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M.S. Thesis In Physics

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**SYNTHESIS AND MAGNETIC CHARACTERIZATION OF $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$
NANOPARTICLES**

by

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Fatma GÖZÜAK

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APPROVAL PAGE

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Mustafa KUMRU
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This is to certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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August 2008

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ABSTRACT

We present a systematic investigation on the structural and magnetic properties of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by using two different methods. A series of Co doped zinc ferrite compounds with the formula $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ were prepared by using Hydrothermal Method ($x = 0.0, 0.3, 0.5, 0.7, 1.0$) and Microwave Combustion Method ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$), respectively.

Metal nitrates and chlorides are used as starting materials to synthesize $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles. XRD, FTIR, TEM and VSM were used for the structural, spectroscopic, morphological and magnetic investigation of products, respectively. The influence of Co content on the lattice parameter a , stretching vibration and magnetization of specimens was investigated. Magnetization measurements have shown that while the materials with high Zn substitution are superparamagnetic at room temperature and ferromagnetic at temperature lower than the blocking temperature, the materials with less Zn substitution are ferromagnetic below room temperature. Magnetizations and the coercivities of the samples decrease with the Zn substitution. The samples synthesized by hydrothermal method showed good magnetic properties than those synthesized by microwave combustion method.

Keywords: Magnetic Nanoparticles; Spinel Compounds; XRD; FTIR; TEM; VSM

**Co_xZn_{1-x}Fe₂O₄ NANOPARÇACIKLARIN SENTEZİ
VE
MANYETİK KARAKTERİZASYONU**

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ÖZ

Bu çalışmada iki farklı metod kullanılarak sentezlenen Co_xZn_{1-x}Fe₂O₄ nanoparçacıklarının yapısal ve manyetik özellikleri üzerine olan sistematik bir araştırma sunuyoruz. Burada, kobalt katkılanmış çinko ferrit bileşikler, Co_xZn_{1-x}Fe₂O₄, x = 0, 0.3, 0.5, 0.7, 1.0 katkılama oranlarında hidrotermal yöntemle, x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 katkılama oranlarında mikrodalga ile yanma yöntemi kullanılarak sentezlenmiştir.

Metal nitratlar ve metal klorürler başlangıç materyalleri olarak ayrı ayrı kullanılmışlardır. Ortaya çıkan ürünlerin yapısal, spektroskopik, morfolojik ve manyetik incelemeleri için XRD, FTIR, TEM ve VSM teknikleri kullanılmıştır. Co miktarının sentezlenen numunelerin; hücre parametresi, gerilme frekansı ve manyetizma üzerine etkisi araştırılmıştır. Manyetizma ölçümleri, yüksek miktarda Zn katkılanması sonucunda, üretilen maddenin oda sıcaklığında süperparamanyetik ve engelleme (blocking) sıcaklığının altındada ferromanyetik olduğunu, az miktarda Zn katkılanmasında ise oda sıcaklığının altında ferromanyetik olduğunu göstermiştir. Zn katkısı artırıldıkça, maddelerin manyetizasyonu ve koersiviteleri azalmıştır. Hidrotermal metotla sentezlenen örnekler mikrodalda yanma metodu ile sentezlenenlere göre daha iyi manyetik özellikler göstermiştir.

Anahtar Kelimeler: Manyetik Nanoparçacıklar, Spinel bileşikler, XRD, FTIR, TEM, VSM.

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CHAPTER 1

GENERAL BACKGROUND

1.1 INTRODUCTION

Nanotechnology can best be considered as the understanding and control of matter at dimensions of roughly 1–100 nm in size [1]. Studies in the synthesis and properties of nanosize materials has detonated over the past decade [2,3]. The unique size dependent properties of nanomaterials are different considerably from the properties of bulk phase materials. At the nanosize; electrical conductivity, mechanical strength and magnetic properties of materials are not the same as they are at bulk size. The physical and chemical properties of the nanomaterials change according to their size and shape or morphology. Hence, material scientists are trying to find simple and effective method to control the size and morphology of nanosize materials. One of the important properties of the nanoscale particles is that the smaller nanoparticle gets, the bigger the ratio of the surface to the volume gets [1].

The formation of domains and domain wall movement determines the behaviour of bulk magnetic materials. However, if the dimensions of the magnetic material is minimized below a critical length, the particles occur as single domains [4]. The formation of single domain particles and quantum size effects and the large surface area of the magnetic nanoparticles changes some of the magnetic properties and causes to exhibit the phenomenon of superparamagnetism [1]. In 1961, Néel suggested that small antiferromagnetic particles can exhibit superparamagnetism and poor ferromagnetism because of uncompensated spins in the

two lattices [5]. Shortly, thermal fluctuations or an applied field can change the magnetic moment of nanosize particle away from the easy axis. Every nanoparticle behaves like a paramagnetic atom. However the nanoparticles have got a well defined magnetic order but with a giant magnetic moment [6]. Explanation and controlling the superparamagnetic properties of nanosize particle is not important only for basic research such as explanation the quantum origins of magnetism. In addition, the explanation and controlling are crucial for practical applications such as high-density information storage, ferrofluid technology, magnetocaloric refrigeration, magnetically guided drug delivery, magnetic resonance imaging (MRI) contrast enhancement agents [7-10]. For instance, in biomedical praxises, magnetic nanosize particles must be superparamagnetic at room temperature in order to avoid agglomeration. However, the superparamagnetic phase must be canceled in high-density information storage otherwise superparamagnetic relaxation of the data bits will cause the magnetic moment of each nanoparticle to fluctuate and as a consequence all stored information will be lost [11].

Nowadays, the synthesis of magnetic nanomaterials has been a field of intense study. Specially, magnetic nanoparticles of spinel ferrites are attractive field in fundamental science, especially for addressing to the basic relationships between magnetic and their crystal chemistry and structure. The relation between the chemical composition, internal structure and physical properties of materials can be shown by courtesy of crystal chemistry. Spinel ferrite systems have got excellent oppornities for understanding and fine-tuning the superparamagnetic properties of nanoparticles by reason of the rich crystal chemistry [1]. To understand and control the magnetic (M_s , M_r , H_c ...i.e.) and mechanical (tensile stress, elongation...i.e.) properties at the atomic level, spinel ferrites (MFe_2O_4 ; $M = Mg, Zn, Co, Ni, Mn, \text{ etc.}$) are ideal magnetic systems [12]. The synthesis of nanocrystalline spinel ferrite has been investigated in latest years on account of their potential applications in high-density magnetic recording, microwave devices, magnetic fluids [13,14]. The other technologic convenient magnetic materials such as iron and metallic alloys have low electrical resistivity. These properties are harmful for applications at high frequencies. An example is the inductor cores in TV circuits. Low electrical resistivity of alloys allows induced currents to pass through the materials. Consequently, in this material heat is produced. This means wasted energy and serius problem. Whereas,

ferrites play this role much better at high frequencies by reason of high electrical resistivity. High permeability and time/temperature stability are important characteristic properties. These characteristics are occurred from microstructure of ferrites [15]. For instance, high permeability can be achieved only in materials by courtesy of large grain size and with residual porosity located at grain boundaries [16]. Former researches showed the grain size is one of the most important parameters which affects the magnetic properties of ferrites. Grain growth kinetics depend strongly on impurity content [17]. The dominated microstructural parameters are important for gaining high permeability. At the same time, the parameters are high sintered density, a large average grain size and clean and stress-free grain boundaries [18]. Little amounts of additives can greatly affect the magnetic and mechanical properties of ferrites [19]. These additives can be a kind of polymer, ethyl alcohol or another spinel ferrites which have different magnetic properties. In addition, ferrites can be used in high frequency and wide-band transformers, quality filter circuits, adjustable inductors, delay lines and other high-frequency electronic circuitry [1]. At the same time, it can be used as an absorbent material to remove sulfur-containing materials from hot-coal gas [20,21]. Moreover, according to other magnetic materials ferrites have more flexible magnetic and mechanical parameters [1]. The performances of spinel ferrites often relate to their stoichiometric ratio and microstructures [22]. An important reason in using ferrites is that they are cheaper than other magnetic metals and alloys [1].

The magnetism of spinel ferrites has been the topic of extensive research [23,24]. They have useful electrical and magnetic properties and applications in information storage systems, magnetic bulk cores, magnetic fluids, microwave absorbers and medical diagnostics. So, the scientists focus their attention on producing magnetic nanoparticles of spinel ferrites by using effective, easy and economic ways [1].

Generally, crystallographic structure of a spinel is a close-packed face-centered cubic array of anions with holes partly filled by cations [24]. The general spinel structure is AB_2O_4 . In this formula A and B denote divalent and trivalent cations. The spinel structure have two cation sites which are tetrahedral and octahedral sites [11]. A tetrahedral site lies in the center of a 4-atom cluster within the crystal (Fig.1.1).

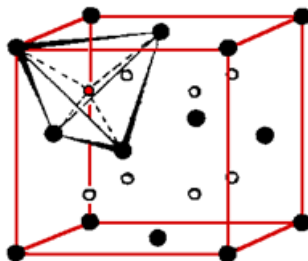


Figure 1.1 The tetrahedral position in the fcc lattice

An octahedral site is a space at the center of a cluster of six atoms that form an octahedron (Fig.1.2).

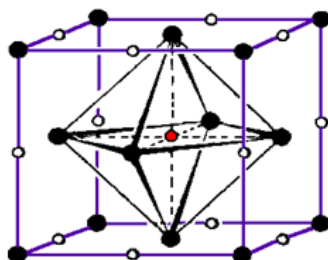


Figure 1.2 The octahedral site in an fcc lattice

There are eight A sites or tetrahedral sites and sixteen B sites or octahedral sites (Fig. 1.3).

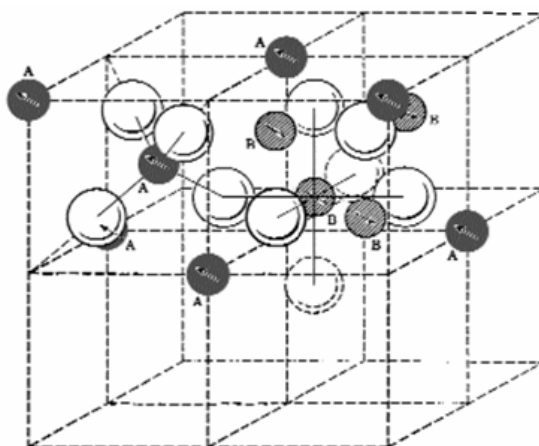


Figure 1.3 The crystal structure of spinel, AB₂O₄

Generally, spinel structure is divided into three types; normal, inverse and mixed spinels structure. When the A-sites are occupied by M^{2+} cations and the B-sites are occupied by Fe^{3+} cations, the ferrite is called a normal spinel (Fig.1.4). Cation distribution of bulk $ZnFe_2O_4$ can be given as an example.

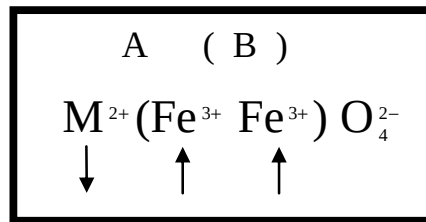


Figure 1.4 Cation distribution in normal spinel ferrites.

If the A-sites is fully filled by Fe^{3+} cations and B-sites are randomly filled by M^{2+} and Fe^{3+} cations, the structure is called inverse spinel sturcture (Fig.1.5). As an example magnetite Fe_3O_4 , $NiFe_2O_4$ and $CoFe_2O_4$ can be given. Cation distribution is showns as follows.

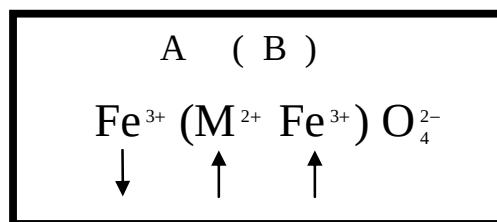


Figure 1.5 Cation distribution in inverse spinel ferrites.

In mixed spinels, M^{2+} and Fe^{3+} cations occupy on both octahedral and tetrahedral sites (Fig.1.6).

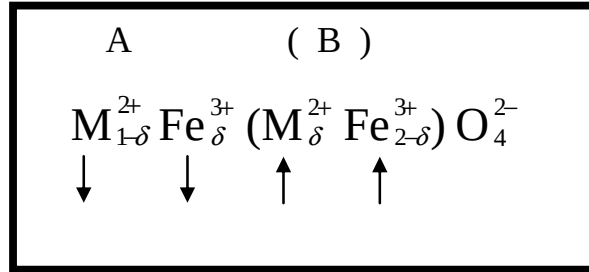


Figure 1.6 Cation distribution in mixed spinel ferrites.

In this formula, δ is the degree of inversion which is the ratio of the divalent M^{2+} ions at the octahedral site. Generally, in spinels the cation distribution has an intermediate inversion degree. This means that both sites contain a fraction of the M^{2+} and Fe^{3+} cations. Magnetically spinel ferrites shows ferrimagnetic ordering and the magnetic attitude of ferrites depends on the spinel structure. The magnetic moment of cation in tetrahedral and octahedral sites are parallel to each other. However, between the A and B sites the direction of the cations are aligned antiparallel with respect to one another. The number of the octahedral sites are twice as tetrahedral sites. Hence, there is a net moment of spins which causes ferrimagnetic ordering for the crystal. The choice of metal cation and the distribution of ions between the A and B sites play important role to get tunable magnetic system [25]. For example, the normal spinel $ZnFe_2O_4$ has antiferromagnetic ordering, however the inverse ferrite $NiFe_2O_4$ exhibit ferrimagnetic ordering below the transition temperature. In the same system, a magnetic transition from a antiferromagnetic to a ferromagnetic behavior (or vice versa) can be occur, if the spinel ferrite has diffrent ion distribution on tetrahedral and octahedral lattice sites [26]. O'Neill et al. reported that when $ZnFe_2O_4$ is annealed at high-temperature a partial site exchange occurs between tetrahedral Zn^{2+} and octahedral Fe^{3+} ions [27].

Generally, cation distribution depends on temperature in most of spinel oxides [28-31]. Because, the changes in temperature alter the size of the particles. Hence, while the grain size decreases, cation distribution changes from the normal spinel to the mixed spinel

type and the magnetization increases. The increase in magnetization with decreasing grain size is result of the increase in cation inversion parameter and hence the strength of superexchange interaction between Fe^{3+} ions in A and B-sites [32]. Magnetic properties of ferrites have been explained by Néel [33]. He suggested that magnetic moments of ferrites are a sum of the magnetic moments of individual sublattices. In the ferrosinels; cations in tetrahedral positions form sublattice A and cations in octahedral positions form B sublattice. In these sublattices, exchange interaction between electrons of ions possesses different value. Mostly, the strongest interaction is the interaction between magnetic ions of sublattices A and B (A-B interaction). A-A interaction is ten times lighter than A-B interaction. Lastly, B-B interaction is the weakest. In here dominant factor is A-B interaction and it leads to complete or partial (non-compensated) antiferromagnetism [33].

As an example; in the inverse spinel ferrites one half of Fe^{3+} cations are occupied in A-sites and another half in B-sites. The magnetic moments of Fe^{3+} cations are mutually compensated and the final magnetic moment of the ferrite is due to the magnetic moment of bivalent cation M^{2+} in the B sites.

