Synthesis and Characterisation of Manganese Ferrite Nanoparticles

A project report submitted

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by

Amantej Kaur Lotay

(Roll no. 301404003)

Under the guidance of

Dr. S. D. Tiwari

SCHOOL OF PHYSICS AND MATERIALS SCIENCE

THAPAR UNIVERSITY

PATIALA-147004

INDIA

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DEDICATED TO MY BROTHER "AADESH"..!!

CERTIFICATE

This is to certify that the project report entitled **"Synthesis and Characterisation of Manganese Ferrite Nanoparticles"** submitted by Ms. Amantej Kaur Lotay is in partial fulfilment for degree of Master of Science in Physics in this University. This work has been done under my supervision. She has not submitted this material for credit towards any other degree at this or any other University.

(Dr. S. D. Tiwari)

Associate Professor

School of Physics and Material Science

Thapar University, Patiala

Countersigned by

Dr. Manoj K. Sharma

Head

School of Physics and Material Science

Thapar University, Patiala

Dr. S. S. Bhatia

Dean of Academic Affairs

Thapar University, Patiala

Declaration

I hereby declare that the project report entitled "Synthesis and Characterisation of Manganese Ferrite Nanoparticles" is the work carried out by me under the supervision of Dr. S.D. Tiwari. I have not submitted this work anywhere else for the award of any degree.

Amantej Kaur.

Amantej Kaur

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Amantej Kaur

Abstract

Manganese Ferrite nanoparticles are synthesised by co-precipitation method. This sample is heated at 800 ^{0}C for three hours in air to prepare another sample of larger crystallite size. Both samples are characterized by X-ray diffractometer, transmission electron microscope and vibrating sample magnetometer. Results on both samples are discussed and compared.

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CHAPTER 1

INTRODUCTION

1.1 Nanoparticles

Particles having size in nanometer range are known as nanoparticles. Behaviour of these particles is different from those of corresponding bulk materials. These systems also have many technological applications. Nanoparticles of different materials have been attracting the attention of researchers because of interesting behaviour exhibited by them and useful applications [1, 2].

1.2 Magnetic nanoparticles

Behaviour of small particles of ferro and ferrimagnetic materials is unique. Property such as superparamagnetism is only shown by sufficiently small particles of these materials [1]. There have been lots of works on magnetic behaviour of these systems. According to Neel, sufficiently small particles of antiferromagnetic are also expected to show superparamagnetism [3].

1.3 Magnetic materials

On the basis of behaviour of materials in external applied magnetic field, all materials can be categories in following categories [4, 5].

1.3.1 Diamagnetic materials

Diamagnetic materials do not have unpaired electrons. Due to this, there is no net magnetic moment. When an external magnetic field is applied then there is an induced magnetization in a direction opposite to the applied magnetic field. In other words, diamagnetic materials are repelled by external magnetic field. The magnetization becomes zero once the applied field is removed.

1.3.2 Paramagnetic materials

Ions in paramagnetic materials possess net magnetic moment because of unpaired electrons. In absence of external magnetic field these moments are randomly oriented and so net magnetization of the system is zero. In an external magnetic field these moments try to align along the field direction and so now the magnetization of the system is non zero. In presence of a very large magnetic field, all moments are aligned along the field direction. In this situation we get maximum magnetization called as saturation magnetization. In low field range the magnetization of paramagnetic materials varies linearly with applied field.

1.3.3 Ferromagnetic materials

In ferromagnetic materials all the spins are aligned in same direction due to ferromagnetic exchange interaction. This interaction is very strong but short range in nature. The dipolar interaction among spins is long range in nature. The system minimizes its energy by diving itself in small regions known as domains. All spins in a domain are along same direction even in absence of any external magnetic field. But in absence of external magnetic field the domains are randomly oriented and so we get zero magnetization. If an external field is applied then all these domains get align along the field and we get saturation in magnetization. Above a critical temperature a ferromagnetic material becomes paramagnetic. This temperature is known as the Curie temperature.

