Synthesis and Characterization of Ferrite Nanoparticles

A project report submitted

in partial fulfillment of the requirements

for the degree of

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Physics

by

Jagriti Garg

(Roll no: 301404008)

Under the guidance of

Dr. S.D. Tiwari

SCHOOL OF PHYSICS AND MATERIALS SCIENCE

THAPAR UNIVERSITY

Patiala, Punjab-147004

India

July 2016

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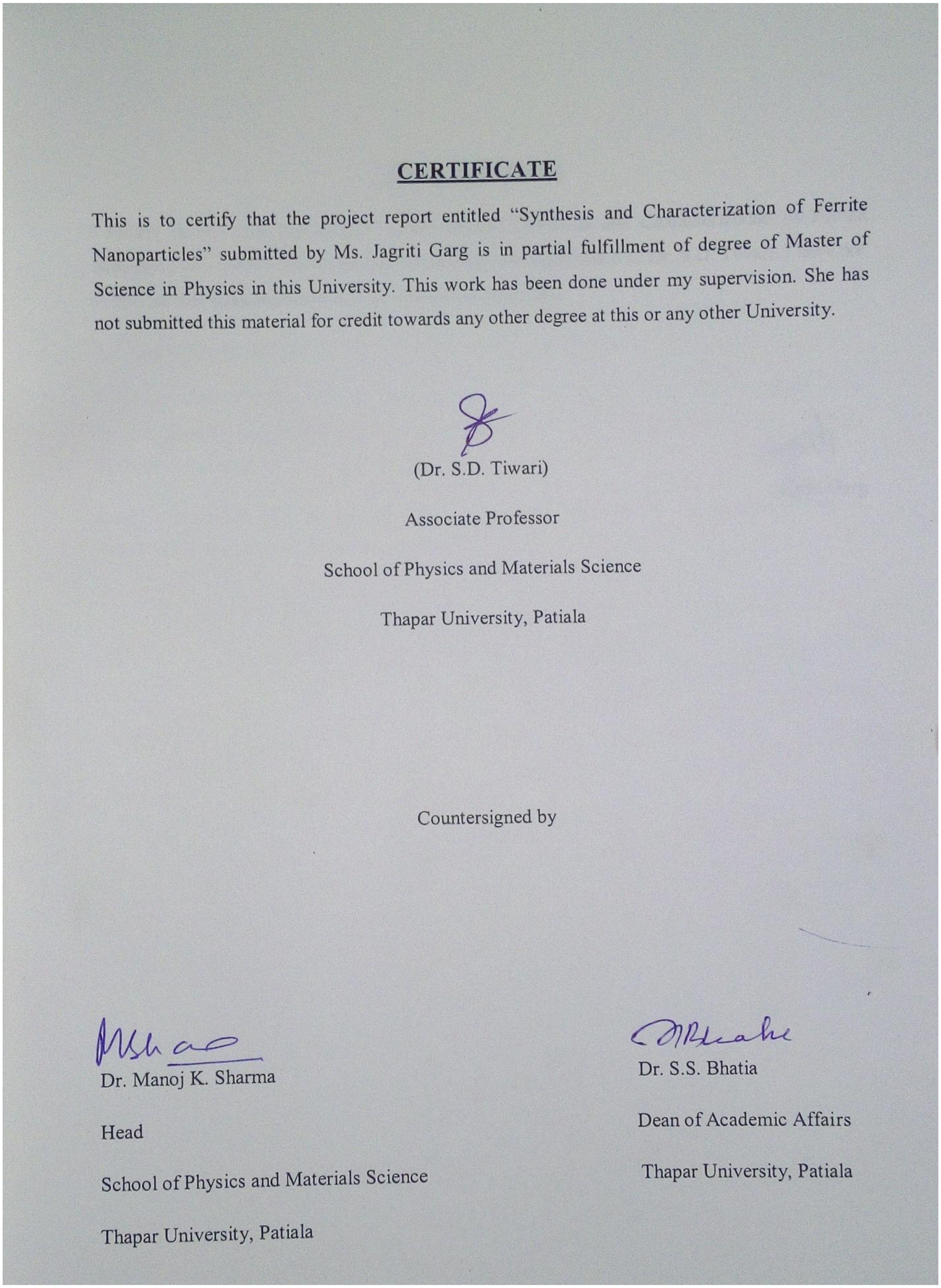