1.2 CLASSIFICATION OF FERRITES

There are two types of magnetic materials, soft and hard. They are described according to their ability to be magnetized and demagnetized, not their ability to withstand penetration or abrasion. They can also be classified according to their coercive field strength into soft an hard materials [1].

$H_c < 10 \text{ A/cm}$: soft magnetic

$H_c > 300 \text{ A/cm}$: hard magnetic (permanent magnets);

1.2.1 Hard Ferrites

Hard materials are difficult to magnetize and demagnetize, so they are used as permanent magnets. In hard materials the hysteresis loop is large (high coercive field strength). Hard ferrite magnets have two different magnetic forms; isotropic and oriented. Isotropic magnets are easy to get desired shape, sintered and magnetized. These magnets have a modest magnetic field and the applications can be found in cycle dynamos and ring magnets. Oriented magnets are shaped under strong magnetic field and then sintered. They have very strong magnetic field and they are applied in loudspeakers, magnets of two wheelers like scooters, etc [34].

1.2.2 Soft Ferrites

Soft ferrites are ceramic electromagnetic materials. The colour of the ferrites is dark gray or black and they are mechanically very hard and brittle. The reason of the magnetic properties of soft ferrites is the interaction between metallic ions occupying particular positions relative to the oxygen ions in its spinel crystalline structure. Due to magnetic domain theory; these interaction form magnetic domains, which are microscopically magnetized regions within the material. When there is no magnetizing force, the magnetic domains are random and the net flux contribution is zero even though local domains are fully magnetized. When there is an external magnetic force, the magnetic domains arrange in the direction of the external magnetic force resulting in a large net magnetic flux contribution [35].

In recent years, spinel ferrite nanoparticles have been prepared using varied methods, such as coprecipitation, the reverse micelle method, microwave plasma synthesis, sol-gel method, ultrasound irradiation, laser pyrolysis techniques, freeze drying, thermal decomposition of organometallic and coordination compounds and hydrothermal methods.

In this work, $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles have been successfully synthesized through two different methods which are Hydrothermal and Microwave. XRD, FTIR, TEM and VSM were used for the structural, morphological and magnetic investigation of the

product. The average crystallite size, L , of the nanoparticles was estimated by Deby Scherrer equation from the X-ray peak broadening (full-width at half maximum, FWHM) of the most intense peak (3 1 1): $L = 0.9\lambda/\beta \cos\theta_B$, where λ is the wavelength of CuK_α (1.54059 Å), θ_B is the angle of Bragg diffraction, and $\beta = B - b$. B is the full width at half maximum (FWHM) and b represents the instrumental line broadening and Particle Size Analyzer. We have observed abnormal magnetic properties such as ‘S’-shape hysteresis loops and non-zero magnetic moments indicating superparamagnetism of the nanoparticles. Low temperature spin glass-like behavior of mainly superparamagnetic $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles at higher temperatures, that were grown by hydrothermal method as will be explained below.

CHAPTER 2

THEORY

2.1 FUNDAMENTALS OF MAGNETISM

All matter is composed of atoms, and atoms are composed of protons, neutrons and electrons. The protons and neutrons are located in the atom's nucleus and the electrons are in constant motion around the nucleus. The magnetic qualities of a matter basically arise from the electrons of the atom which have two kinds of electron movement, spin and orbital. Electrons carry a negative electrical charge and produce a magnetic field as they move through space. A magnetic field is produced whenever an electrical charge is in motion. The strength of this field is called the **magnetic moment** and each movement has a magnetic moment associated with it. The response of a material to a magnetic field (**H**) is characteristic of the magnetic induction or the flux density (**B**). The magnetization (**M**) is the effect that a material has upon the magnetic induction in a magnetic field. Thus, a general equation relating these three magnetic quantities, magnetic field, magnetic induction and magnetization, can be established by

$$B = \mu_0 (H + M) \quad (2.1)$$

$$B = \mu H \quad (2.2)$$

where μ_0 is a universal constant of permeability in a free space and μ is the permeability of a material [36]. Permeability is the degree of magnetization of a material that responds linearly to the field that is applied on the material. From equation (2.1), it is clear that $\mu_0 \mathbf{H}$ is the magnetic induction generated by the field alone and $\mu_0 \mathbf{M}$ is the additional magnetic induction contributed by a material.

The magnetic susceptibility (χ) is the ratio of magnetization to magnetic field.

$$\chi = M / H \quad (2.3)$$

Hence, from the above equations, the permeability and susceptibility of a material are correlated with this formula;

$$\mu = \mu_0 (1 + \chi) \quad (2.4)$$

The susceptibility is an important variable in characterization of magnetic properties of a material. The magnitude of the susceptibility and its temperature and field dependencies provide a measure of magnetic behavior of different types of magnetic materials [36,37].

2.2 CLASSES OF MAGNETIC MATERIALS

The origin of magnetism comes from the orbital and spin motions of electrons and how the electrons interact with one another. In most atoms, electron's spins are in opposite directions and occur in pairs (Fig.2.1). Therefore, when electrons are paired together like that, their opposite spins cause their magnetic fields to cancel each other. As a result, no net magnetic field exists. Alternately, materials with some unpaired electrons will have a net magnetic field and will react more to an external field.

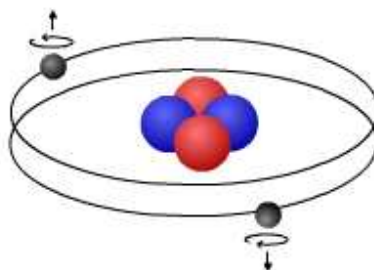


Figure 2.1 Representation of electrons' spins. [37].

The best way to identify the different types of magnetism is to describe how materials respond to an external magnetic field. Materials can react quite differently to the presence of an external magnetic field and this reaction is dependent on a number of factors, such as the atomic and molecular structure of the material, and the net magnetic field. Besides, this may be surprising to some, but all matter is magnetic. It's just that some materials are much more magnetic than others. The main difference is that in some materials there is no collective interaction of atomic magnetic moments, however in other materials there is a very strong interaction between atomic moments.

The magnetic behavior of materials can be grouped into the following six major groups:

1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism
4. Antiferromagnetism
5. Ferrimagnetism
6. Superparamagnetism

Materials in the first two groups are not magnetically ordered and they don't exhibit collective magnetic interactions. Materials in the remaining four groups show long-range magnetic order below a certain critical temperature. Generally, ferromagnetic and

ferrimagnetic materials are what we consider as being magnetic (ie., behaving like iron). The last four are so weakly magnetic that they are usually thought of as "nonmagnetic" [37,38].

2.2.1 Diamagnetism

All materials have diamagnetic properties and diamagnetism is their fundamental property. Generally, diamagnetism has usually very weak and negative susceptibility (Fig.2.2). Diamagnetic substances are made of atoms which have no net magnetic moments (ie., all the orbital shells are paired and there are no unpaired electrons). Diamagnetic properties come out from the realignment of the magnetic moment of the electrons under the influence of an external magnetic field. Thereupon, the material does not retain the magnetic properties when the external field is removed. In the periodic table, most of the elements, including copper, silver, and gold, are diamagnetic [37,38] .

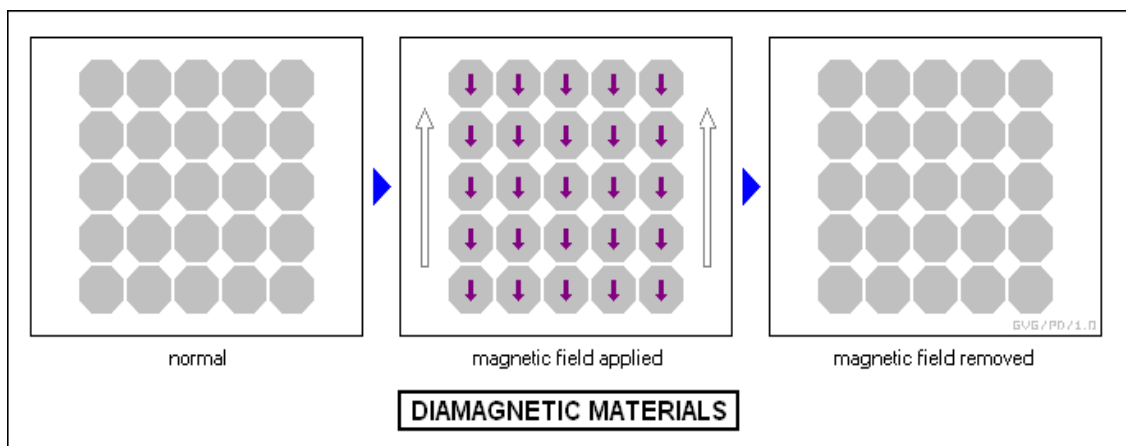


Figure 2.2 The directions of magnetic moments of diamagnetic atoms, when an external magnetic field is applied and then it is removed [39].

The susceptibility of diamagnetic material could be expressed by using a simple Langevin theory :

$$\chi = -\frac{NZe^2r^2}{mc^2} \quad (2.5)$$

where N is the number of atoms per unit volume Z is the number of electron, e is the charge of electron, r is the orbital radius and c is the speed of light [36].

Note that when the magnetic field is zero the magnetization will be zero. The other typical behavior of diamagnetic materials is that the susceptibility doesn't depend on temperature as shown in Fig.2.3. Most organic compounds and most materials are diamagnetic, including Cu, B, S, N₂ [38,36].

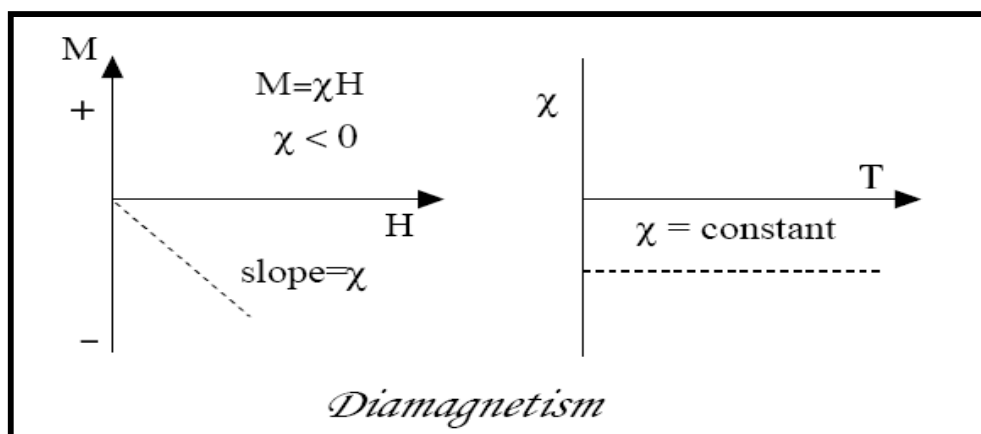


Figure 2.3 Magnetization vs. Magnetic Field and Susceptibility vs. Temperature graphs for Diamagnetic Materials [38].

2.2.2 Paramagnetism

In the simplest case, in a material composed atoms of an element with a magnetic moment, the atoms align themselves randomly, ensuring that their magnetic moments cancel out. However, some material hold nonzero magnetic moment. Because of unpaired electrons in partially filled orbitals, this class of materials have some of the atoms or ions in the material have a net magnetic moment.

If the material is placed across a magnetic field and the atoms are free to move, they will align with the magnetic field, resulting in a net positive magnetization and positive susceptibility. O_2 , NO, Cr and Mn are just several examples of the paramagnetic materials. Nevertheless, the individual magnetic moments do not act on each other magnetically, and like diamagnetism, when the field is removed the magnetization will be zero (Fig. 2.4). So many materials are like that known as "paramagnetic"; numerous rare earth elements have paramagnetic properties [38,39].

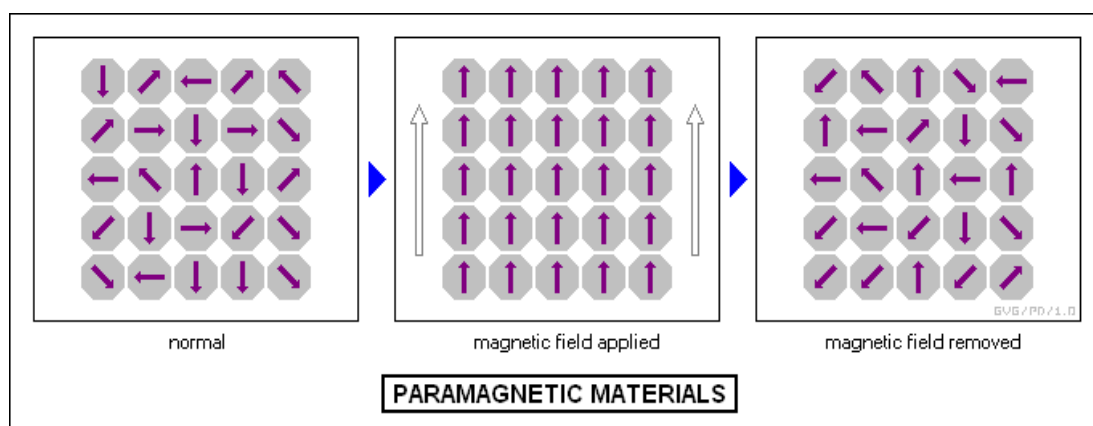


Figure 2.4 Direction of magnetic moments of paramagnetic atoms, when an external magnetic field is applied and then it is removed [39].

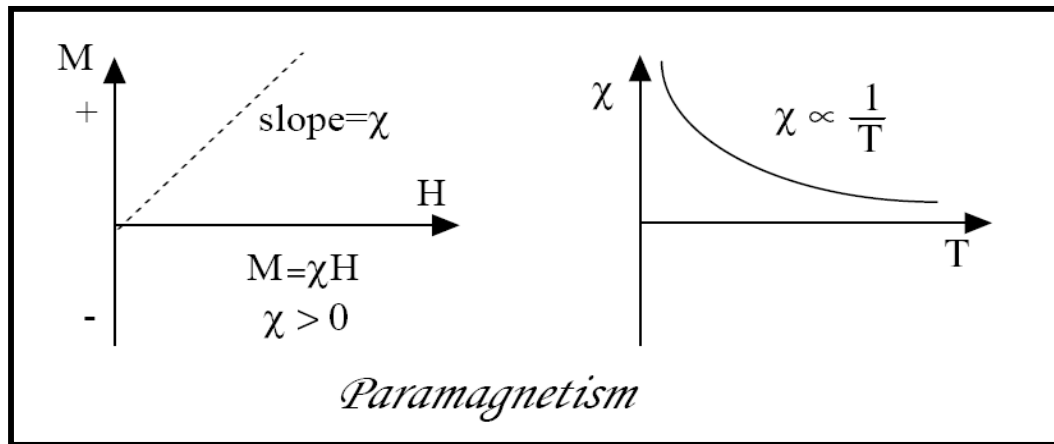


Figure 2.5 Magnetization vs. Magnetic Field and Susceptibility vs. Temperature graphs for Paramagnetic Materials [38] .

The susceptibility of a paramagnetic material is inversely proportional to temperature (see Fig.2.5), which is known as Curie law

$$\chi = C / T \quad (2.6)$$

where C is the Curie constant [36].