1.3.4 Antiferromagnetic materials

In antiferromagnetic materials neighbouring spins of similar magnitude are aligned in opposite direction due to antiferromagnetic exchange interaction. This arrangement of spins gives zero magnetization. Above a critical temperature a given antiferromagnetic material becomes paramagnetic. This temperature is known as Neel temperature.

1.3.5 Ferrimagnetic materials

In ferrimagnetic materials, the adjacent spins of unequal magnitude align themselves in the opposite direction giving rise to a non zero magnetization. Behaviour of ferrimagnetic materials is almost similar to those of ferromagnetic materials. These materials also become paramagnetic above a critical temperature.

1.4 Manganese Ferrite

Researchers have been working on different types of ferrites due to their interesting behaviour and probable applications which include magnetic sensors, magnetic fluids, magnetic resonance imaging, generators etc. [6]. Ferrites are very useful in high frequency devices. Due to their high electrical resistivity the induction of eddy current and resulting energy loss can be minimized.

Among all ferrites those of transition metal ferrites are the most researched ferrite materials. These can be easily prepared by several methods including co-precipitation, thermal treatment, sol gel, sonochemical synthesis etc. The ferrites having ferrimagnetic cubic spinel structure are among the highly attracting materials because of their interesting electrical and magnetic properties [7].

The spinel structure has the configuration of AB_2O_4. This can be represented as a cubic closed packing of oxygen ions. This is shown in Figure 1.7. A represents tetrahedral site and B represents octahedral sites. Both sites are taken up by cations. The general formula of the ferrites spinel structure can be written as $(M^{2+})[Fe_2^{3+}]O_4$. Here M^{2+} represent metals ions such Fe^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Mg^{2+}. In the spinel structure of ferrites, the Fe^{3+} ions occupy the octahedral positions while M^{2+} ions occupy tetrahedral positions.

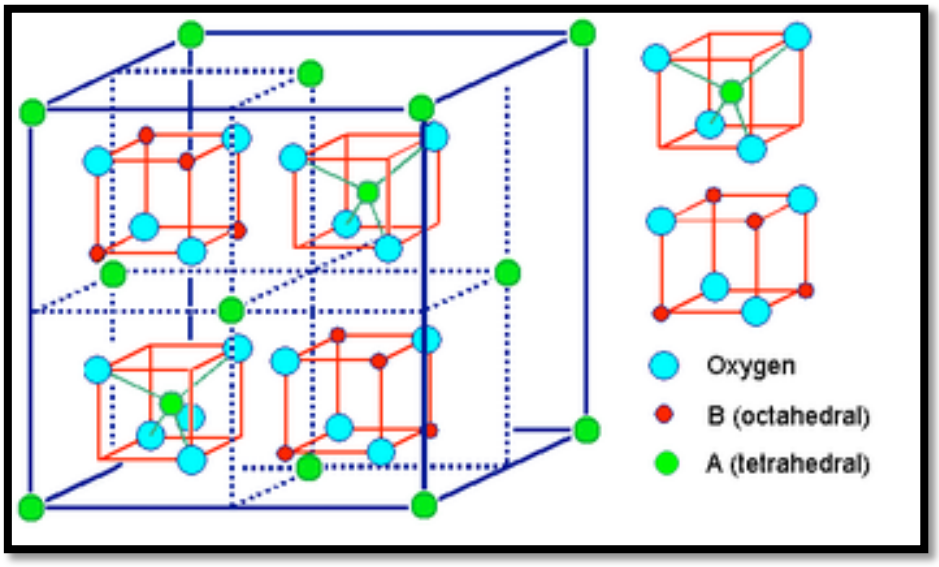

Figure 1.1: Spinel structure [8].

1.5 Literature Review

Tang et al. (1991): Manganese Ferrite was prepared at room temperature and at different temperatures using co-precipitation method. Particles prepared at room temperature had crystallite size of 2 nm but when these particles were heated the crystallite size and the particle size both were increased [9].

Rath et. al. (1999): They studied the synthesis of nanosized Zn-Mn Ferrite particles from metal chloride solution through a hydrothermal precipitation method. Magnetic behaviour of the sample was also studied [10].

Misra et al. (2004): They studied magnetic behaviour of nanocrystalline nickel, zinc and manganese ferrite prepared by reverse micelle synthesis method [11].