CERTIFICATE

This is to certify that the project report entitled "Synthesis and Characterization of Ferrite Nanoparticles" submitted by Ms. Jagriti Garg is in partial fulfillment of 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 Materials Science

Thapar University, Patiala

Countersigned by

Dr. Manoj K. Sharma

Head

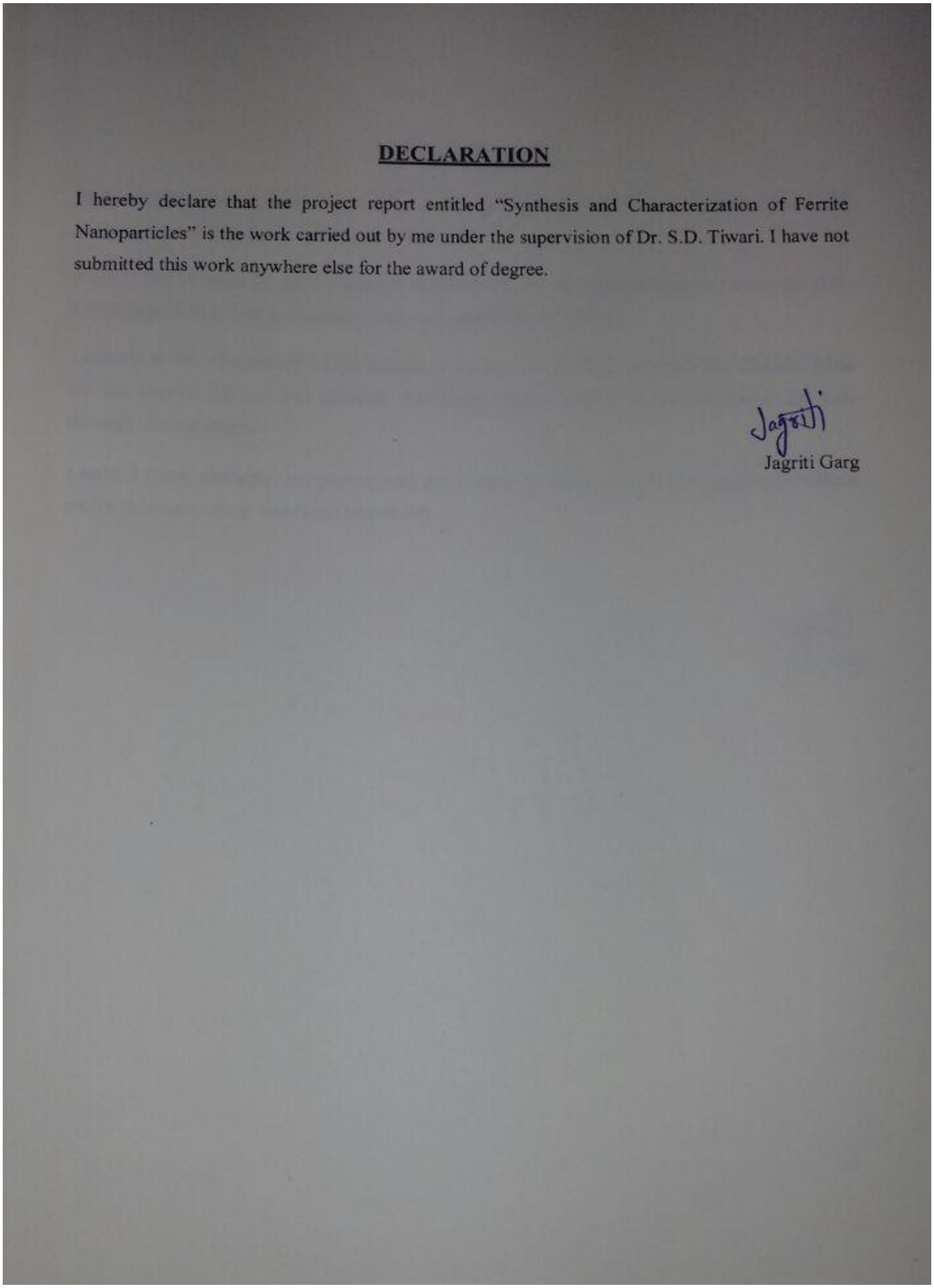
School of Physics and Materials Science

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 Characterization of 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 degree.