2.2.3 Ferromagnetism

Ferromagnetic materials are very different from diamagnetic and paramagnetic materials in many various ways. Ferromagnetic materials have a net magnetic moment as a result of some unpaired electrons in their atoms. Unlike paramagnetic materials, the atomic moments in these materials show very strong interactions. These interactions are produced by electronic exchange forces and result in the exchange coupling between neighboring moments. These exchange couplings causes the moments to align parallel with each other. Therefore, the ferromagnetic materials usually can gain a large magnetization in a relatively weak magnetic field, since all magnetic moments are easily aligned together. Exchange forces are very strong, equivalent to a field on the order of 1000 Tesla, or approximately a 100 million times the strength of the earth's field. Even if magnetic field is removed ferromagnetic materials exhibit parallel alignment of magnetic moments (Fig.2.6) resulting in large net magnetization [36,38].

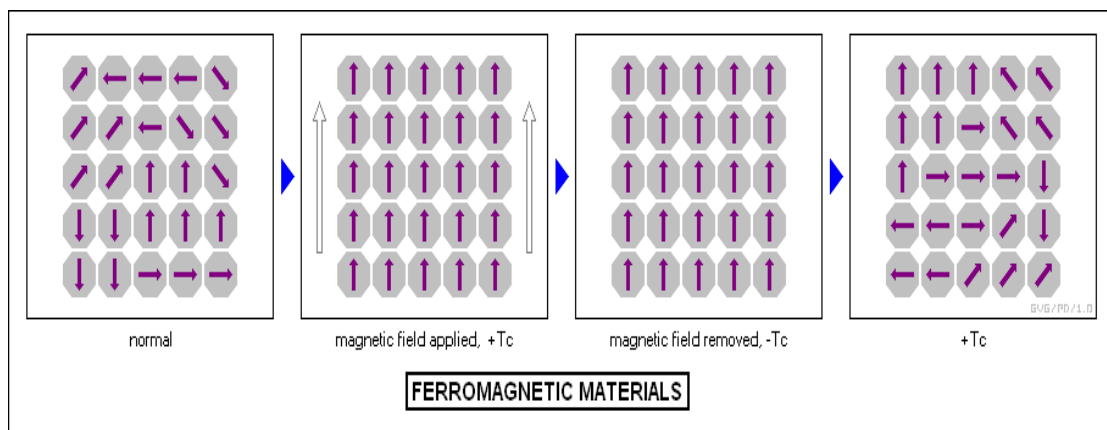


Figure 2.6 Direction of magnetic moments of ferromagnetic atoms, when an external magnetic field is applied and then it is removed [39].

Ferromagnetic materials get their strong magnetic properties due to the presence of magnetic domains. In these domains, great numbers of atom's moments are aligned parallel so that the magnetic force within the domain is strong. When the domains are nearly randomly organized, the net magnetic field for the part as a whole

will be zero and the ferromagnetic material will be in the unmagnetized state. When a magnetic field is applied, the domains become aligned parallel to produce a strong magnetization within the part. Some examples of ferromagnetic materials are iron, nickel, and cobalt [37].

2.2.3.1 Magnetic Domains

Ferromagnetic materials do not get their magnetic properties only from their magnetic moments of atoms. At the same time, small regions known as magnetic domains contribute to magnetization of the material. In each domain, all of the atomic moments are coupled together in a favorable direction. Magnetic domains can be detected by using Magnetic Force Microscopy (MFM) and images of the domains like the one shown below in Fig.2.7 ;

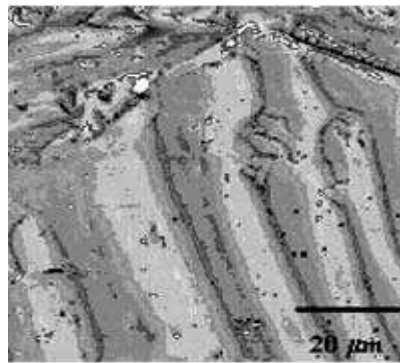


Figure 2.7 Magnetic Force Microscopy (MFM) image showing the magnetic domains in a piece of heat treated carbon steel [37].

Ferromagnetic materials obtain saturation magnetization in each of the domains without an external magnetic field being applied so they are said to be characterized by "spontaneous magnetization". The domains in ferromagnetic materials develop themselves and are randomly oriented relative to each other. So the bulk material may not show any signs of magnetism, although the domains are magnetically saturated.

When the magnetic domains within the material are aligned, ferromagnetic materials become magnetized. This can be provided by placing the material in a strong external magnetic field. Some or all of the domains of ferromagnetic materials can become aligned. When the more domains that are aligned, the magnetic field will be stronger in the material. When all of the domains are aligned, the material could be

called magnetically saturated. When a material is magnetically saturated, external magnetization force will not contribute to its internal magnetization level [37].

In addition, the susceptibility of a ferromagnetic material does not obtain the Curie law, but displayed a modified behavior defined by Curie-Weiss law .

$$\chi = C / (T - \theta) \quad (2.7)$$

where C is the Curie constant and θ is called Weiss constant. For ferromagnetic materials, the Weiss constant is exactly alike to the Curie temperature (T_C). At temperature below Curie temperature, the magnetic moments are well arranged, whereas above Curie temperature, material fails to obtain magnetic ordering and shows paramagnetic character. Fe, Co, and Ni are common ferromagnetic materials [36].

2.2.3.2 Curie Temperature

In spite of the fact that electronic exchange forces in ferromagnets are very strong, thermal energy finally overcomes the exchange forces and shows a randomizing effect. When heat is given to material again without the presence of a magnetic field, the material will turn back into domains again and lose its residual magnetic properties. This event occurs at a special temperature that is called the Curie temperature (T_C). Pierre Curie is the scientist who discovered the phenomenon in 1895. Below the Curie temperature, the ferromagnetic material structure is ordered and above the temperature, it is disordered. At the Curie temperature, the saturation magnetization will be zero.

In the mineral identification, the Curie temperature is also an distinctive property and is a diagnostic parameter. However, it is not foolproof identification because so many magnetic minerals, in principle, can have the same Curie temperature [39].

2.2.3.3 Hysteresis

In addition to the Curie temperature, ferromagnets can have residual memory of an applied magnetic field once and after it is removed. This event is called hysteresis and a graph of the variation of magnetization with magnetic field is called a hysteresis loop (Fig.2.8).

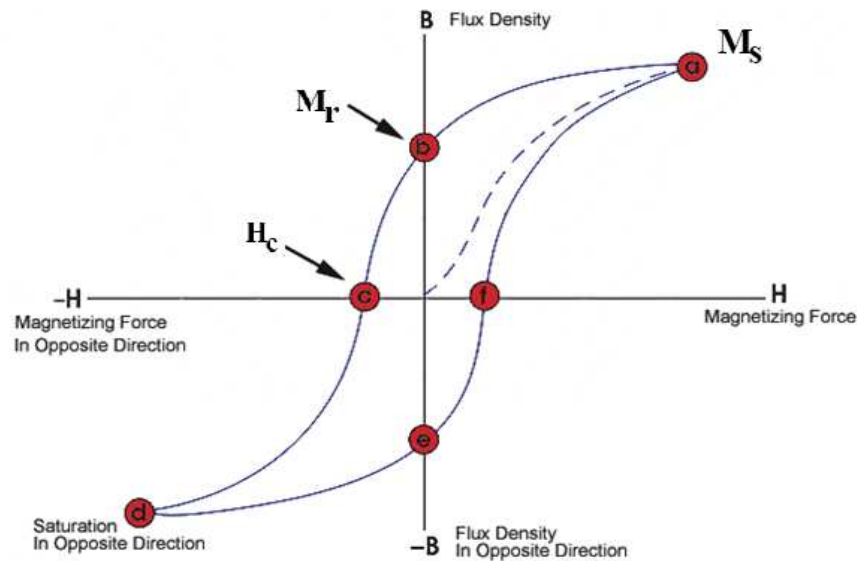


Figure 2.8 The Hysteresis Loop [37].

The loop is generated by measuring the magnetic flux of a ferromagnetic material while the magnetizing force is changed. A ferromagnetic material that has never been previously magnetized or has been thoroughly demagnetized will follow the dashed line as H is increased. As the line demonstrates, the greater the amount of current applied ($H+$), the stronger the magnetic field in the component ($B+$). At point "a" almost all of the magnetic domains are aligned and an additional increase in the magnetizing force will produce very little increase in magnetic flux. The material has reached the point of magnetic saturation. When H is reduced to zero, the curve will move from point "a" to point "b." At this point, it can be seen that some magnetic flux remains in the material even though the magnetizing force is zero. This is referred to as the point of retentivity on the graph and indicates the remanence or level of residual magnetism (M_r) in the material. (Some of the magnetic domains remain aligned but some have lost their alignment.) As the magnetizing force is reversed, the curve moves to point "c", where the flux has been reduced to zero. This is called the point of coercivity (H_c) on the curve. (The reversed magnetizing force has flipped enough of the domains so that the net flux within the material is zero.) The force required to remove the residual magnetism from the material is called the coercive force or coercivity of the material.

As the magnetizing force is increased in the negative direction, the material will again become magnetically saturated but in the opposite direction (point "d"). Reducing $\mathbf{H}$ to zero brings the curve to point "e." It will have a level of residual magnetism equal to that achieved in the other direction. Increasing $\mathbf{H}$ back in the positive direction will return $\mathbf{B}$ to zero. Notice that the curve did not return to the origin of the graph because some force is required to remove the residual magnetism. The curve will take a different path from point "f" back to the saturation point where it will complete the loop. From the hysteresis loop, a number of primary magnetic properties of a material can be determined.

1. Retentivity (M_r) - A measure of the residual flux density corresponding to the saturation induction of a magnetic material. In other words, it is a material's ability to retain a certain amount of residual magnetic field when the magnetizing force is removed after achieving saturation. (The value of $\mathbf{B}$ at point b on the hysteresis curve.)

2. Saturation Magnetization (M_s) - M_s is measured in the laboratory by applying a magnetic field of 1-2 Tesla. This field strength is usually sufficient to saturate most magnetic minerals. Upon reducing the field to zero, the magnetization does not go to zero but persists as a saturation remanence.

3. Coercive Force (H_c) - The amount of reverse magnetic field which must be applied to a magnetic material to make the magnetic flux return to zero (The value of $\mathbf{H}$ at point c on the hysteresis curve) [37].

2.2.4 Antiferromagnetism

Antiferromagnetic material aligns the magnetic moments in a way that all moments are antiparallel to each other (Fig.2.9), which is totally opposite to ferromagnetic ordering. Antiferromagnetic materials also have zero remanence, no hysteresis, but a small positive susceptibility that varies in a peculiar way with temperature. The clue to antiferromagnetism is the behavior of susceptibility above a critical temperature, called the Néel temperature (T_N). Above T_N , the susceptibility obeys the Curie- Weiss law for paramagnets but with a negative intercept indicating negative exchange interactions. The antiferromagnetic susceptibility is followed by

Curie-Weiss law with a negative θ as in equation (2.7). Common examples of materials with antiferromagnetic ordering include MnO, FeO, CoO and NiO [36].

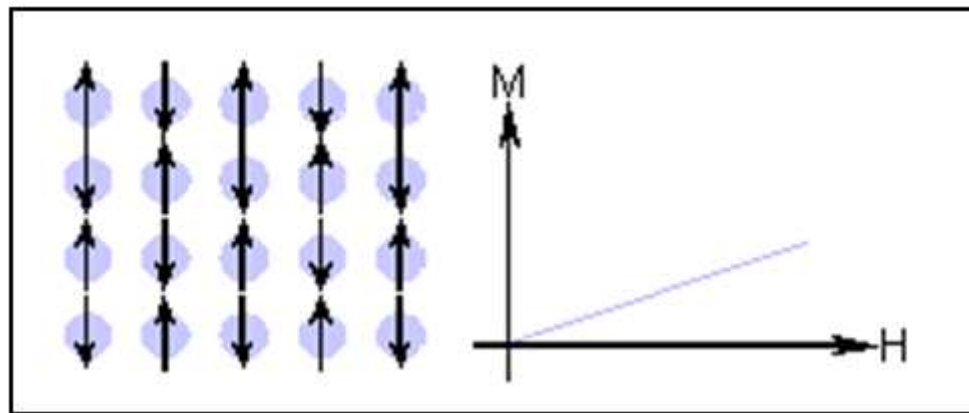


Figure 2.9 Graph of Magnetization vs. Magnetic Field for Antiferromagnetic Materials [40].

Slight deviations from ideal antiferromagnetism can exist if the anti-parallelism is not exact. If neighboring spins are slightly tilted ($<1^\circ$) or canted (Fig.2.10), a very small net magnetization can be produced.

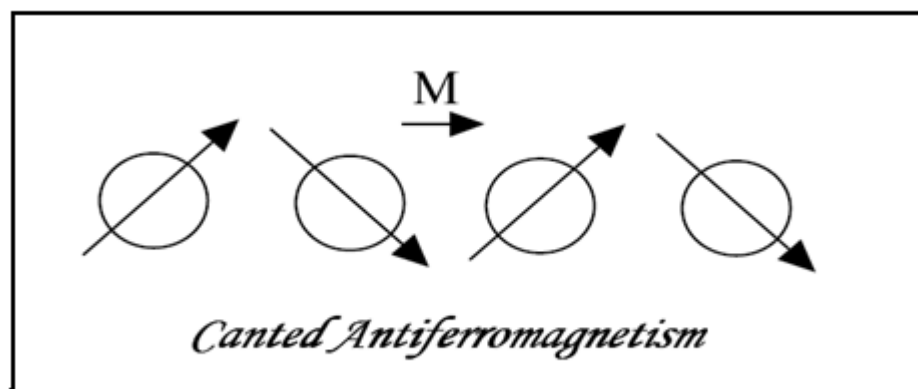


Figure 2.10 Canted spins [38].

This is called canted antiferromagnetism and hematite is a well known example. Canted antiferromagnets exhibit many of the typical magnetic characteristics of ferro- and ferrimagnets (e.g., hysteresis, remanence, Curie temperature) [38].

2.2.5 Ferrimagnetism

Ferrimagnetic material has the same antiparallel alignment of magnetic moments as an antiferromagnetic material does. However, the magnitude of magnetic moment in one direction differs from that of the opposite direction. As a result, a net magnetic moment remains in the absence of an external magnetic field. The susceptibility of a ferrimagnetic material obeys Curie-Weiss law and has a negative θ . Cubic spinel ferrites probably are the most common ferrimagnetic materials [36].

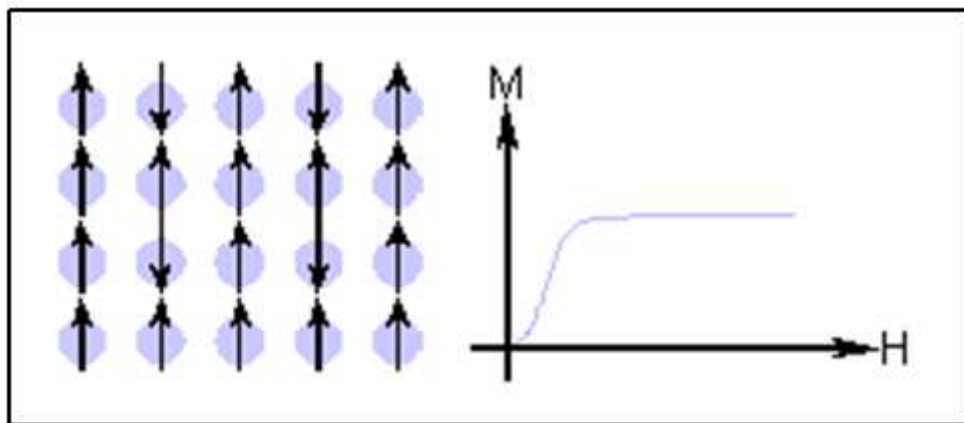


Figure 2.11 Graph of Magnetization vs. Magnetic Field for Ferrimagnetic Materials [40].

