nanoparticles using complexing media such as starch. Non-spherical mesoscopic iron oxides are also candidate materials for studying the shape, size, and strain induced modifications of various physical properties viz. optical, magnetic, and structural. Magnetic and optical properties of spherical as well as non-spherical iron oxide nanoparticles are subjected to detailed investigations. The role of a complexing medium like starch in aiding the directional growth of \(\gamma\text{Fe}_2\text{O}_3\) is studied. Thermo-gravimetric and Fourier Transform Infrared spectroscopic studies are conducted to identify the impurity phases present.

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6.1 Introduction

Mesoscopic magnetic iron oxides have attracted the attention of scientists for a variety of reasons. Magnetic iron oxides are candidate materials for audio, video and compact memories.\cite{1} Recently efforts are underway to find new applications of these materials - as drug delivery agents, as superparamagnetic iron oxide (SPION) particles for hyperthermia, contrast enhancing agents in magnetic resonance imaging (MRI)\cite{2} and also as biosensors.\cite{3} They are biocompatible and inexpensive. From a fundamental point of view, magnetic iron oxides are ideal templates for studying ferrimagnetism at the nano level since they possess an ideal two sub lattice with magnetic ions on either sites.

Magnetic iron oxides belong to the class of inverse spinels having their cation distributed on the octahedral sites (B) and tetrahedral sites (A). Maghemite or gamma ferric oxide also crystallizes in the inverse spinel structure. The structure of maghemite is said to possess a vacancy ordered spinel structure with vacancies situated exclusively on the octahedral sites.\cite{4}

The preparation of gamma iron oxide from precursors is tricky because the material turns easily in to its nonmagnetic phase during synthesis if adequate precautions are not taken.

Nonsphericity is an essential criterion for enhancing signal to noise ratio during recording.\cite{5,6} But \(\gamma\text{ Fe}_2\text{O}_3\) is a cubic crystal and does not easily crystallizes in to elongated ellipsoidal particles. Earlier, workers have attempted to synthesize nonspherical precursors using complexing medium.\cite{7} Nucleation will be greatly influenced by external conditions, like pH, temperature and constant stirring. Complexing agents like starch retard the growth of the precursors in the crystallographic a-directions, so that growth proceeds in the c-directions, leading to needles.\cite{8} However, with the advent of nanoscience and nanotechnology, shape and size induced
modifications of various properties like optical, magnetic, structural properties is a rich area of physics where quantum mechanical phenomenon like quantum size effects can be investigated on candidates materials like gamma iron oxide.\textsuperscript{[9]} It is also known that size dependent magnetic properties manifest itself in to superparamagnetism and single domain characteristics. Reduction of size results in large red shift in Fe$_3$O$_4$ nanoparticles.\textsuperscript{[10]}

Most of earlier studies on nonspherical particles are limited to the synthesis of nonspherical $\gamma$Fe$_2$O$_3$ particles. Most of the particles lie well above the nanometer dimension.\textsuperscript{[7]} However, size, shape and strain dependent optical and magnetic properties are a virgin area where the effect of size and shape can be studied in a single shot if nanosize particles can be synthesized. Such a study assumes importance because of the resulting magneto optical properties of the nanocrystals.

In this chapter spherical and elongated mesoscopic gamma iron oxide particles are synthesized employing a novel technique and using starch/water/ethylene glycol as Complexing agents. Their structural, magnetic, optical properties are evaluated. Emphasis is laid in studying the shape induced optical properties of gamma iron oxide nanoparticles. Thermo Gravimetric (TG) and FTIR analysis are carried out to probe the retention of organic residues in the sample. Attempts are made to correlate the optical, magnetic properties with size and shape.