Jagriti

Jagriti Garg

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Jagriti Garg

Abstract

Nanoparticles of magnetite are synthesized by co-precipitation method at room temperature. This as prepared sample is heated at 800 ºC in air for three hours to prepare another sample of larger crystallite size. Structural and morphological characterizations of both samples are done by X-ray diffraction and transmission electron microscope. Magnetic behaviors of samples are studied using vibrating sample magnetometer. Observations on both samples are discussed and compared.

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Chapter 1

INTRODUCTION

1.1 Nanoparticles

Particles having size in nanometer range are called nanoparticles. These act as a bridge between bulk material and atomic structure. They have different properties in comparison to corresponding bulk material. Majority of researchers are working on different types of nanoparticles because of their unique behavior and important technological applications [1, 2].

1.2 Magnetic Materials

Magnetic materials show some response to external applied magnetic field. Behavior of these materials is very interesting. Magnetic materials also have many applications in our life [2]. On the basis of effect of external applied magnetic field all materials can be classified in following categories [3, 4].

1.2.1 Diamagnetism Diamagnetic materials always oppose the external applied magnetic field. When we apply the magnetic field, orbiting electrons produce magnetization in a direction opposite to the applied field. There will not be any magnetization in absence of external applied magnetic field. Examples of diamagnetic materials are bismuth, zinc, copper, silver, gold, diamond etc.

1.2.2 Paramagnetism In paramagnetism materials the ionic magnetic moments are oriented in random direction giving rise to zero magnetization. If an external magnetic field is applied then the magnetic moments try to align along the field direction. In presence of a very high strength magnetic field, all moments get aligned along the field direction. This gives maximum magnetization known as the saturation magnetization. The magnetization of the system becomes zero once the applied field is removed.

1.2.3 Ferromagnetism These materials are strongly attracted by applied magnetic field. All magnetic moments inside ferromagnetic materials are aligned in same direction because of a strong, but short range, ferromagnetic exchange interaction among them. This arrangement remains unchanged even if the applied field is removed. The effect of dipolar interaction, being long range in nature, among moments is also there. Both interactions simultaneously result in formation of randomly oriented domains. All moments in a domain are aligned in same direction. Above a transition temperature a given ferromagnetic material becomes paramagnetic. This transition temperature is called the Curie temperature. Examples of ferromagnetic materials are iron, nickel, cobalt etc.

1.2.4 Antiferromagnetism

In antiferromagnetic materials the neighboring moments of equal magnitude are aligned in opposite direction due to strong antiferromagnetic exchange interaction. Due to this these materials give net zero magnetization in absence of any external magnetic field near 0 K. Above a critical temperature an antiferromagnetic material becomes paramagnetic. This transition temperature is called the Neel temperature. Examples of antiferromagnetic materials are FeO, MnO, CoO, NiO etc.

1.2.5 Ferrimagnetism

In these materials the neighbouring moments of unequal magnitude are aligned in opposite direction. Due to this imbalance in magnitude of moments we get a net magnetization by these materails. Above a critical temperature these materials also become paramagnetic. Examples of ferrimagnetic materails are ferrites.

1.3 Ferrites

Ferrites are ceramic compounds consisting of ferric oxide and one or more other divalent metal oxides [5]. The general molecular formula of ferrite is $M^{2+} O Fe^{3+}_2 O_3$, where M represents divalent metal like Fe, Mn, Co, Ni etc. These materials are ferrimagnetic in nature. Ferrites are also chemically stable and show high electrical resistivity. Because of high chemical stability, these materials exhibit interesting optical, electrical, chemical and magnetic properties. Due to high resistivity of ferrites, these offer low eddy current, low dielectric losses etc. Due to low eddy current, ferrites have several important applications in area of electronics.