In ionic compounds, such as oxides, more complex forms of magnetic ordering can occur as a result of the crystal structure. One type of magnetic ordering is called ferrimagnetism. A simple representation of the magnetic spins in a ferrimagnetic oxide is shown above (Fig. 2.11).

Ferrimagnetism is therefore similar to ferromagnetism. It exhibits all the hallmarks of ferromagnetic behavior: spontaneous magnetization, Curie temperatures, hysteresis, and remanence. However, ferro- and ferrimagnets have very different magnetic ordering. Magnetite is a well-known ferrimagnetic material. Indeed, magnetite was considered a ferromagnet until Néel in the 1940's, provided the theoretical framework for understanding ferrimagnetism [38].

2.2.6 Superparamagnetism

It is well known that a bulk magnetic material is composed of magnetic domains. The magnetization inside each domain is uniform, but varies from domain to domain as they are separated by an interface layer known as the domain wall. By reducing the dimension of a magnetic material, the size of the domains is accordingly decreased and their structures may change in terms of domain wall width and wall structures. As far as the energy is concerned, when the size reaches a critical length, the magnetic material only possesses a 'single domain', since the energy cost for the formation of domain walls becomes energetically unfavorable, that is, the energy gain from the formation of domain walls is higher than the energy reduction by dividing the single domain into even smaller domains [36].

Size reduction in magnetic materials resulting in the formation of single-domain particles also gives rise to the phenomenon of superparamagnetism [41]. Superparamagnetic materials could exhibit both, ferromagnetic and paramagnetic behaviors under some particular conditions and occurs only when the material is composed of very small crystals (generally in the order of 1nm to 20 nm). Such materials exhibit ferromagnetic or ferrimagnetic properties in bulk, but will present a paramagnetic behavior when the material reaches the Curie temperature and the thermal energy is enough to align the magnetic dipoles and the resulting fluctuations in the direction of magnetization causes the induced magnetization go to zero [42-44].

The absence of saturation, remanent magnetization and coercivity at high temperature region in M-H curve indicates the superparamagnetic nature of the particles, which relax back their spins by rotation on removal of applied magnetic field so as to give a zero net magnetic moment. In this case even though the temperature is below the Curie temperature and the thermal energy is not sufficient to overcome the coupling force between neighboring atoms, the thermal energy is sufficient to change the direction of magnetization of the entire crystallite [45]. It is also known that fine particles are easy to activate thermally and overcome magnetic anisotropy. Nanoparticles lost their hysteresis property above blocking temperature and magnetic moments follow the same direction with applied magnetic field. So that the magnetic

moments do not have any remnant magnetization and a hysteresis loop to observe coercive field.

In other words, above the Curie point superparamagnetism occurs when thermal fluctuations or an applied field can easily move the magnetic moments of the nanoparticle away from the easy axis, the preferred crystallographic axes for the magnetic moment to point along. Each particle behaves like a paramagnetic atom, but with a giant magnetic moment, as there is still a well defined magnetic order in each nanoparticle [41,46]. The magnetic susceptibility of superparamagnetic materials is between that of ferromagnetic and paramagnetic materials [47].

2.3 EXCHANGE INTERACTION AND MAGNETIC ANISOTROPY

The theory of ferro- and ferrimagnetism is based on two mechanisms, magnetic anisotropy and exchange forces. These forces are so strong that these material are spontaneously magnetized, even in the absence of an applied field.

The dependence of magnetic properties on a preferred direction is called magnetic anisotropy. There are several different types of anisotropy:

1. Magnetocrystalline Anisotropy
2. Stress Anisotropy
3. Shape Anisotropy
4. Surface Anisotropy

Magnetic anisotropy strongly affects the shape of hysteresis loops and controls the coercivity and remanence. Anisotropy is also of considerable practical importance because it is exploited in the design of most magnetic materials of commercial importance [38] .

2.3.1 Magnetocrystalline Anisotropy

Magnetocrystalline anisotropy is an intrinsic property of a ferrimagnet, independent of grain size and shape and it can be most easily seen by measuring magnetization curves along different crystal directions. In another words, magnetocrystalline anisotropy is the energy necessary to deflect the magnetic moment

in a single crystal from the easy to the hard direction. The easy and hard directions arise from the interaction of the spin magnetic moment with the crystal lattice (spin-orbit coupling) and shows various symmetries.

The magnitude of the magnetocrystalline anisotropy determines the magnetization in response of the magnetic field. Large magnetocrystalline anisotropy energy of a magnetic material is called hard magnetic material and shows a large coercivity in hysteresis measurement. A magnetic material with small magnetocrystalline anisotropy energy is referred to soft magnetic material and has a small value of coercivity [36,38].

2.3.2 Stress Anisotropy

In addition to magnetocrystalline anisotropy, there is another effect related to spin-orbit coupling called magnetostriction. Magnetostriction arises from the strain dependence of the anisotropy constants. Upon magnetization, a previously demagnetized crystal experiences a strain that can be measured as a function of applied field along the principal crystallographic axes. A magnetic material will therefore change its dimension when magnetized.

The inverse affect, or the change of magnetization with stress also occurs. A uniaxial stress can produce a unique easy axis of magnetization if the stress is sufficient to overcome all other anisotropies [38].

2.3.3 Shape Anisotropy

The third type of anisotropy is due to the shape of a mineral grain. It is called Shape anisotropy and it is induced from magnetostatic energy which originates from the classical interactions between magnetic dipoles and is an extrinsic property. A magnetized body will produce magnetic charges or poles at the surface. This surface charge distribution, acting in isolation, is itself another source of a magnetic field, called the demagnetizing field. It is called the demagnetizing field because it acts in opposition to the magnetization that produces it.

For example, take a long thin needle shaped grain. The demagnetizing field will be less if the magnetization is along the long axis than if is along one of the short axes. This produces an easy axis of magnetization along the long axis. A sphere, on the other

hand, has no shape anisotropy. The magnitude of shape anisotropy is dependent on the saturation magnetization.

For magnetite, smaller than about 20 microns, shape anisotropy is the dominant form of anisotropy. In larger sized particles, shape anisotropy is less important than magnetocrystalline anisotropy [36,38].

2.3.4 Surface Anisotropy

Surface anisotropy is caused by the existence of a surface that represents a discontinuity for magnetic interactions. Such surface effects become more significant as the size of magnetic nanomaterials decrease, because the increasing numbers of atoms are on the surface layer of a particle. In order to take into account surface effect, Néel first proposed the surface anisotropy [48]. Recent theoretical studies indicated that spins at surface are dictated by the local crystal field, a lower coordination number and a broken magnetic exchange bond. Thus, surface spins are often canted and/or disordered [49-51] .

Judging from the surface effect is dependent on the size and often correlated to the nanoparticle size effect. Surface anisotropy generally leads the surface to be magnetically harder than the core of the particle [36].

2.4 SPINEL FERRITES

2.4.1 Spinel Structure

Spinel is an important class of mixed-metal oxides, which has the general chemical composition of AB_2O_4 . Normally A is a divalent atom of radius between 80 and 110pm, such as Mg, Fe, Mn, Zn, and Cu. And B is a trivalent atom of radius between 75 and 90pm, such as Ti, Fe, Al, and Co [52]. The crystal structure for many important magnetic oxides is based on spinel structure, which is named after the mineral spinel $MgAl_2O_4$ [36].

2.4.2 Magnetic Properties of Spinel Ferrites

Variation of the cation distribution between the A and B sites may lead to different magnetic properties even though the chemical composition may not change.

As far as the magnetic ordering in spinel ferrites is concerned, since the metal cations in spinel ferrites are mutually separated by larger oxygen anions, the direct interactions between cations are at least very weak. Magnetic properties of ferrites have been explained by Neel [53], who postulated that magnetic moments of ferrites are a sum of magnetic moments of individual sublattices. At the same time, an indirect exchange, so called superexchange interaction as originally proposed by Néel [54] becomes strong enough to order the magnetic moments.

In the ferros spinels these are: sublattice A consisting of cations in tetrahedral positions and sublattice B with cations in octahedral positions. The magnetic moments for all metal cations in A sites are orientated parallel with respect to each other and the magnetic moments for all cations in B sites are aligned parallel with one another as well. The magnetic moment orientation of cations between A and B sites, however, is antiparallel to each other in spinel ferrite. (in the figure above) As there are twice as many of B sites as A sites, a net magnetic moment results. Therefore, the magnetic structure of spinel ferrite is ferrimagnetic ordering. Exchange interaction between electrons of ions in these sublattices has different value. Usually interaction between magnetic ions of sublattices A and B (A–B interaction) is the strongest. A–A interaction is almost ten times weaker and B–B interaction is the weakest. The dominant A–B interaction leads to complete or partial (non-compensated) antiferromagnetism (ferrimagnetism) [53].

In addition, the superexchange interaction is also strongly dependent on the geometry of arrangement such as distance and angles of cations in A and B sites [36].

2.5 CHARACTERIZATION METHODS

2.5.1. Fourier Transform InfraRed (FTIR) Spectroscopy

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two

unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

Unknown materials can be identified by using FT-IR. At the same time, It can determine the quality or consistency of a sample and the amount of components in a mixture.

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis [55].

2.5.2. X-Ray Powder Diffractometry

The interaction of X-ray radiation with crystalline sample is governed by Bragg's law, which indicates a relationship among the diffraction angle (Bragg angle), x-ray wavelength, and interplanar spacing. According to Bragg, the x-ray diffraction can be visualized as x-rays reflecting from a series of crystallographic planes as shown in Fig.2.12. The path differences introduced between a pair of waves traveled through the neighboring crystallographic planes are determined by the interplanar spacing. As the total path difference is equal to $n\lambda$ (as n being an integer and λ being the wavelength), the constructive interference will occur and a group of diffraction peaks can be observed and give rise to x-ray patterns. The quantitative account of Bragg's law can be expressed as:

$$n\lambda = 2d \sin \theta \quad (2.7)$$

where d is the interplanar space, λ is the wavelength, and θ is the Bragg angle shown in Fig.2.12.

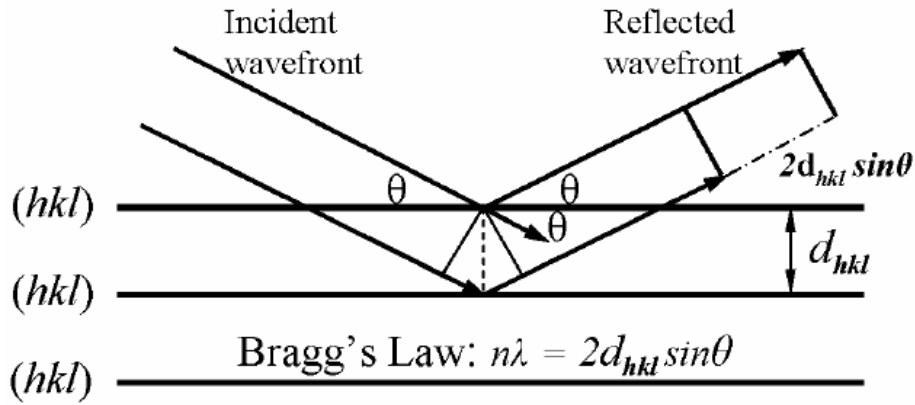


Figure 2.12 Geometrical illustrations of crystal planes and Bragg's law [36].

One of the more frequent applications of XRD analysis is to determine the crystalline size and lattice strain in nanocrystalline materials. The peak broadening in X-ray diffraction patterns for nanomaterials is the result of the finite size effect. For a finite size nanocrystal, the number of x-ray radiation reflected from successive lattice planes that add up to produce constructive or destructive interference becomes finite and therefore they can not reinforce or cancel out completely. Additionally, some other factors such as inhomogeneous lattice strains, variations in the lattice constants from one crystallite to another and structural faults can also yield the broadening of the diffraction peaks.

The size of nanomaterials can be derived from the peak broadening and calculated by using the Scherrer equation (2.8), provided that the nanocrystalline size is less than 100nm.

$$d = K\lambda / (\beta \cos \theta) \quad (2.8)$$

where d is the average crystalline dimension perpendicular to the reflecting phases, λ is the x-ray wavelength, θ is the Bragg angle, and β is the finite size broadening. K is a constant close to unity that is related both to the crystalline shape and to the way β is defined, i.e., either as the full width at half-maximum (FWHM) or as the integral breadth i.e. the ratio of the peak area to peak maximum [56-58].

2.5.3 Transmission Electron Microscopy (TEM)

Modern Transmission Electron Microscopy (TEM) has become a versatile and indispensable tool in exploration of nanomaterials. The complementary imaging, diffraction and spatial resolution microanalysis techniques in TEM provide the information on chemical composition, crystal structure, electronic and /or magnetic structure, size and shape of nanomaterials.

The versatility of transmission electron microscopy for the analysis of materials primarily originates from the various interactions when electron beams undergo within the solid specimen. For example, the transmitted electrons are used to visualize the internal crystal structure by bright and dark field imaging and orientation and identification of crystals in selected area electron diffractions. The elemental and chemical information can be simultaneously derived from the analysis of the characteristic x-ray radiations.

2.5.4. Vibrating Sample Magnetometry (VSM)

Many different magnetometers have been devised to measure and characterize magnetic materials. Of these, the VSM is by far the most common instrument because it offers the best combination of performance capabilities, and can accommodate a large range of samples with widely different properties.

The Vibrating Sample Magnetometer (VSM) is the basic instrument for characterizing magnetic materials. Since its invention some forty years ago, it has become the workhorse in both laboratory and production environments for measuring the basic magnetic properties of materials as a function of magnetic field and temperature. Computer control and automation was introduced to the VSM two decades ago, but otherwise there have been no major advancements in performance until quite recently.

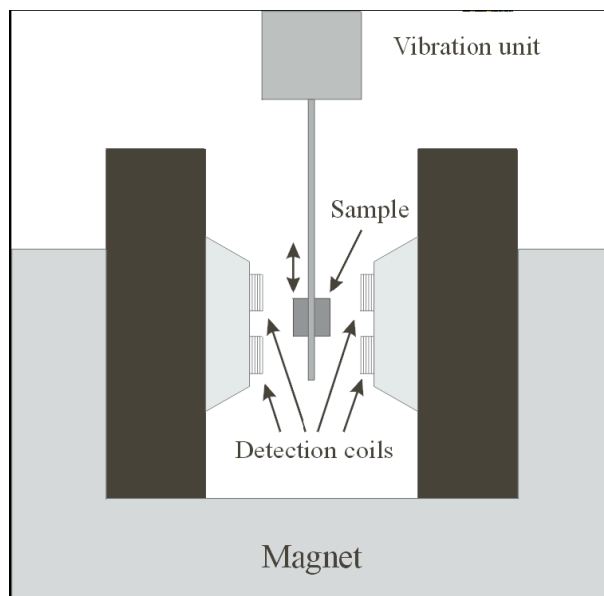


Figure 2.13 Schematic diagram of the VSM.