Amighian et al. (2006): They studied behaviour of manganese ferrite prepared by co-precipitation method. The sample was annealed at 1050 ^{o}C in argon atmosphere followed by rapid air quenching [12].

Arelaro et al. (2008): They investigated the influence of Mn^{2+}, Fe^{2+}, Co^{2+} cations on the effective magnetic anisotropy of ferrite system [13].

Lu et al. (2009): They found that Manganese doped superparamagnetic iron oxide nanoparticles were used to form ultrasensitive MRI contrast agents for liver imaging [14].

Yang et al. (2010): They reported the magnetic resonance imaging applications of manganese ferrite nanoparticles prepared by thermal decomposition method [15].

Naseri et al. (2011): They reported magnetic behaviour of manganese ferrite prepared by thermal treatment method [16].

Elahi et al. (2012): They reported magnetic properties of manganese ferrite prepared by co-precipitation method. NaOH was used as precipitant [17].

Goswami et al. (2013): They studied the synthesis of manganese ferrite by sonochemical method. It was found that the particle size, coercivity and saturation magnetisation increase with the calcination temperature [18].

Hashemian et al. (2015): They studied the synthesis and characterization of manganese ferrite nanoparticles by chemical co-precipitation method at pH 9 [19].

CHAPTER 2

METHODOLOGY

2.1 Synthesis

In this work manganese ferrite nanoparticles are synthesised by co-precipitation method [9]. For this, solutions of sodium hydroxide, Fe^{3+} ions and Mn^{2+} ions are prepared. The metal ions solutions are mixed in appropriate ratio. This solution is added drop wise to the solution of sodium hydroxide while continuously stirring till the pH of the solution reaches to 12. The solution is kept as such for 20 minutes and then kept in oven at 90 ^{o}C for 90 minutes. This is then allowed to cool. The precipitate is washed several times with distilled water and dried in oven. Resulting flakes are ground to get fine powder sample. A part of this sample is heated at 800 ^{0}C in air for three hours to form another sample.

2.2 Characterisation Techniques

2.2.1 X-Ray Diffraction

X-ray diffraction analysis is based on constructive interference of monochromatic X-ray beams diffracted from a crystalline material. A systematic arrangement for this is shown in following figure.

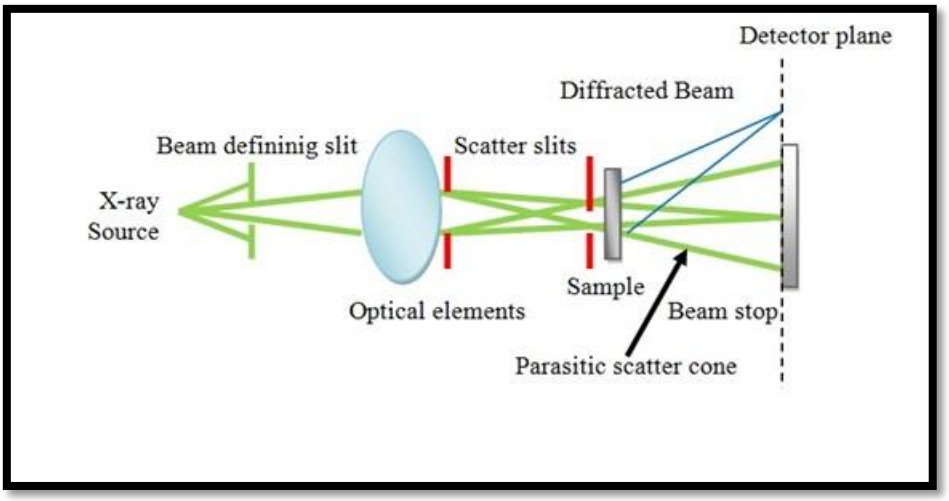

Figure 2.1: Systematic diagram of X-ray diffractometer [20].

The constructive interference between the diffracted x-ray beam takes place when

$$2dSin\theta = n\lambda,$$

where λ is wavelength of x-ray beam and n is order of diffraction. This relation is called Bragg's law. Following figures shows systematic representation of x-ray diffraction from parallel atomic planes.