1.3 Literature review

Tang et al. (1991): Preparation of manganese ferrite particles using co-precipitation method followed by digestion process was discussed in detail [6].

Kim et al. (2001): Synthesis of iron oxide nanoparticles was done using co-precipitation method. Particle size was found to be about 60 nm. They also synthesized different samples under different conditions. Magnetic properties of samples were also studied [7].

Liu et al. (2004): They prepared ultrafine and well dispersed magnetic nanoparticles in aqueous solution using controlled co-precipitation method. Citrate ion was used to control the particle size [8].

Hong et al (2006): Microwave method was used to synthesize magnetic Fe_3O_4 nanoparticles. Samples under microwave irradiation have more complete crystalline structure than those aged for 7 days at room temperature. Magnetic measurements showed that samples under microwave irradiation had higher value of saturation magnetization [9].

Silva et al. (2007): Magnetite nanoparticles have been successfully synthesized in the presence of carrageenan polysaccharides. Carrageenan give rise to smaller particles and the average size depends on the concentration and nature of the polysaccharide used [10].

Shen et al. (2009): Fe_3O_4 nanoparticles were prepared from the waste water purification. It was found that pH and temperature greatly affect the mechanism [11].

Wu et al. (2011): They synthesized magnetite nanoparticles by ultrasonic chemical co-precipitation. Results showed that the magnetite particles have cubic structure with high level of crystallinity. Particles also exhibit superparamagnetism [12].

Petcharoena et al. (2012): Ammonium hydroxide was used as precipitating agent to synthesize magnetite. Cubic spinel structure of magnetite nanoparticles reflects from diffraction peaks. Saturation magnetization of nanoparticles was 60 emu/g [13].

Tajabadi et al. (2012): Effect of alkaline media concentration and temperature on magnetite synthesis was studied. Magnetite nanoparticles were prepared under N_2 atmosphere [14].

Hariani et al. (2013): Fe_3O_4 nanoparticles were synthesized by co-precipitation method to remove procion dye. Here divalent and trivalent iron salts with sodium hydroxide were used [15].

Dudchenko et al. (2014): Magnetite was prepared by potassium hydroxide and ammonium hydroxide in aqueous solution at 80 ºC. Magnetization measurements revealed that the saturation magnetization was less when potassium hydroxide was used for synthesis [16].

Vedernikova et al. (2015): High temperature structure transformation in magnetite nanoparticles was studied. The samples showed cubic inverse spinel structure with size ranging from 9 to 26 nm [17].

Almasy et al. (2015): They synthesized magnetite with wet milling and co-precipitation method. Magnetic behavior of samples were also studied [18].

Chapter 2

Experimental work

2.1 Synthesis

There are many physical and chemical methods for the preparation of nanoparticles. A chemical method to prepare sample is used [6]. Ferrite nanoparticles are synthesized by co-precipitation method. For this, iron chloride hexahydrate, ferrous sulphate heptahydrate, sodium hydroxide and distilled water are used. An aqueous solution containing ferric and ferrous ions in appropriate ratio is added drop wise to aqueous sodium hydroxide solution while continuous stirring till the pH of system reaches 12. The resulting precipitate is washed with water and dried in oven. The dried flakes are ground to get fine powder sample of Fe_3O_4. A part of this powder is heated at 800 ºC for three hours in air.

2.2 Characterization Techniques

2.2.1 X-ray Diffraction

X-ray diffraction is a non destructive analytical technique which gives the information about crystallographic structure of a sample [3]. A monochromatic beam of X-rays having wavelength λ is incident on the sample. Bragg's diffraction occurs at an angle θ when

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

where d is inter planer spacing and n is order of diffraction. Diffraction of x-ray beam is systematically shown in following figure.