The VSM, shown schematically in Fig. 2.13, employs an electromagnet which provides the magnetizing field (DC), a vibrator mechanism to vibrate the sample in the magnetic field, and detection coils which generate the signal voltage due to the changing flux emanating from the vibrating sample. The output measurement displays the magnetic moment M as a function of the field H [59].

CHAPTER 3

EXPERIMENTAL

3.1 CHEMICAL SUBSTANCES

The following chemicals were used in the synthesis.

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH , $\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$, where n is approximately 8 to 9 (PEG-400), $\text{CH}_3\text{CH}_2\text{OH}$ (absolute ethanol), H_2O (distilled water), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ (Urea), KBr (Potassium bromide) are all analytical grade and used as received.

Spectroscopic grade of KBr was used for making IR pellets. It was dried at 80-100 °C for 2 hours before using. All chemicals used were from commercial sources (Merck and Fluka) and reagent grade quality.

3.2 INSTRUMENTATION

3.2.1. Fourier Transform Infrared (FTIR)

Mattson Satellite Infrared Spectrometer was used in the region 400- 4000 cm^{-1} . Spectra of solid samples were obtained from KBr pellets using KBr sample ratio = 100mg/3mg.

3.2.2. X-ray Powder Diffraction (XRD)

X-ray powder diffraction analysis was conducted on a Huber JSO-DEBYEFLEX 1001 Diffractometer (XRD) using $\text{Cu K}\alpha$ (operated at 40 kV and 35 mA).

3.2.3. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy, TEM. Transmission Electron Microscopy analysis was performed using a FEI Tecnai G2 Sphera Microscope. A drop of diluted sample in alcohol was dripped on the TEM grid. Following drying, the sample was loaded into a TEM column for analysis. Particle size distribution was obtained from three micrographs, counting a minimum of 150 particles.

3.2.4. Vibrating Sample Magnetometer (VSM)

Magnetic measurements were carried out with the Quantum Design Model 6000 Vibrating Sample Magnetometer (VSM) option for the Physical Property Measurement System (PPMS) and parameters like specific saturation magnetization (M_s), coercive force (H_c) and remanence (M_r) were evaluated.

3.2.5. Microwave Oven

Arçelik brand microwave oven with max 2.450 GHz was used.

3.2.6. Furnace

Carbolite brand furnace with max 1500 °C heat capacity was used.

3.2.7. Oven

Ecocell brand (with max 300 °C heat capacity) and Memmert mark was used.

3.2.8. pH-meter

ORION-model 210A pH meter was used.

3.2.9. Teflon Autoclave

Two types of teflon autoclaves which had 15 and 50 mL capacity were used.

3.3. EXPERIMENTAL PROCEDURE

3.3.1. Synthesis of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1.0$) by Using Hydrothermal Method

The chemical reagents used in the work are sodium hydroxide, ferric chloride, cobalt chloride and zinc chloride. All the reagents were used without further purification. In Table 3.1 stoichiometric amounts of metal chlorides (in gr) used for hydrothermal synthesis of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles are given. Amount of ferric chloride is constant (5.40 g) for each Co content. The $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ powders with x varying from 0 to 1 were elaborated by using a hydrothermal route: a precursor solution was prepared by aqueous dissolution of mix chlorate sources and sodium hydroxide under stirring for about 20 min, then 30 g PEG-400, heated and melted, was put to the mixture, followed by addition a certain amount of NaOH until the pH reached to 9.

After continuous stirring for an hour, a homogeneous solution could be obtained. The mixed solution was poured into a Teflon lined stainless-steel autoclave with a filling degree of 80%. The autoclave was kept at 150°C temperatures for 12-15 h, then cooled to room temperature naturally. The products were filtered and washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 90 °-100 °C for 12-24 h until the product was dried.

Table 3.1 Stoichiometric amounts of metal chlorides (in gr) used for the hydrothermal synthesis of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles.

x(number of moles)	$\text{CoCl}_2.6\text{H}_2\text{O}$	ZnCl_2	Product
0.0	0	1.363	ZnFe_2O_4
0.3	0.714	0.954	$\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$
0.5	1.19	0.682	$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$
0.7	1.666	0.409	$\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$
1.0	2.38	0	CoFe_2O_4

3.3.2. Synthesis of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) by Using Microwave Method

In an appropriate ratio, analytical grade of cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ at six different composition and constant amount of ferric nitrate (2.02) $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and urea (1g) were mixed to obtain precursor solutions, $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) (see Table 3.2). The crucible containing the solution was introduced into a microwave oven. Initially, the solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases (N_2 , NO_2 , CO_2). After the solution reaches to the point of spontaneous combustion, it begins to burn and releases lots of heat, vaporizes all the solution instantly and becomes solid burning at the temperature over 1000°C . The entire combustion process takes only 5 min to produce ferrite powders in a microwave oven.

Table 3.2 Stoichiometric amounts of metal nitrates with urea (in gr) used for the Microwave synthesis of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles .

X (number of moles)	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Product
0.0	0	0.744	ZnFe_2O_4
0.2	0.146	0.595	$\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$
0.4	0.291	0.446	$\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$
0.6	0.437	0.297	$\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$
0.8	0.582	0.150	$\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$
1.0	0.730	0	CoFe_2O_4

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1.0$) NANOPARTICLES SYNTHESIZED BY HYDROTHERMAL METHOD

4.1.1. FT-IR Measurements

Figure 4.1 shows the FTIR spectra of hydrothermally produced $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.3, 0.5, 0.7$ and 1.0). Two main broad metal-oxygen bands are seen in the IR spectra of all spinels, and ferrites in particular. The highest one, ν_1 , generally observed in the range $600\text{-}500\text{ cm}^{-1}$, corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, $\text{M}_{\text{tetra}}\leftrightarrow\text{O}$, whereas the ν_2 – lowest band, usually observed in the range $450\text{-}385\text{ cm}^{-1}$, is assigned to octahedral-metal stretching, $\text{M}_{\text{octa}}\leftrightarrow\text{O}$ [60,61]. Due to the limitation of our FTIR instrument below 400 cm^{-1} , ν_3 (328 cm^{-1}) and ν_4 (below 300 cm^{-1}) were not detected [62,63]. As it can be seen from the figure 4.1, the intensive broadband peak around 3450 cm^{-1} is due to $\text{O}\leftrightarrow\text{H}$ stretching vibration interacting through H bonds. The second one, observed at $\sim 1600\text{ cm}^{-1}$, is less intensive and the maximum of the third H_2O absorption band at $\sim 900\text{-}1000\text{ cm}^{-1}$ indicates strong hydrogen bridges [64]. The $\nu(\text{C}=\text{O})$ stretching vibration of the carboxylate group (CO_2) is observed around 1400 cm^{-1} and the band at 1050 cm^{-1} would state for nitrate ions traces.

The IR spectra (Fig. 4.1 (a)) for ZnFe_2O_4 has two significant absorption peaks at around 558 cm^{-1} which are ascribed to tetrahedral Zn^{2+} stretching and 425 cm^{-1} which can be

attributed to the vibration iron species (Fe^{+3}) in an octahedral site. The band was observed at 1095 cm^{-1} indicates C–O bond for pure ethylene glycol. This C–O bond shifts indicate that the O from C–O coordinates with Zn and Fe on the surface of zinc ferrite nanocrystals. The surfactant molecules in the adsorbed state are influenced by the field of solid-state surface. As a result, the characteristic bands shifted to a lower frequency region. In the previous reports [65–68], it has been accepted that the functional head groups of the surfactant have coordination bond or strong interaction with nanoparticles, and thus kinetically control the growth rates of various faces of crystals, which can control the morphology.

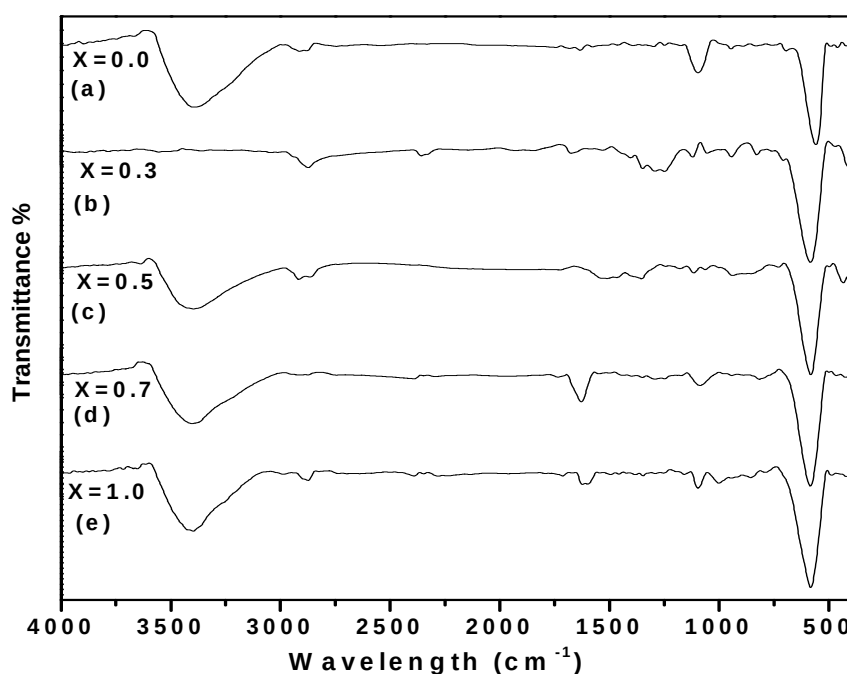


Figure 4.1 FTIR spectra of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ samples, synthesized by Hydrothermal Method, at different composition (a) $x=0.0$, (b) $x=0.3$, (c) $x=0.5$, (d) $x=0.7$, (e) $x=1.0$.

Fig. 4.1 (b) shows the IR spectrum of the sample for $x = 0.3$. In comparison with the IR spectrum shown in Fig. (a), the absorption at 3450 cm^{-1} disappeared, which was a consequence of complete evidence of the presence of moisture. At the same time, the bands at 1095 cm^{-1} and 558 cm^{-1} shift to 1244 cm^{-1} and 583 cm^{-1} .

IR spectrum for the samples obtained at $x = 0.5$ is shown in Fig. 4.1 (c); in comparison with IR bands at $x = 0.0$ and $x = 0.3$, the shift was observed in the

absorption band at 558 cm^{-1} to 586 cm^{-1} and little difference was observed with the other band at 583 cm^{-1} . In this spectrum, again the intensive broadband, around 3450 cm^{-1} is due to $\text{O}\leftrightarrow\text{H}$ stretching vibration interacting through H bonds was observed. In addition, the band observed at 1095 cm^{-1} decreases drastically in intensity and shifts to 1114 cm^{-1} .

In Fig. 4.1 (d) three main bands are found. First one is the intensive broadband which is due to $\text{O}\leftrightarrow\text{H}$ stretching vibration around 3450 cm^{-1} and the second band which indicates C–O bond is around 1090 cm^{-1} . The last band which are ascribed to tetrahedral stretching is at 590 cm^{-1} . Besides, extra fourth peak was observed at $\sim 1630\text{ cm}^{-1}$, is less intensive and the maximum of the third H_2O absorption band at $\sim 900\text{--}1000\text{ cm}^{-1}$ indicates strong hydrogen bridges.

Fig. 4.1 (e) is so similar to Fig. 4.1 (d) in several ways however there is little differences. Also, this spectrum have three main bands, the intensity of two bands which were observed at $\sim 1630\text{ cm}^{-1}$ and $\sim 1090\text{ cm}^{-1}$ decreased. The other broad band which are ascribed to tetrahedral stretching at 590 cm^{-1} slightly change to 593 cm^{-1} .

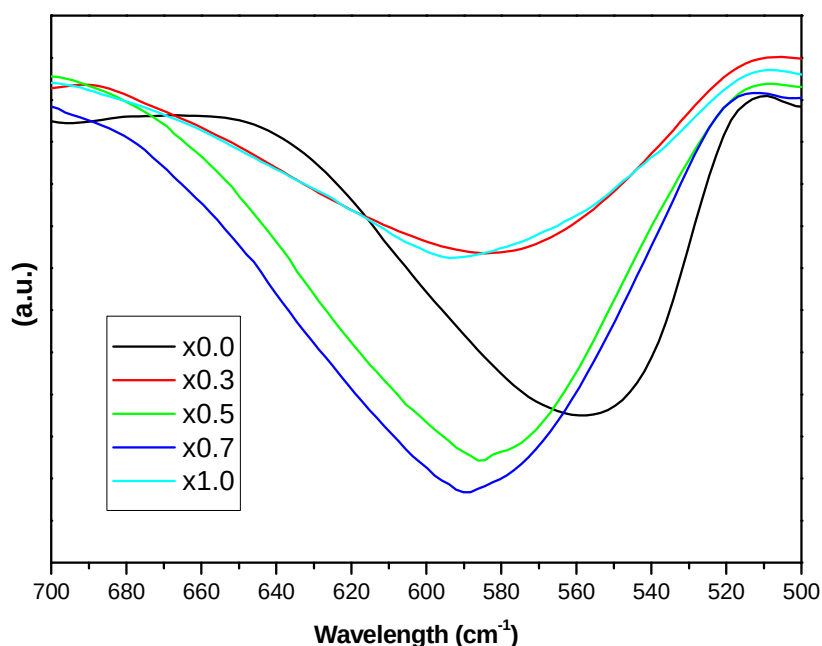


Figure 4.2 ν_1 band on IR spectra of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, synthesized by Hydrothermal Method, as a function of the Co content (x).

As a result, in the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ solid solutions, when Zn^{2+} are replaced by smaller Co^{2+} ions with lower atomic weight, the ν_1 vibration shifts to higher wavenumber, as shown in Fig. 4.2, Fig. 4.3 and Table 4.1.

Table 4.1 FTIR vibrations for $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ compounds synthesized by Hydrothermal Method.

Compound	ν_1 (cm^{-1})
ZnFe_2O_4	558
$\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$	579
$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	586
$\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$	590
CoFe_2O_4	593

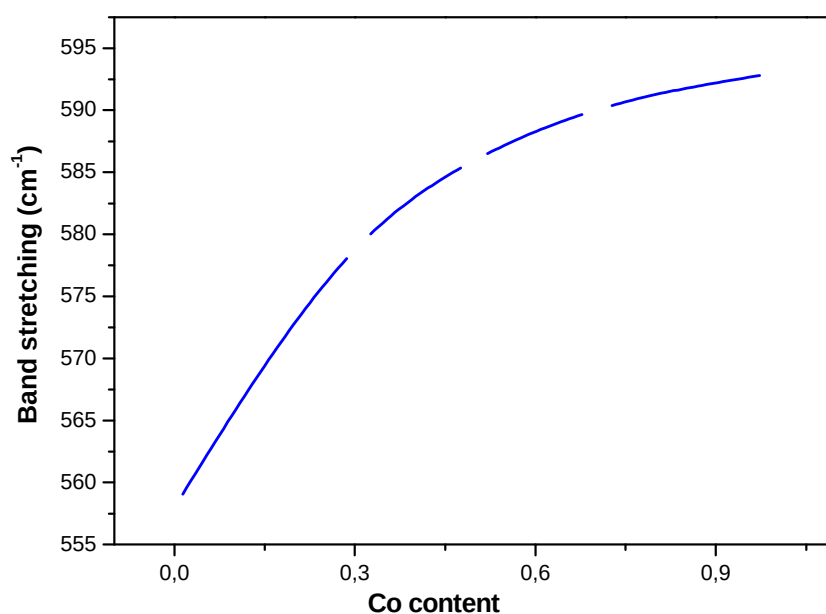


Figure 4.3 Variation of the band ν_1 with the composition (x) of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ synthesized by Hydrothermal Method.