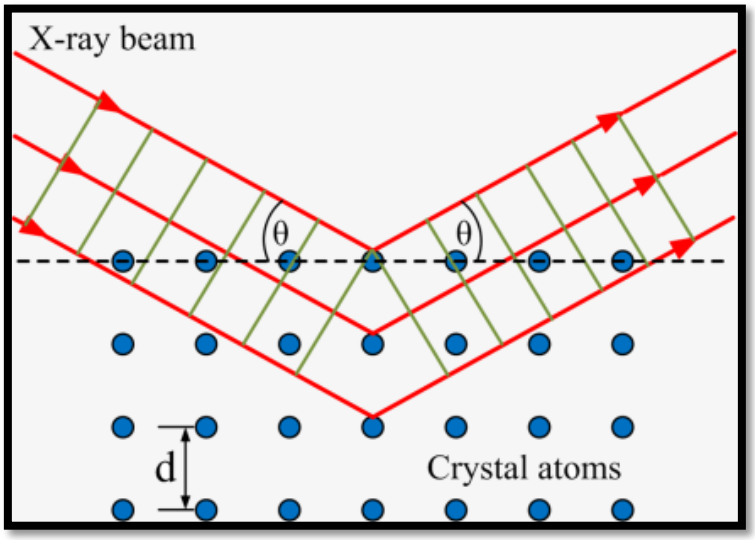

Figure2.2: Diffraction of x-ray beam [21].

2.2.2 Transmission Electron Microscope

An optical microscope uses a beam of light to get magnified image of an object. The resolving power of any microscope is limited by the wavelength of radiation used and so it cannot be increased beyond a limit for the conventional optical microscope. The transmission electron microscope uses a beam of energetic electrons to get magnified image of a thin specimen. The wavelength of de Broglie waves associated with moving electrons can be decreased by increasing energy of electrons in the beam. In this manner the resolving power of transmission electron microscope can be varied. In this high sensitive microscope a series of magnetic lenses is used to deflect the electron beam. Magnetic lenses are current carrying coils. Following figure shows a systematic representation of transmission electron microscope.

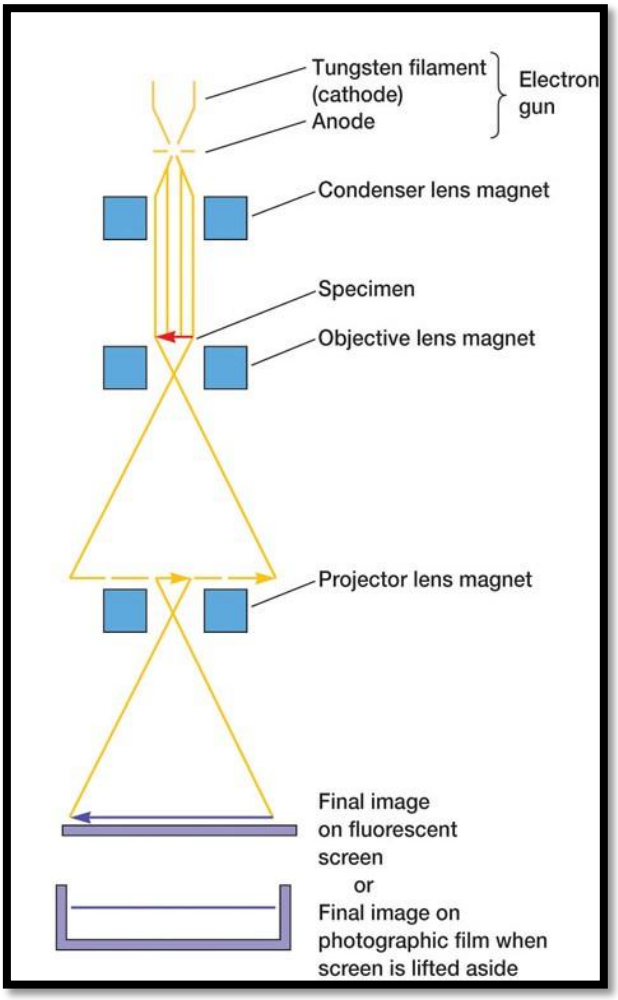

Figure 2.3: Schematic diagram of transmission electron microscope [22].