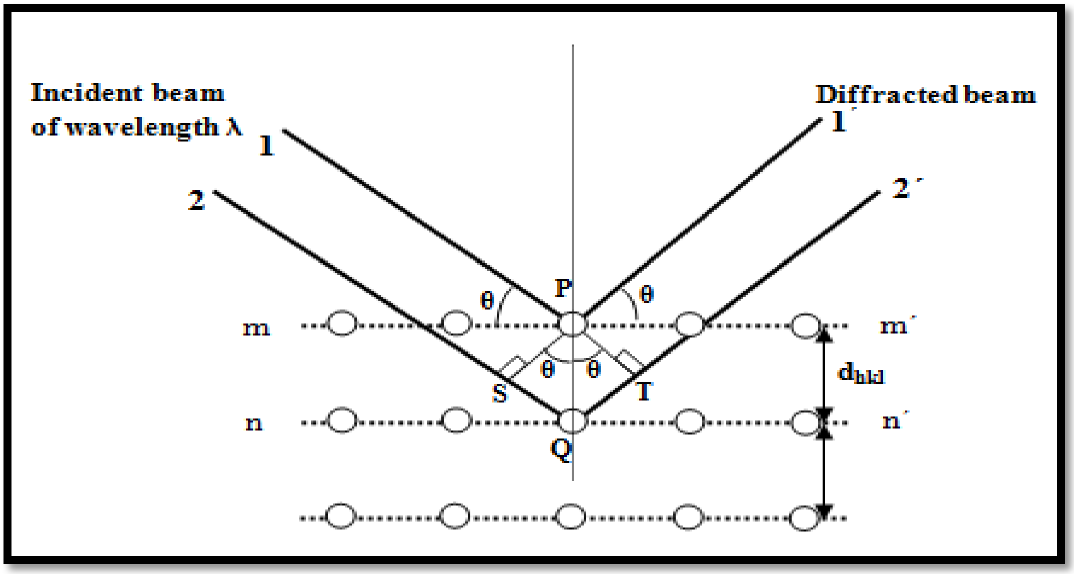

Figure 2.1: Diffraction of X-ray beam [19].

2.2.2 Transmission Electron Microscope

Transmission electron microscope is a powerful and important tool for material characterization. In this an energetic beam of electrons is allowed to pass through a thin specimen. The transmitted electron beam gives information about the crystal structure of the material. In this instrument several magnetic lenses, which are current carrying coils, are used for bending of the electron beam [20].

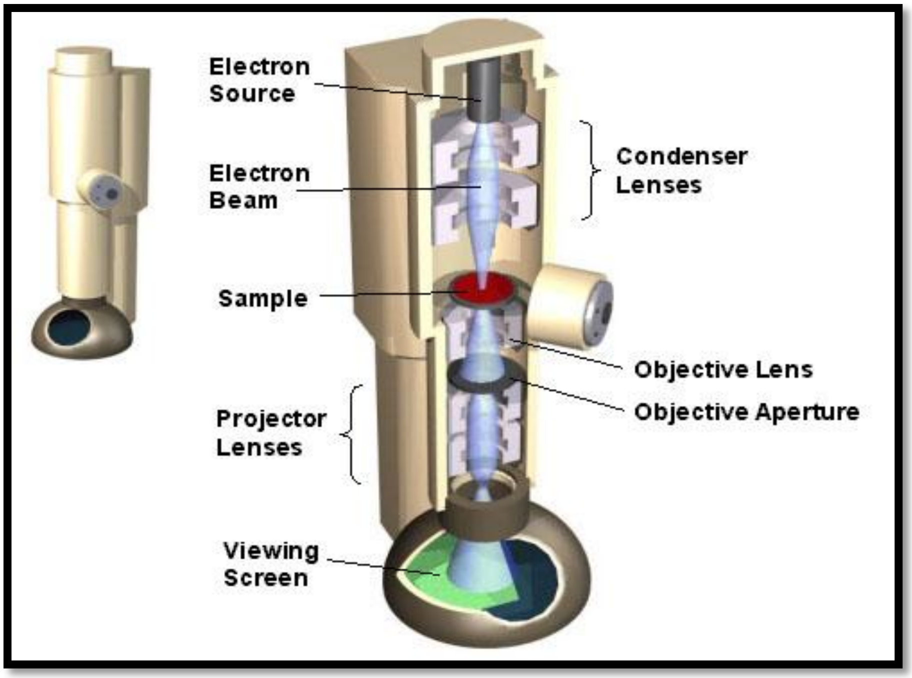

Figure 2.2: Transmission Electron Microscope [21].