6.2. Experimental

6.2.1 Preparation of spherical $\gamma$Fe$_2$O$_3$ nanoparticles

In order to prepare spherical $\gamma$Fe$_3$O$_4$ particles, 20\% of starch solution is prepared by adding 20 g of soluble starch in to 100cc of hot water. The resultant solution is heated with constant magnetic stirring to 50$^\circ$C till it became transparent. 25g of anhydrous ferrous sulphate is dissolved in 75 cc
starch solution. This solution was heated to 70°C. To this solution 0.2 molar ethylene glycol is added. It is presumed that ethylene glycol inhibits the growth of the particles along one particular direction. Addition of ethylene glycol must be drop wise with constant stirring in order to ensure the formation of spherical particles. These particles are filtered off and dried in a furnace at 370°C dried in ambient atmosphere to ensure the formation of $\gamma Fe_2O_3$.\textsuperscript{[11]} This leads to a brown magnetic powder confirming the formation of $\gamma Fe_2O_3$ nanoparticles.\textsuperscript{[12]} These samples are hereafter named N-1.

6.2.2 Preparation of ellipsoidal $\gamma Fe_2O_3$

The above procedure for the synthesis of spherical iron oxide particles is modified to prepare ellipsoidal gamma iron oxide (hereafter named N-2) in the sense, that instead of ethylene glycol and starch, water and starch are employed as the complexing for this medium. 25g of anhydrous ferrous sulphate was dissolved in 75 cc starch solution. This solution was heated to 70°C. To this solution 0.2 molar solution of oxalic acid is added to precipitate nonspherical ferrous oxalate precursors from the medium. It is found that as the concentration of starch increases aspect ratio also increases.

6.2.3 Characterization

The structural analysis and the identification of the phase are conducted using an X-ray diffractometer (Rigaku Dmax-C) using Cu Kα radiation ($\lambda = 1.5418$ Å). A scanning rate of 5° min$^{-1}$ is applied in the 2θ range of 10° - 70°. The grain size is estimated by employing Debye-Scherer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

6.1
where $\lambda$ is the wavelength of X ray used, $\beta$ is the FWHM of the XRD peak with maximum intensity and $\theta$ is the angle of diffraction. A JOEL JEM 2200 FS electron microscope using an accelerating voltage of 200 kV is used to deduce the particle size distribution of nanoparticles. The Transmission Electron Microscope (TEM) images, High Resolution Transmission Electron Microscope (HRTEM) images and Energy Dispersed Spectra (EDS) are recorded for morphological and compositional studies. Room temperature magnetic properties are obtained from the hysteresis loop recorded in a Vibrating Sample Magnetometer (VSM) model EG&G Par 4500. A Thermo Nicolette Avatar 370 DTGS model spectrophotometer using the KBr method was used to record the FTIR spectrum of the samples. A Jasco V 530 UV – Visible spectrophotometer was used to determine the diffused reflectance studies. DTG studies are conducted using Perkin Elmer Thermal Analysis in the Nitrogen atmosphere in the temperature range 30 – 550 °C.

6.3 Results and Discussion

6.3.1 Structural and Morphological Studies using XRD and TEM

The x ray powder diffraction pattern of the spherical (N-1) and the nonspherical (N-2) Iron Oxide nanoparticles are depicted in Figure 6.1. and they represent a spectrum typical of an inverse spinel. The planes are identified and listed. The peaks (111), (220), (311), (400), (511) and (440) correspond to that of $\gamma$Fe$_2$O$_3$ (ICDD: 39-1346).
There are no indications for the existence of any impurity phase, corresponding to $\alpha Fe_2O_3$. However, the base line is found to be shifted due to the presence of amorphous phase probably due to the organic inclusion of the samples. The average particle size was determined from line broadening and the spherical particles have an average size of 10 nm. TEM images of N-2 indicate that the formations of nonspherical particles (Figure 6.3), while particles coded N-1 are spherical in shape (Figure 6.2). The spherical particles have an average size of 10 nm. Nonspherical particles have an average length of 19 nm and breadth 9 nm with an average aspect ratio of 2.
It is evident from Figure 6.2.b that the particles are highly crystalline and well separated by grain boundaries. Diffusion of lattice planes into the grain boundary is also noted. The EDS indicates the presence of Iron from Iron Oxide nanoparticles. The particle size distribution for spherical particles is determined for spherical particles and a histogram depicting the size distribution is shown in Figure 6.2.d.
Figure 6.3: (a) TEM image, (b) HRTEM image, (c) EDS of N-2.