2.2.3 Vibrating Sample Magnetometer

This instrument measures magnetization of a given sample. First, the sample is magnetized by applying an external magnetic field. Now this magnetized sample is allowed to vibrate inside a pick up coil. An emf is induced across this coil due to Faraday's law of induction. This emf is directly proportional to the magnetization of sample. After suitable calibration the magnetization of sample can be measured in desired unit as function of temperature, applied magnetic field and time [23].

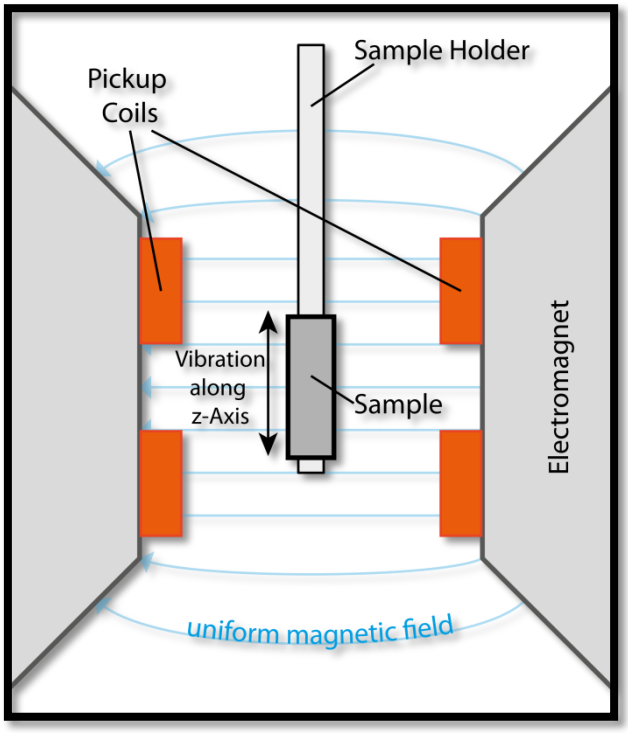

Figure 2.4: Schematic diagram of vibrating sample magnetometer [24].

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Structural characterisation

The structural characterisation of both samples is done using X-ray diffraction and transmission electron microscopy.

3.1.1 X-Ray Diffraction

Room temperature X-ray diffraction pattern of as prepared manganese ferrite is shown in Figures 3.1. This pattern shows that the sample in single phase manganese ferrite [9]. The peaks are seen to be broadened. It indicates that the sample in nanocrystalline. The average crystallite size is calculated using the modified Scherer formula [25]. It turns out to be about 20 nm.