2.2.3 Vibrating Sample Magnetometer

Vibrating Sample Magnetometer is used to measure magnetization of materials as a function of temperature, applied magnetic field and time [22]. In this instrument, the sample is placed in external applied magnetic field to get magnetized. Now this sample is allowed to vibrate in vertical direction inside a pick up coil. This causes an induced emf across the coil. This emf is directly proportional to the magnetization of sample. After appropriate calibration, the magnetization of sample can be measured as function of temperature, applied magnetic field or time.

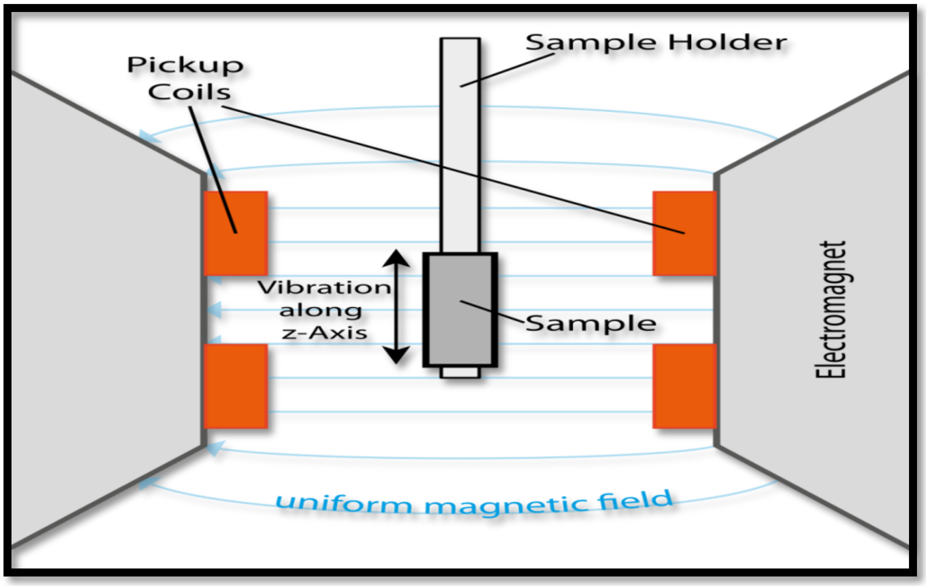

Figure 2.3: Vibrating Sample Magnetometer [22].

Chapter 3

Results and Discussion

3.1 Structural characterization

3.1.1 X-ray Diffraction

Room temperature x-ray diffraction pattern of synthesized powder sample is shown in Figure 3.1. From this pattern we find that the sample is single phase Fe_3O_4. The diffraction peaks are seen to be broadened. It indicates that the sample is nanocrystalline. The average crystallite size is calculated using Scherer formula. It turns out to be about 10 nm.