Figure 6.3 depicts the TEM, HRTEM, and EDS images of non-spherical iron oxide particles. The discrepancy in particle size as determined by XRD and TEM could be because of the fact that only large crystallites contribute to the Bragg peak.\cite{13} It can be seen from Figure 6.3.b that although the crystal lattice of particles are well defined, the Miller indices are interlocked (buckled) and lattices planes have a small bending in the grain boundary. These are evidence for the occurrence of high internal strain with in the lattice.\cite{14}
6.3.2 Magnetization studies using VSM

The hysteresis loop for spherical (N-1) and nonspherical iron oxide particles (N-2) are shown in figure 6.4. Nonspherical particles exhibit a saturation magnetization of 30 emu/g while spherical particles display a saturation magnetization of 37 emu/g and a coercivity of 105 Oe. Enhancement of coercivity for sample N-2 and decrease in its saturation magnetization with respect to N-1 are other evidences for the deviation from sphericity of sample N-2. If the particles are spherical, the same applied field would have magnetized it to the same extent. If it is not, the same applied field will magnetize it along a long axis. Hence the strength of the applied magnetic field along the short axis is such that it produces the same true field inside the specimen. Thus shape alone is the source of magnetic anisotropy.¹⁵

![Figure 6.4: Room temperature M(H) curves for (a)N-1, (b)N-2.](image)

Thus it can be inferred from the magnetization curves of N-1 and N-2 that increase in coercivity in the case of N-2 is mainly due to the elongation of grains. These ellipsoidal particles may cause a small amount of spin freezing in random directions. This is one of the reasons attributed to the decrease in saturation magnetization value for N-2. The magnetization
curve of N-1 shows almost negligible remanence and small coercivity showing their superparamagnetic nature.

Additional evidence for superparamagnetism exhibited by N-1 can be obtained by simulating the magnetization curve using the Langevin function \( L(x) \). Here it is assumed that the individual grains are single crystals with the number of crystals equal to the number of domains. We have Langevin function represented by

\[
L(x) = \coth x - \frac{1}{x} \quad 6.2
\]

Size plays a crucial role in deciding the overall magnetization. The variation of particle size is also then to be taken into account. Since the equation 2 is not taking any consideration to the distribution of particle size, it cannot explain the collective behaviour of an ensemble of nanoparticles with a size distribution having finite width. The size distribution obtained from TEM is used for simulation. After giving due provision for \( b \) (width of the size distribution histogram) the Langevin function can be modified as,\[161\]

\[
L(x) = \frac{1}{2bx} \int_{x(1-b)}^{x(1+b)} \int L(x') dx' \quad 6.3
\]

\[
= \frac{1}{2bx} \ln \left\{ \frac{(1-b) \sinh[x(1+b)]}{(1+b) \sinh[x(1-b)]} \right\} \quad 6.4
\]

The simulated Langevin function using Eq.(4) is carried out and is shown in Figure 6.
The fitting (Figure 6.5) is carried out after giving due weightage for particle size distribution. Thus simulated curve (linear) fits very well (particularly at average sizes) with experimental curve (dotted).

### 6.3.3 TG-DTG Studies

Bulk maghemite in the micron regime possess a saturation magnetization of \(~74\ \text{emu/g}\) \cite{15} and coercivity of 250 Oe, \cite{11} and they are generally multidomain in character. However, as particle size reduces they became single domain and exhibit superparamagnetic characteristics. Although we have procured evidence for superparamagnetism by Langevin fitting, the reduction in magnetization is to be probed by supplementary techniques. For this TG DTG studies are carried. The TG-DTG curves are shown in Figure 6.6.
Figure 6.6: TG-DTG curve for N-1.

TG curve shows a continuous weight loss on heating. A substantial weight loss corresponding to 8% at 450 °C is observed. The net weight loss is around 14% when the temperature reaches 550 °C. There is a possibility of a small fraction of the polymer (particularly starch which can remain there till 1000 °C) being retained in the sample which normally does not decompose at these temperatures. If due weightage is provided to the retention of polymeric residues, in the final gamma ferric oxide the observed saturation magnetization can be accounted for.