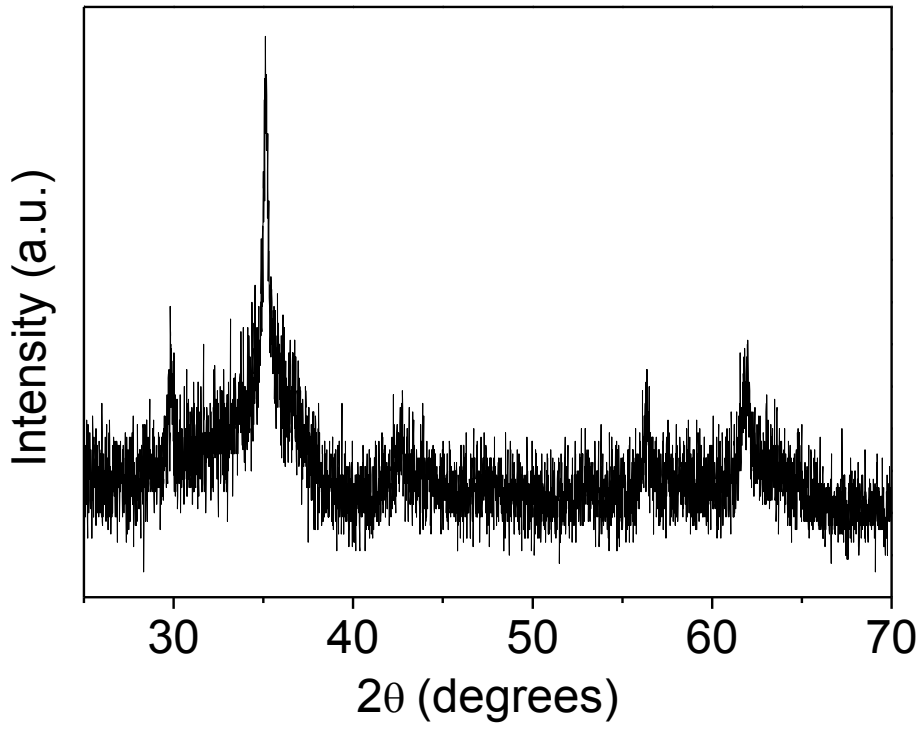

Figure 3.1: X-ray diffraction pattern for manganese ferrite nanoparticles.

The x-ray diffraction pattern of heated manganese ferrite sample consists of sharp peaks. It indicates that the crystallite size is now very large due to heating the as prepared sample at 800 ^{0}C for three hours in air.

3.1.2 Transmission Electron Microscopy

Figure 3.2 shows transmission electron micrograph of manganese ferrite nanoparticles. From this image we find that the particles are of different shapes and sizes. The average particle size is also seen close to average crystallite size.

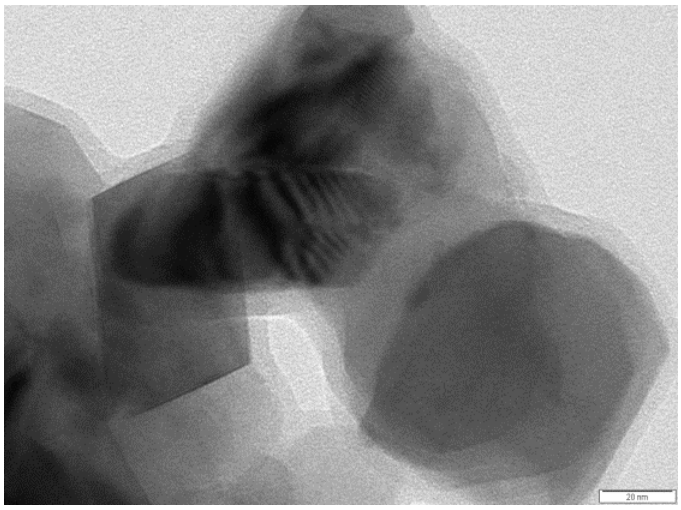

Figure 3.2: Transmission electron micrograph of manganese ferrite nanoparticles.

3.2 Magnetization

Magnetization of both samples as a function of applied magnetic field measurement at room temperature are measured using a vibrating sample magnetometer. The data are shown in Figures 3.3 and 3.4. From Figure 3.3 we see that the magnetization saturates and there is no hysteresis. These indicate that the as prepared sample of manganese ferrite nanoparticle is superparamagnetic in nature at room temperature. Figure 3.4 shows magnetization vs. applied magnetic field curve at room temperature for heated manganese ferrite sample. We see that the area of hysteresis loop is now no more zero. Also the value of magnetization for this sample is more than that of original sample. This increase in magnetization is due to increase in crystallite size caused by heating the sample at 800 ^{0}C for three hours in air.