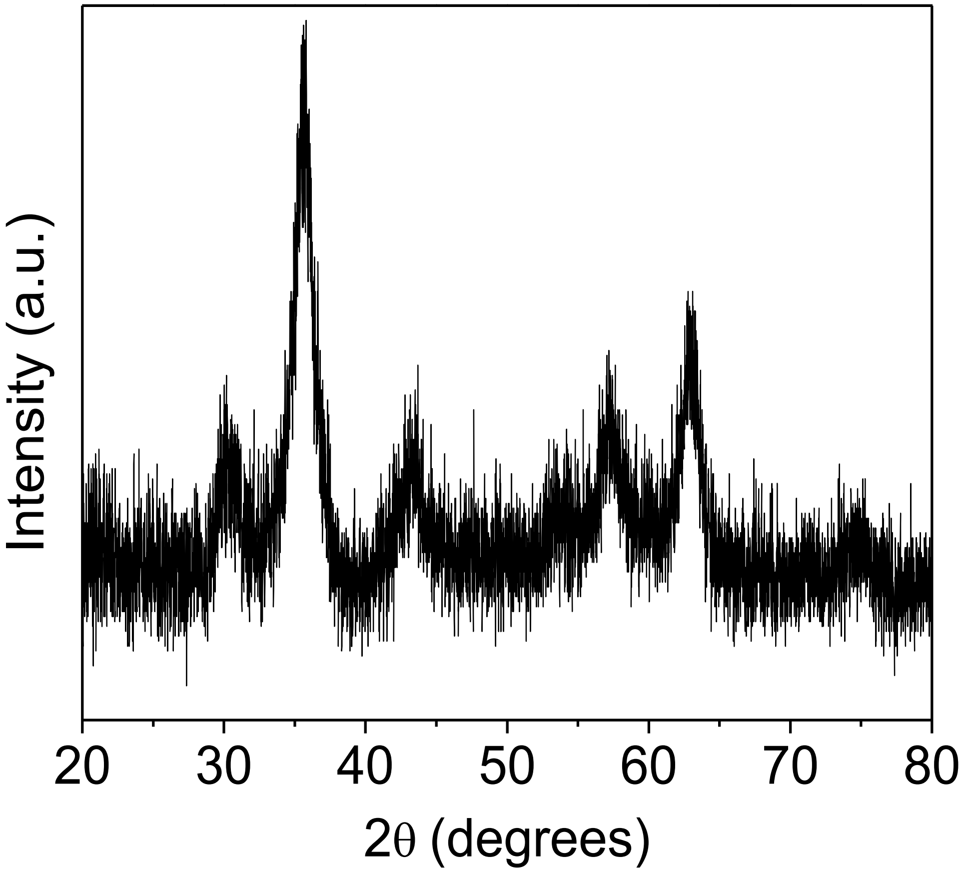

Figure 3.1: X-ray diffraction pattern of Fe_3O_4 nanoparticles.

One more sample having larger crystallite size is also prepared by heating the as prepared sample at 800 ºC for three hours in air. The diffraction peaks are found to be sharp.

3.1.2 Transmission Electron Microscopy

Particle size of synthesized Fe_3O_4 sample is analyzed with the help of transmission electron microscope. Figure 3.2 shows transmission electron micrograph of the sample. From this figure it is clear that the particles are of different shapes and sizes.

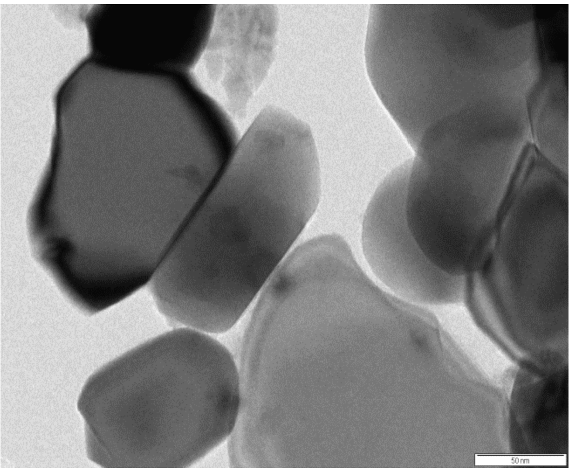

Figure 3.2: Transmission electron micrograph of Fe_3O_4 nanoparticles.

3.2 Magnetization

The magnetization as a function of applied magnetic field, for both samples, at room temperature is measured using a vibrating sample magnetometer. These measurements are shown in Figures 3.3 and 3.4. From Figure 3.3 it is seen that the magnetization saturates and area of M-H loop is zero. This indicates that the Fe_3O_4 nanoparticles sample is superparamagnetic in nature. Figure 3.4 shows room temperature M-H loop for heated Fe_3O_4 sample. Clearly, now the area of the loop is not zero. The value of magnetization has also increased. These are due to increase in crystallite size of the sample.