4.1.2 X-ray Measurements

Figure 4.4 shows the XRD powder patterns of as hydrothermally synthesized $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles with $x = 0, 0.3, 0.5, 0.7,$ and 1.0 . All XRD peaks are correspondent with the JCPDS card no 89-1012 (ZnFe_2O_4) and 22-1086 (CoFe_2O_4). Analysis of the diffraction pattern confirms the formation of cubic spinel structure for all samples. The peaks indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0) and (5 3 3) planes of a cubic unit cell, correspond to cubic spinel structure.

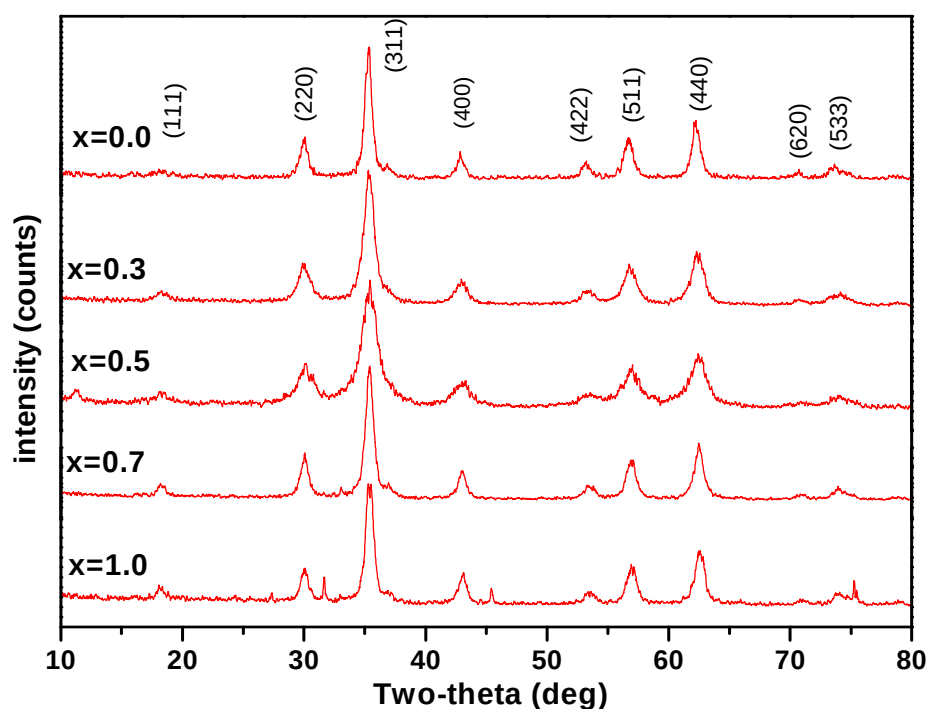


Figure 4.4 XRD powder patterns of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by Hydrothermal Method

The average crystallite diameter, L , was estimated by the Scherrer formula from the full-width at half maximum (FWHM) of the most intense peak (3 1 1). Though all

the samples were prepared under identical condition, the crystallite size was not the same for all Co concentrations. This was probably due to the preparation condition followed here which give rise to different rate of ferrite formation for different concentrations of cobalt, favoring the variation of crystallite size. As seen in Table 4.2, the particle size of the sample is found as 12 nm at $x = 0.0$ Co content and as 11.1 nm at $x = 1.0$ Co content. Firstly, the particle size of the samples is decreasing as Co additive is increasing up to the point ($x = 0.5$) then, the size starts to rise again.

Table 4.2 Particle size of samples, synthesized by Hydrothermal Method, for $x = 0.0, 0.3, 0.5, 0.7, 1.0$.

Sample	Particle Size (nm)
ZnFe_2O_4	12
$\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$	9.4
$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	8.1
$\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$	10.9
CoFe_2O_4	11.1

Table 4.3 Lattice Constants ($\text{\AA}$) of samples, synthesized by Hydrothermal Method for $x = 0.0, 0.3, 0.5, 0.7, 1.0$.

Sample	Lattice Constant ($\text{\AA}$)
ZnFe_2O_4	8,436
$\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$	8,424
$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	8,415
$\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$	8,405
CoFe_2O_4	8,390

Fig. 4.5 and Table 4.3 shows that the lattice constant decreases from 8.436 to 8.390 $\text{\AA}$ with increase in cobalt concentration. The lattice constant (a_0) was found to decrease with the increase in Co content, which suggested the formation of a

compositionally homogeneous solid solution. The lattice constant (a_0) was found to be within the range of the lattice constants of ZnFe_2O_4 and CoFe_2O_4 . This decrease could be also attributed to the substitution of the small sized Co cation for the large sized Zn cation. The lattice constant obtained for CoFe_2O_4 ($8.390\text{\AA}$) is close to the known of bulk CoFe_2O_4 ($8.395\text{\AA}$) [69]. The lattice constant for Co–Zn ferrites is very close to the values reported by Lee et al [70].

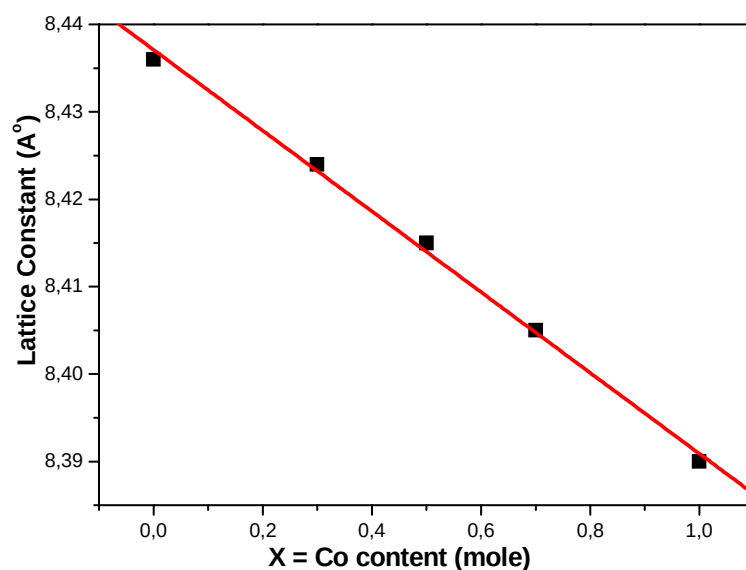
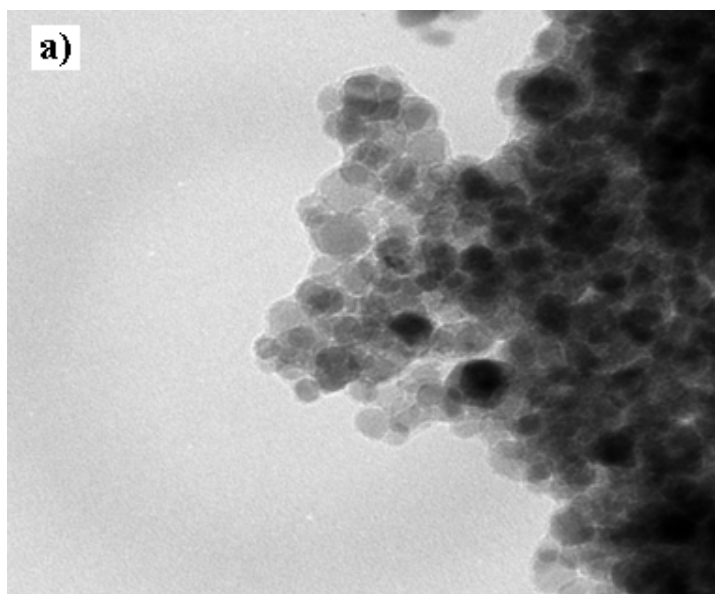


Figure 4.5 Variation of Lattice constant of hydrothermally synthesized $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles.

4.1.3 TEM Measurements

Fig. 4.6 shows TEM images of products $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ obtained at different Co contents. Particles are strongly aggregated despite sonication. It has been reported that PEG can increase the attraction among the polymer chains by coordination and cause the aggregation of nanoparticles (due to the rapid growth of nucleation) to larger diameter [65,71]. This may help to explain the observed aggregation.

TEM micrograph of as-synthesized zinc ferrite (ZnFe_2O_4) nanoparticles is given in Fig. 4.6.(a). Particles have spherical morphology and their size vary in the range of 7–21 nm, with almost a normal distribution centering around 13 nm. Average particle size is calculated as 12 ± 3 nm from the TEM micrographs by counting a minimum of 150 nanoparticles.



In Fig. 4.6 (b), we can see that the size of $\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles are homogeneously distributed. The magnitude of the nanoparticles change in the range of 7-10 nm and the shape of product is mainly spherical and some tend to form quasi spherical particles. Also in this sample PEG prevent to the aggregation of the nanoparticles.

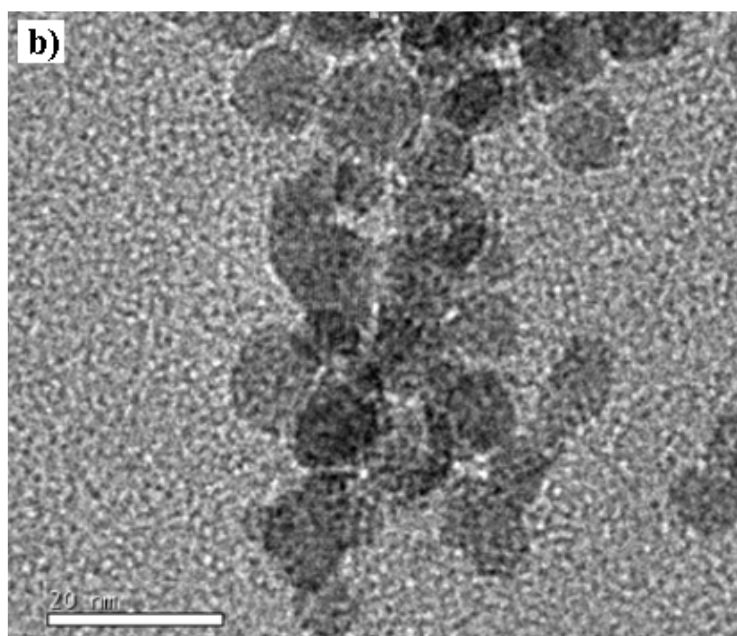


Figure 4.6 TEM micrograph of; a) ZnFe_2O_4 , b) $\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ synthesized by Hydrothermal Method

In Fig. 4.7 (c) the TEM micrograph of the sample $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ is given. Even then the micrograph shows distorted spherical particles with a particle size distribution of 5-10 nm. The residual part of decomposed PEG can also be seen in the micrograph.

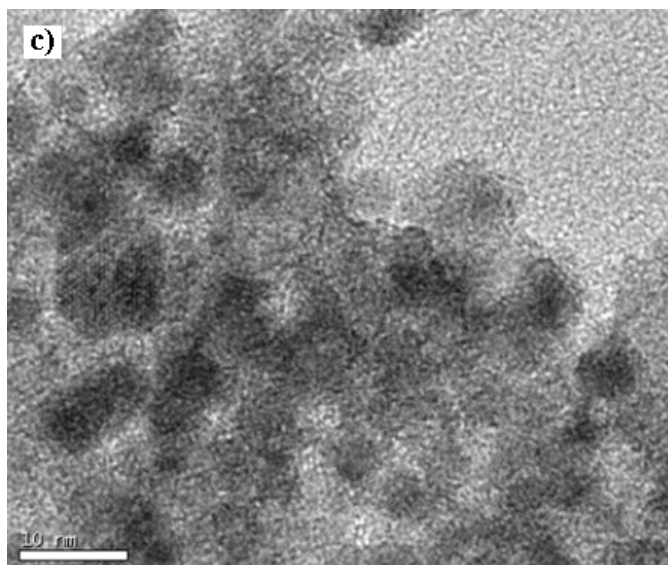


Fig. 4.7 (d) shows the TEM images of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles. In this sample, the distribution of the nanoparticle sizes are not homogeneous. Particle sizes are changing in the range of 5-40 nm.

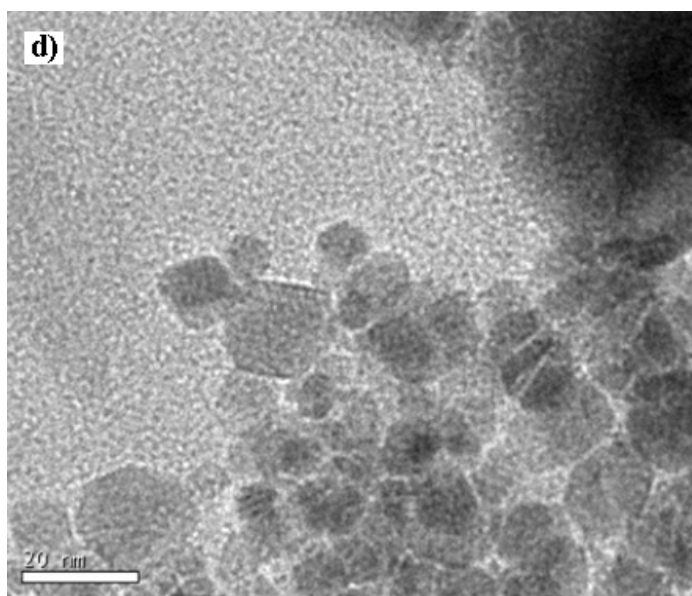


Figure 4.7 TEM micrograph of ; c) $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and d) $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ synthesized by Hydrothermal Method.

TEM micrograph of hydrothermally synthesized cobalt ferrite (CoFe_2O_4) nanoparticles are given in Fig.4.8. Particles don't have exactly spherical shapes and their size vary in the range of 7–25 nm.

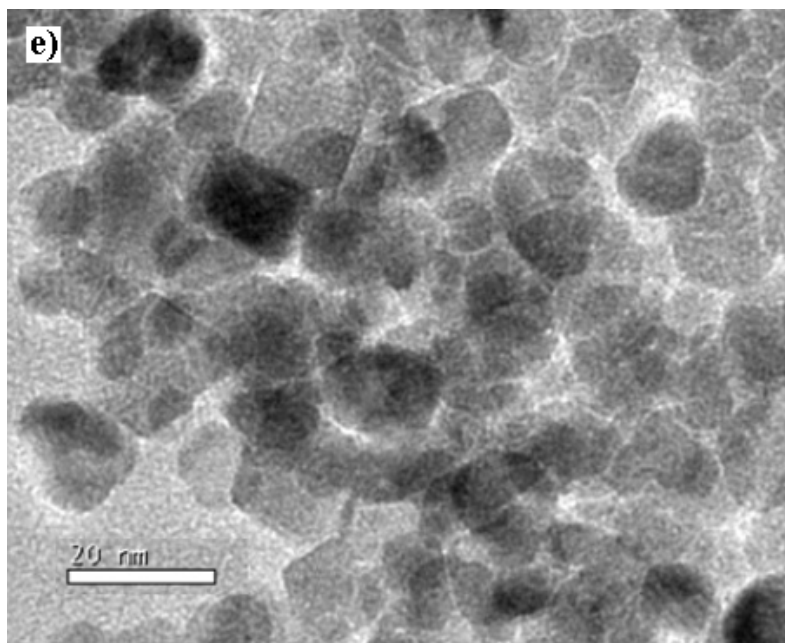


Figure 4.8 TEM micrograph of ; e) CoFe_2O_4 synthesized by Hydrothermal Method.