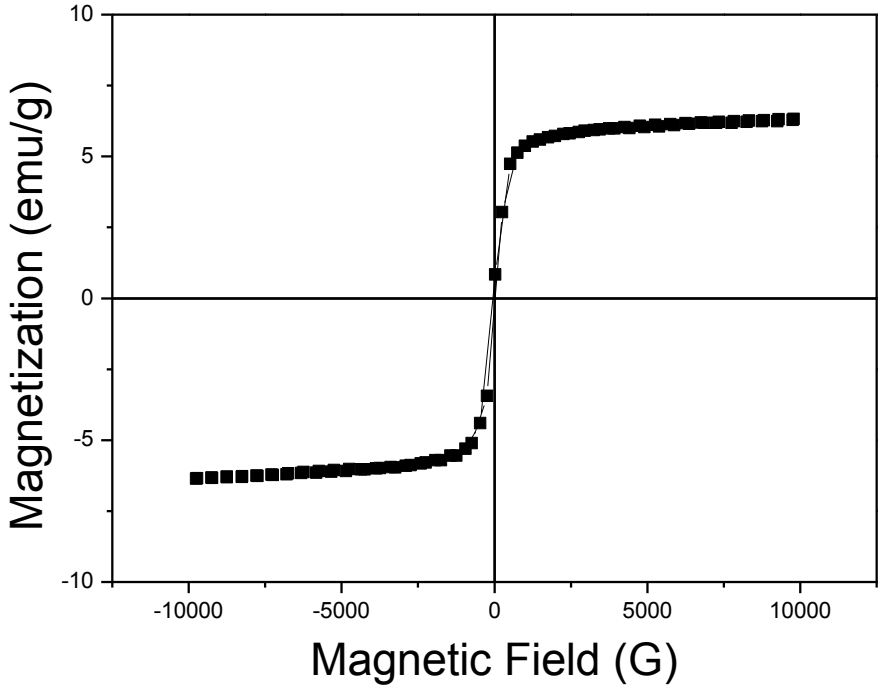

Figure 3.3: Magnetisation as a function of applied magnetic field for manganese ferrite nanoparticles.

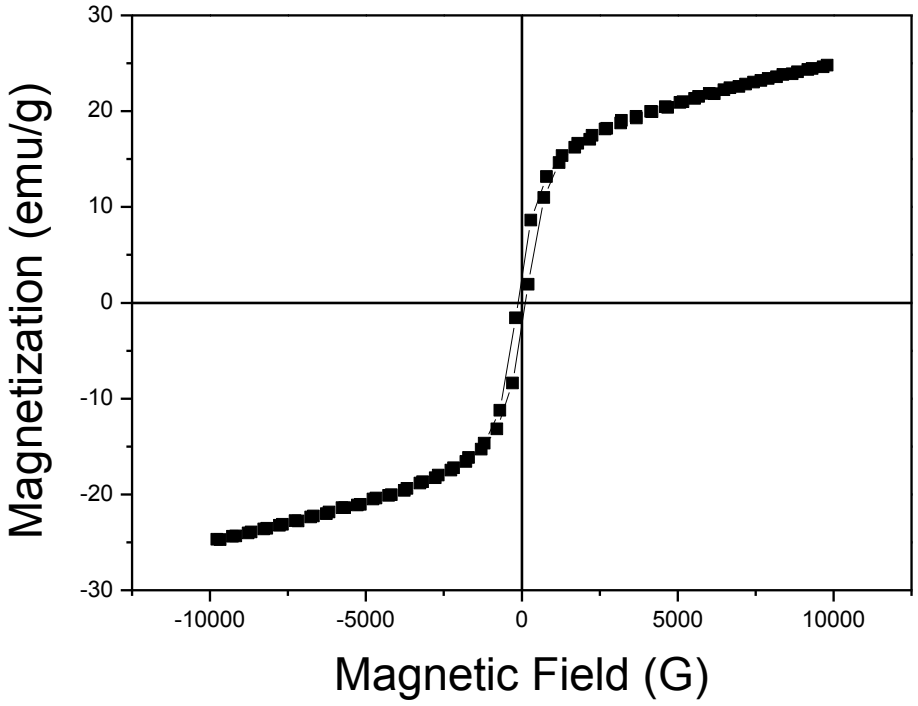

Figure 3.4: Magnetization as a function of applied magnetic field for heated manganese ferrite sample.

CHAPTER 4

CONCLUSION

In this work nanoparticles of manganese ferrite were synthesised by co-precipitation method. This samples is heated at 800 ^{0}C in air for three hours to prepare another sample of manganese ferrite. Samples are characterized by x-ray diffraction, transmission electron microscope and vibrating sample magnetometer. The as prepared sample is found to be superparamagnetic at room temperature. The behaviour of heated sample is not seen to be superparamagnetic due to much larger crystallite size. Also the magnetization of system increases with increase in crystallite size.

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