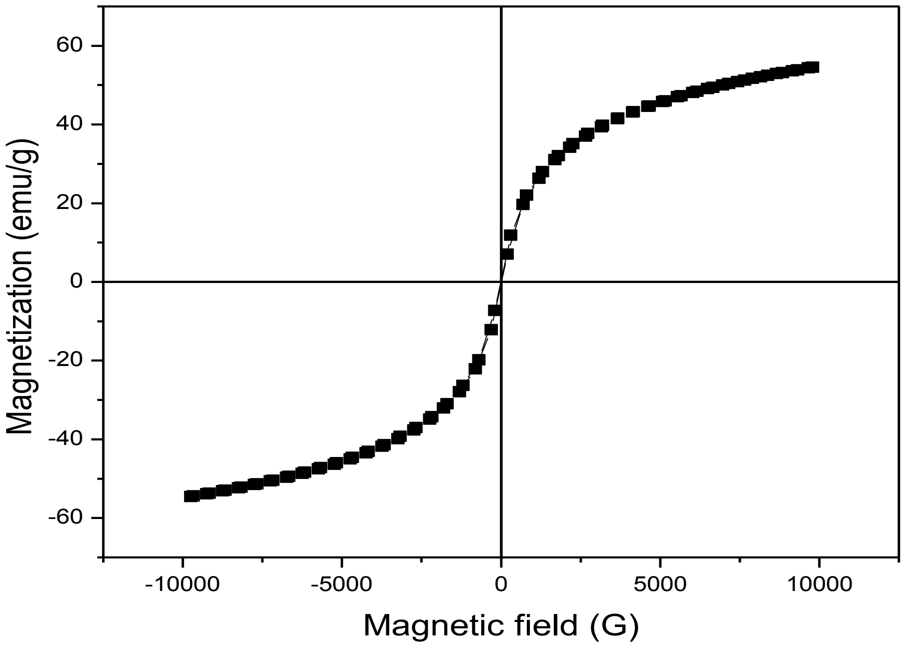

Figure 3.3: Magnetic field versus magnetization loop for Fe_3O_4 nanoparticles at room temperature.

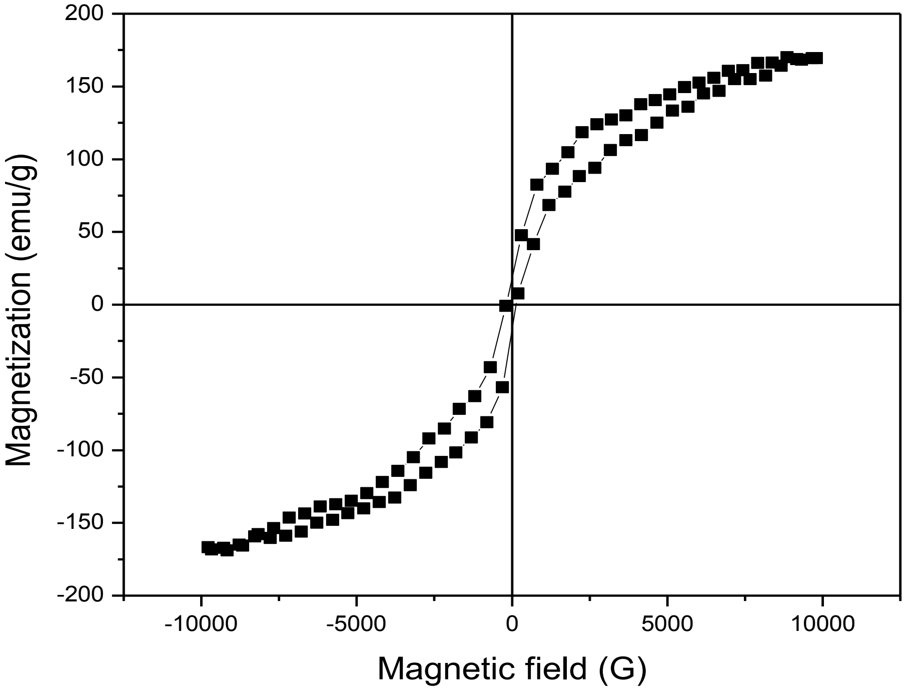

Figure 3.4: Magnetic field versus magnetization loop for heated Fe_3O_4 sample at room temperature.

Chapter 4

Conclusion

In this work, ferrite nanoparticles were synthesized by co-precipitation method. This sample was heated at 800 ^{0}C for three hours in air to prepare another ferrite sample having larger crystallite size. The average crystallite size and particle size for as prepared ferrite sample were found to be about 10 nm. Magnetic behavior of both samples were also studied and compared. The as prepared ferrite sample was found to be superparamagnetic at room temperature whereas the heated ferrite sample was not found to be superparamagnetic at room temperature due to larger crystallite size.

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