4.1.4 Magnetic Measurements

All magnetic measurements have been carried out by using Quantum Design Vibrating Sample Magnetometer (QD-VSM). The samples were cooled either in the presence of an external magnetic field (Field cooling case-FC) or in zero field (Zero field cooling case-ZFC) and, the magnetic hysteresis curves were recorded by sweeping the external field between ± 10 kOe at different temperatures. Also, temperature variation of the magnetization were recorded between room temperature and 10 K.

4.1.4.1 ZnFe_2O_4 Nanoparticles

Figure 4.9 shows the M-H curves taken at different temperatures. As can be seen from Fig.4.9, the value of magnetization sharply increases with the external magnetic field strength at low field region and, however, it can not reach a saturation state yet in

the presence of a relatively strong magnetic field of even 10 kOe, which is consistent with the earlier works [72-a,72-b]. Also the magnetization increases by decreasing temperature.

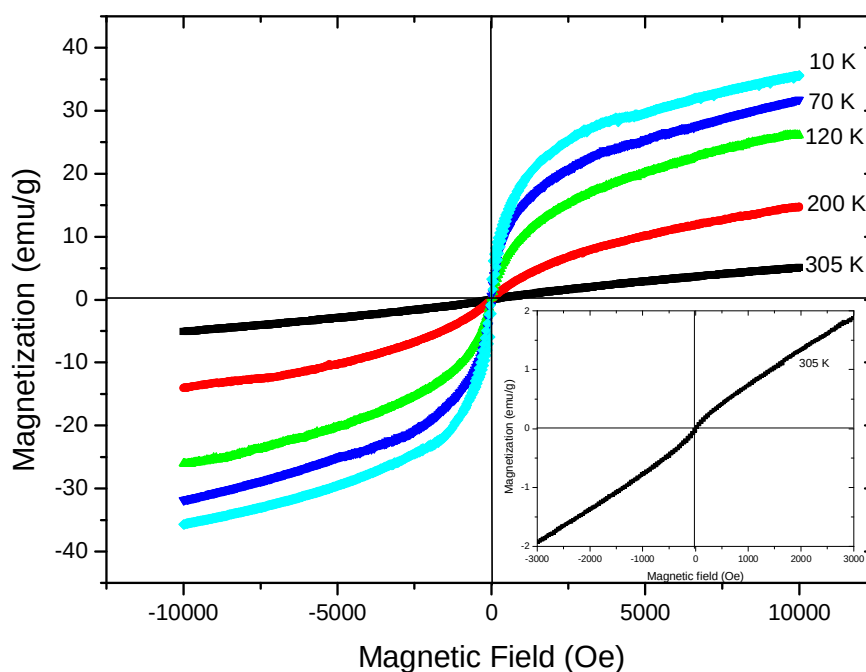


Figure 4.9 M-H curves taken at different temperatures for ZnFe_2O_4 .

The high field side of the curves are almost linear with the external field. The measured value of saturation magnetization decreases with increasing temperature as well. This behavior implies the co-existence of ferromagnetic and antiferromagnetic interactions. The non-saturated magnetization suggests the existence of strong antiferromagnetic inter-cluster interactions mixed with ferromagnetic interactions [73,74-a,74-b] inside the clusters. This (co-existence of ferromagnetic and antiferromagnetic) can also cause the canted spin structures inside the clusters. By increasing the applied field, the ferromagnetic part tends to saturate, whereas the antiferromagnetic part increases linearly, resulting in lack of saturation of magnetization even at 10 kOe magnetic field.

Typical superparamagnetic ‘S’-like shape of hysteresis curves (without open loops- coercive forces are zero) were observed at high temperature region. Those ‘S’-like shape loops can be divided into two parts: curvature parts and linear parts. The

linear parts can be attributed to the antiferromagnetic phase of the sample, while the curvature parts may originate from the change of the inversion parameter induced by the preparation technique when the particle size decreases to the nanometer scale [72,73]. At lowest temperature a 40 Oe coercive field was also observed.

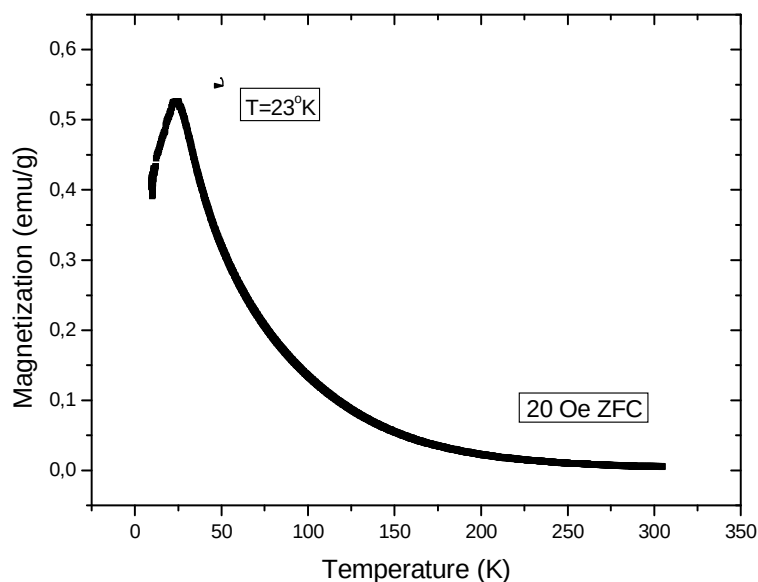


Figure 4.10 M-T curve of ZnFe₂O₄ nanoparticles with applied field of 20 Oe.

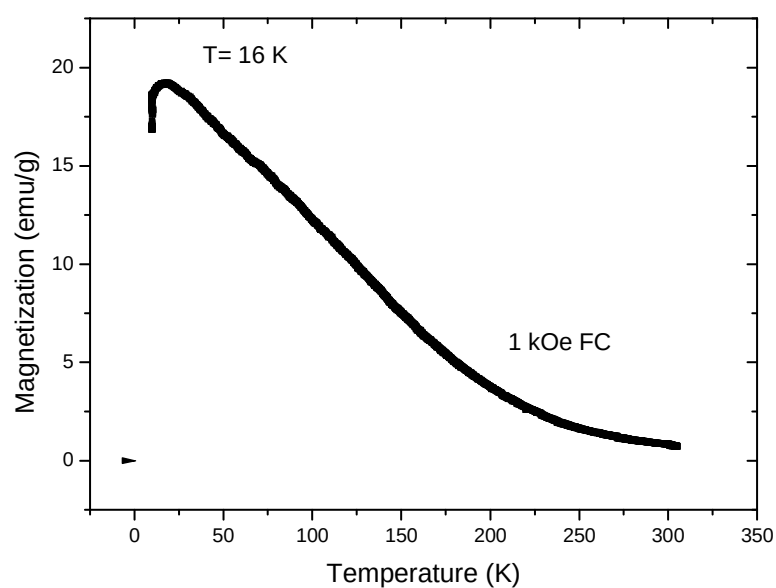


Figure 4.11 FC M-T curve of ZnFe₂O₄ nanoparticles with applied field of 1 kOe.

Fig. 4.10 and Fig. 4.11 displays the M-T curves of the sample at the applied field of 20 Oe and 1 kOe, respectively. It is found that for the ZFC curve with a measurement field of 20 Oe increases with decreasing temperature, exhibits a maximum at around 23 K and start to decrease below this temperature. The decrease in magnetization below this temperature may indicate that there are strong antiferromagnetic inter-cluster interactions between the particles [72,73,74-b]. While in the case of the FC curve with 1 kOe magnetic field applied, the peak (kink) shifts down to about 16 K, which is due to magnetic ordering of clusters resulting a decrease of spin-canting with increasing the applied field [75].

Alternatively, the decrease in magnetization at higher temperatures and linear increase with external field could be explained with super-paramagnetic response of individual magnetic clusters that can be ferro-magnetic or ferrimagnetic in nature. In this view, un-compensated spins of antiferromagnetic clusters give rise to finite and giant effective spins that response to external field like a super-paramagnetic systems. However, since there is antiferromagnetic interactions both in intra-clusters and interclusters spins, and size (effective moment) distribution of the particles, the resultant overall magnetic behavior would naturally be expected to be considerably different than that of conventional super-paramagnetic systems. This results supports predictions of Oliver and Chinnasamy et al. For Spin-glass-like behavior for nanosized ZnFe_2O_4 particles [45,73,76,77].

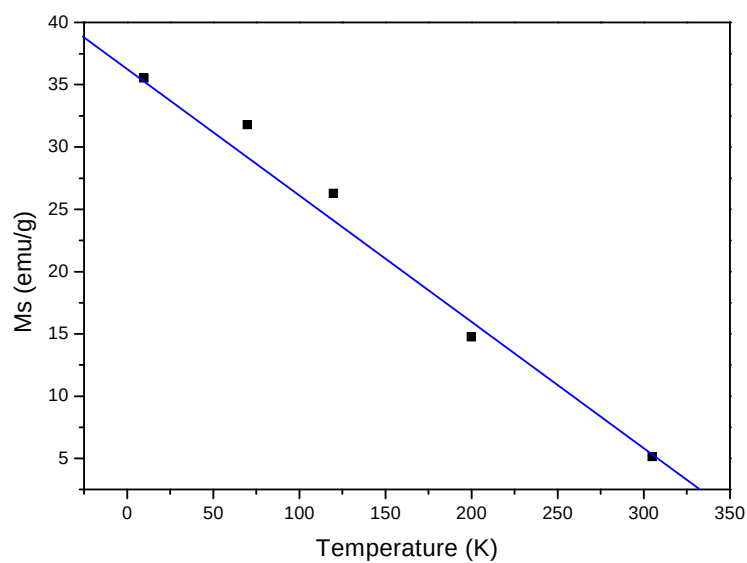


Figure 4.12 M_s values of ZnFe_2O_4 nanoparticles at various temperatures.

Figure 4.12 shows the temperature variation of the saturation magnetization (M_s) which are obtained by extrapolating M vs. $1/H$ plot to $1/H = 0$. M_s values linearly decrease with temperature.

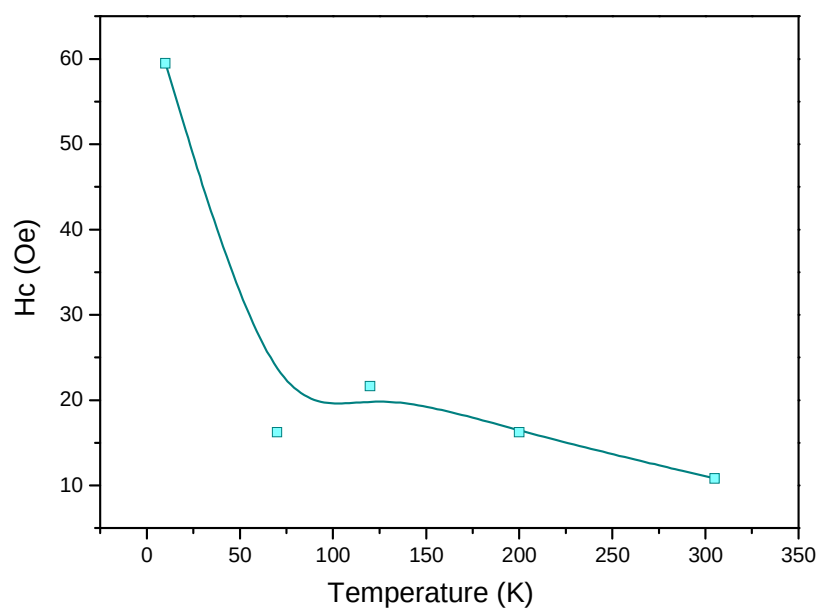


Figure 4.13 H_c values of ZnFe_2O_4 nanoparticles at various temperatures.

Figure 4.13 shows that the coercive field (coercivity) of ZnFe_2O_4 increases as the temperature is lowered. While the coercivity is less at high temperatures, it reaches very high values at the lowest temperature. In the coercive field, H_C , which presents, with decreasing temperature, a maximum at 120 K, a minimum at $T = 70\text{K}$ (corresponding to the temperature of the maximum of MZFC) and finally it increases very rapidly, at lower temperatures .

Since ZnFe_2O_4 usually forms an inverse spinel structure and has very high anisotropy energy constants, K_1 and K_2 , and is sensitive to temperature in the lower temperature region, the increase in the coercive field of ZnFe_2O_4 is much greater. The large values of the coercive field is associated with the increase in the effective anisotropy field (K_{eff}), where $K_{\text{eff}} = 4pM_sH_{\text{irr}}$. This can be attributed due to random freezing of nanoparticles in locally canted states, for which the random anisotropy energy will act as a pinning potential [73,78].

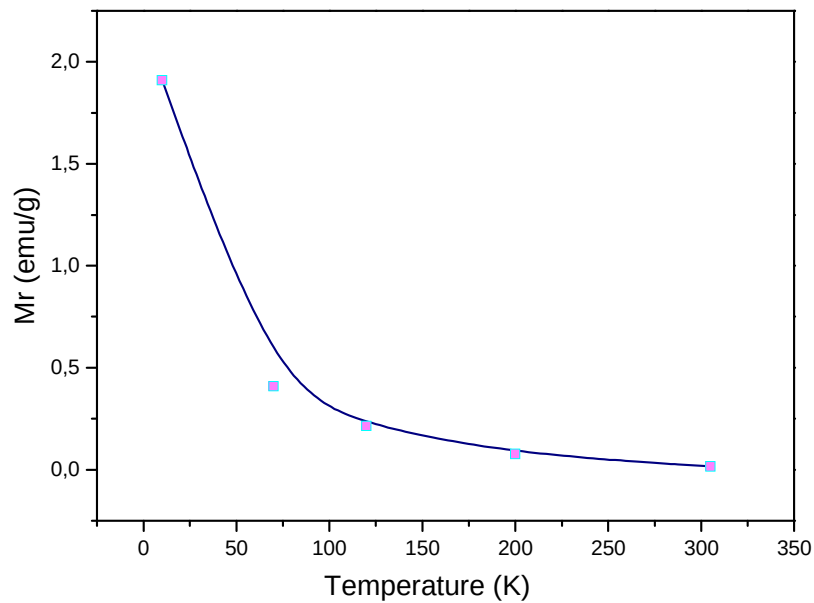


Figure 4.14 Mr values of ZnFe_2O_4 nanoparticles at various temperatures.

Figure 4.14 shows the temperature variation of the remnant magnetization of the sample. As can be seen from the figure, the remnant magnetization of the sample decreases with the temperature. In the cubic system of ferromagnetic spinels, the magnetic order is mainly due to a super-exchange interaction mechanism occurring between the metal ions in the A and B sublattices [73,78].

Figure 4.15 shows the temperature dependence of the normalized magnetization (M_r/M_s). As can be seen from the figure, M_r/M_s curve decreases sharply up to 100 K and then decreases slowly at high temperature regions. This means that the magnetic anisotropy of the sample increases by decreasing the temperature.