6.3.4 FT-IR Studies

FT-IR studies are carried out on N-1 and N-2 samples in order to ascertain the presence of starch. The spectrum is charted in Figure 6.7.
The peak at 3384.82 corresponds to \(-\text{OH}\) group and the broadening shows the presence of hydrogen bonding. This strengthens the evidence for the presence of starch in the samples.\(^{17}\) This \(-\text{OH}\) group with hydrogen bonding is coming from starch. Peaks between 500 and 700 cm\(^{-1}\) correspond to Fe-O bonds.\(^{18}\)

### 6.3.5 Energy band gap calculation

Band gap calculation plays an important role in characterising the materials at nano level. In the case of nanoparticles, various factors like lattice strain, plasmonic confinements, surface and shape effects and quantum confinement effects can alter and engineer the band gap and hence, the determination of band gap plays a seminal role in nanoparticle characterisation. Diffused Reflectance Spectroscopic (DRS) studies of samples N-1 and N-2 are conducted using UV-Visible NIR Spectrophotometer. Energy band calculations are carried out using the relation.\(^{19}\)
\[ \alpha = \sum \alpha = \sum \frac{A_i (h\nu - E_{gi})^{m_i}}{h\nu} \]  \hspace{1cm} 6.5

where the value of $E_{gi}$ and $m_i$ correspond to the energy and the nature of the particular optical transition with absorption coefficient $\alpha_i$. For allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, the value of $m_i$ corresponds to $\frac{1}{2}$, 2, 3/2 and 3, respectively.\cite{20} Since the particles are nanocrystalline, the values of $E_{gi}$ and $m_i$ are determined without presuming the nature of electronic transition.\cite{21} Eq.5 can be rewritten in the following form

\[ \frac{d (\ln (\alpha h\nu))}{d (h\nu)} = \frac{m}{(h\nu - E)} \]  \hspace{1cm} 6.6

The plot of $\frac{d (\ln (\alpha h\nu))}{d (h\nu)}$ versus $h\nu$ will produce discontinuity at a particular value of $h\nu = E$ where a possible electronic transition can occur corresponding to the bandgap $E = E_{gi}$. Figure 6.8 (a) and (b) show the above plots for samples N-1 and N-2 respectively.

![Figure 6.8: Bandgap calculation from differential plot; (a) for N-1, (b) for N-2.](image-url)
The red shifted electronic band (~0.24 eV) is due to the presence of ellipsoidal particles which are under very high stress. This is further supported by HRTEM (Figure 3.b.). This shows that, although the crystal lattice of particles is well defined, the Miller indices are buckled (Figure 3.b.). The nature of electronic transition is found using ln(αhv-E) vs ln(αhv) curves (figure 6.9) and it is found that the slope of the curves is ~0.5. This indicates that the electronic transition involved is ‘allowed direct’.

![Figure 6.9: ln(hv-E) vs ln(αhv) curves for; (a) N-1, (b) N-2.](image)

From the lattice constants for spherical and nonspherical γFe₂O₃ particles unit cell compression of (ΔV/V) -10% was observed in the case of nonspherical particles. Stress increases as the size is reduced. The reduction in bandgap is governed by the narrowing of the direct bandgap due to the enhanced pressure from the surface tension, where pressure P=2γ/r, γ is the surface tension and r is the size of the grain. So the strain induced modification of band gap provides a phenomenological explanation for the anomalous red shift observed in mesoscopic iron oxide particles. The effect of matrix or any other impurities in the red shift has been removed, since the entire measured band gaps are well above the red shifted value.
Conclusion

The employment of a complexing medium like starch for the synthesis of nonspherical iron oxide particles can be modified to tailor the aspect ratio of nonspherical nanoparticles of gamma ferric oxide, since shape controlled particles are of interest both from a fundamental and application point of view. The observed reduction in saturation magnetization with respect to the saturation magnetization of bulk maghemite is due to the presence of superparamagnetism and residual organic impurities in the final product.

Strain induced modification of band gap is possible by carefully controlling the acicularity of these particles. Shape control can also induce anisotropy and thus modify the coercivity of these particles. A simple phenomenological explanation was provided to explain the red shift found in the optical band gap of nonspherical maghemite particles.
References