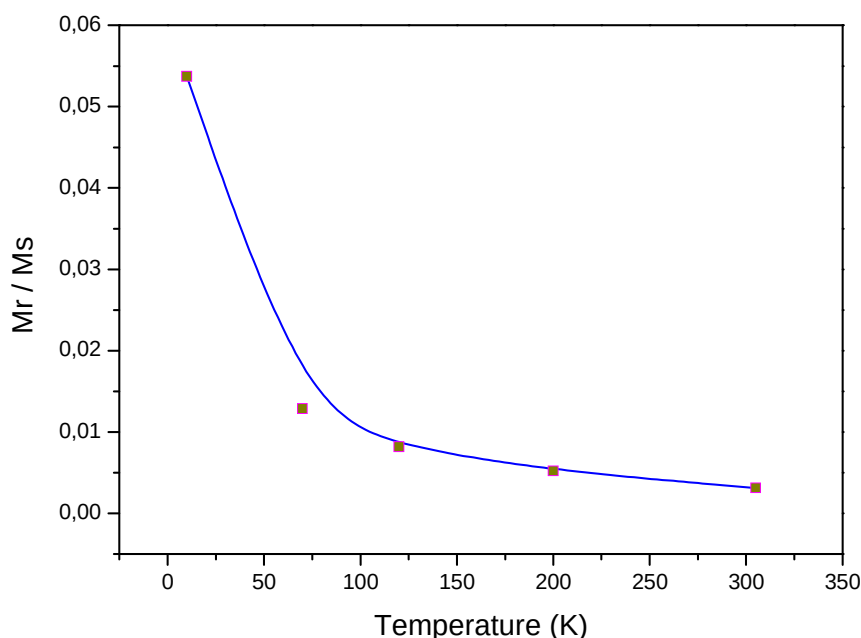


Figure 4.15 M_r/M_s values of ZnFe_2O_4 nanoparticles at various temperatures.

As a result, ZnFe_2O_4 nanoparticles were prepared by hydrothermal method. The characterization results show that the samples have 13 nm size. The magnetization measurements have shown that the particles are superparamagnetic at room temperature. Typical superparamagnetic ‘S’-like shape of hysteresis curves (without open loops- coercive forces are zero) were observed at high temperature region. The nanoparticles have also shown spin-glass like behavior. Changes in the magnetic properties, i.e. M_s , H_c , M_r , can be attributed to the formation of a dead layer on the surface, the existence of random canting of particle surface spins, non-saturation effects due to random distributions of particle size, deviation from the normal cation distribution, presence of adsorbed water, etc. All these factors may reduce the magnetic properties of nanoparticles. The deviation of cation distribution in nanoparticles from the bulk also influences the temperature dependence of magnetization [73,78,79].

4.1.4.2 $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ Nanoparticles

Figure 4.16 shows the hysteresis loops of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at different temperatures. The magnetization strongly increases with the external magnetic field strength at low field region and almost linearly increases at the high field region. However, it can not reach a saturation state in the presence of a strong magnetic field of even 45 kOe. Also the magnetization increases with decreasing temperature. While the M-H curve does not show hysteresis and remnant magnetization at high temperature region, there is a large coercivity below the blocking temperature. The coercivity of the nanoparticles increases with the decrease in temperature. At the applied magnetic field of 45000 Oe the induced magnetization as observed from the magnetization curves is found to increase from 8emu/g for the room temperature to 27 emu/g for the temperature of 10 K. Also the coercivity first increases from 0 Oe at room temperature to 6300 Oe at 10 K.

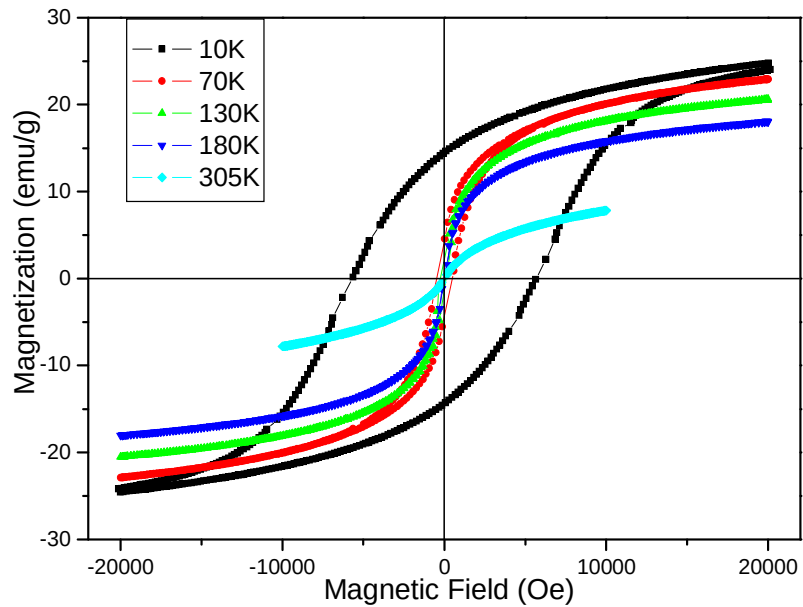


Figure 4.16 M-H curves taken at different temperatures for $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles.

The absence of saturation, remnant magnetization and coercivity at high temperature region in M-H curve indicates the superparamagnetic nature of the particles, which relax back their spins by rotation on removal of applied magnetic field so as to give a zero net magnetic moment. In this case even though the temperature is below the Curie temperature and the thermal energy is not sufficient to overcome the coupling force between neighboring atoms, the thermal energy is sufficient to change the direction of magnetization of the entire crystallite [80].

The absence of coercivity at room temperature could be attributed to the presence of Zn atoms in the otherwise ferromagnetic cobalt ferrite phase, for the presented composition [81]. These anomalous behaviors can be defined by the core-shell model of the particles. In the core-shell model of nanophase materials, the spin structure can be divided into two parts, the spin structure belonging to the core of the particle, and the surface-spin structure. They both play an important role in order to decide the magnetic properties of the system, but the role of the surface-spin structure becomes more important as the size is reduced. While the core spin-structure is ordered and is the major deciding factor for the saturation value of magnetization, the highly disordered surface-spin structure plays an important role in deciding how the saturation is approached. In the present case, we observe very slow approach to saturation showing the existence of the disordered spin configuration existing at the surface of magnetic nanoparticles [82].

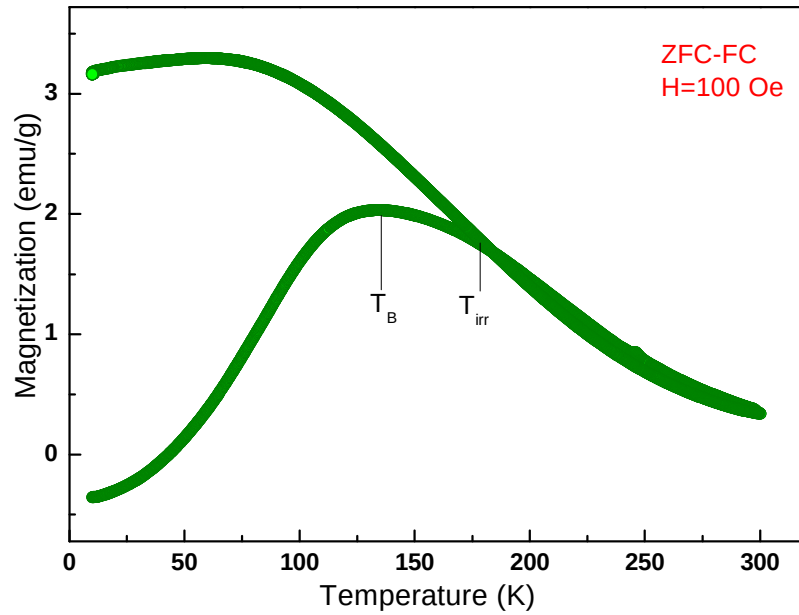


Figure 4.17 M-T curve of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with applied field of 100 Oe.

Temperature dependence of magnetization for zero field cooling (ZFC) and field cooling (FC) cases are shown in Fig. 4.17. The magnetization of the sample increases by decreasing temperature and for high temperature regime, both measurements show the same behaviour. By decreasing the temperature further, while FC curve continuous to increase, ZFC curve reaches to a maximum magnetization of 2 emu/g at 130 K and then starts to decrease by decreasing the temperature. The temperature at which the magnetization is maximum for ZFC case is called as blocking temperature. The separation between the ZFC and the FC curves gives an indication that there is a non-equilibrium magnetization below 180K for the ZFC case, and represents the irreversibility temperature, T_{irr} . In general, T_{irr} reperesents the blocking temperature of particles with the highest energy barrier and T_{max} is related to the average blocking temperature. The difference between T_{max} and T_{irr} corresponds to the width of the blocking temperature distribution [83].

As well known, a bulk ferromagnetic compound is generally multi-domain in nature below its ferromagnetic transition temperatures. Although formation of domain walls adds to its energy, the multi-domain character reduces the total magnetization and

hence the magneto-static energy to zero, leading to the minimization of the total energy of the system. This multi-domain character of a ferromagnetic system can be lost if the particle size is decreased below a critical size, at which the division of the aligned spins within a ferromagnetic system into domains no longer leads to the minimization of its total energy. The ferromagnetic particles are then termed as single domain with their magnetic spins aligned along one of the easy directions of magnetization. An increasing fraction of atoms lie at or near the surface as the particle size decreases and then surface spin effects and interface effects become more and more significant [84-86].

Because of the presence of missing bonds, fluctuations in number of atomic neighbors and inter-atomic distances and defects, the surface is characterized by topological and magnetic disorder. Such disorder propagates from the surface to the particle core, actually making no longer valid the picture of the particle as a perfectly ordered single domain, whose spins rotate in a synchronous way as a large single spin and cause the increase of effective magnetic surface anisotropy [87-90].

The resulting magnetic behavior of very small particles is complex and the effect of the interplay of some surface related phenomena is not well understood yet: surface anisotropy, which can also give a dominant contribution to surface-core exchange interaction (exchange anisotropy, different magnetic phases), the total particle anisotropy, in the case of and competition between core and surface effects.

Like the bulk ferromagnetic systems, the single domain ferromagnetic systems also show hysteresis in their M–H behavior (finite coercive field and remnant magnetization) and thermomagnetic irreversibility (TMI) between their ZFC and FC plots. There is, however, an important difference; in the case of bulk form the hysteresis and the TMI result from the energy barrier associated with restriction in the domain wall formations and movements, whereas that in the case of single domain form they result from energy barrier associated with restriction in orientation process of the single domain spins as imposed by the anisotropy energy of the system.

The anisotropy energy is defined as $E = KV \sin^2\Theta$, where V is the volume of the particle, Θ is the angle between the actual direction of magnetization and the easy direction of magnetization, and K is anisotropy constant. Hysteresis in the single

domain ferromagnetic particles vanishes when the particle size becomes so small that the maximum anisotropy energy (KV for $\Theta = 90^\circ$) becomes close to the thermal energy, so that the process of flipping of the single domain spin becomes uninhibited [91].

This state of the ferromagnetism is called ‘superparamagnetism’ as it does not show any hysteresis in its M – H behavior and like in the case of paramagnetism, the magnetization never gets saturated even at very high applied field. When superparamagnetic particles are cooled below certain temperature they transform to ferromagnetic state. The thermal energy at this temperature becomes significantly less than the anisotropy energy (KV) and thus cannot facilitate uninhibited flipping of the single domain spins. As a result, the ferromagnetic onset temperature decreases with decrease in size of the single domain particles [84, 92- 95].

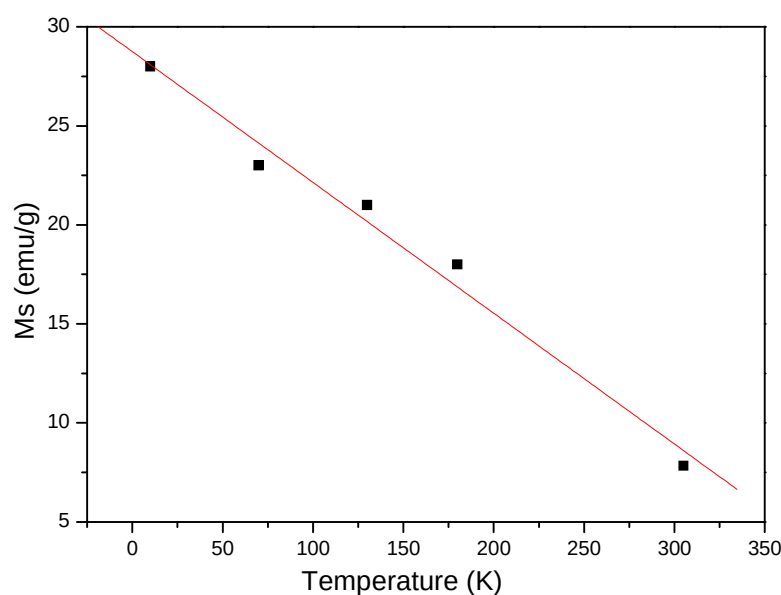


Figure 4.18 M_s values of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

Figure 4.18 shows the saturation magnetization values of the sample which are obtained by extrapolating M vs. $1/H$ plot to $1/H = 0$ at different temperatures. It is deduced that the saturation magnetization of the sample is almost linearly decreasing with the temperature. While the saturation magnetization of the sample is 18 emu/g at

around the blocking temperatures, it gradually increases by decreasing the temperature and reaches to a value of 28 emu /g at 10 K.

Temperature variation of the remnant magnetization is also shown in Fig.19. It is observed that the remnant magnetization of the sample is also decreasing by the temperature and vanishes above the blocking temperature. The value of remnant magnetization at 130 K is 2.37 emu/g while it is almost 14.50 emu/g at lowest temperature.

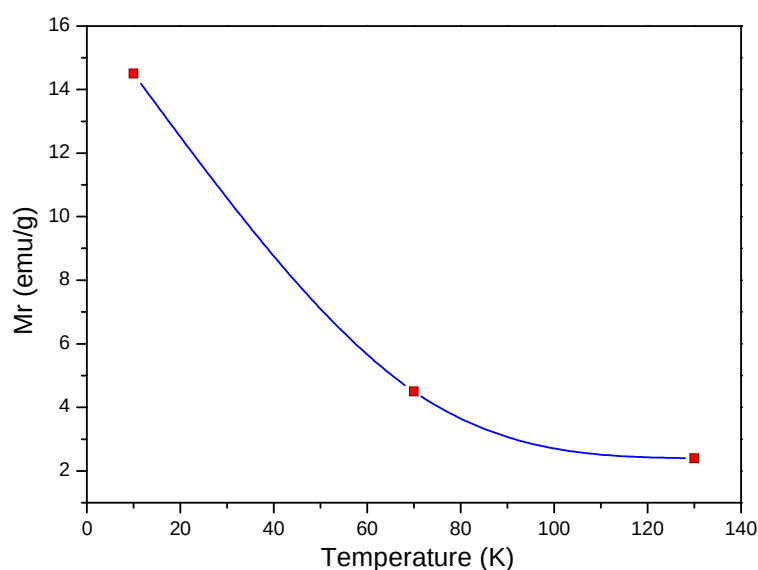


Figure 4.19 Mr values of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

Temperature dependence of the coercive field, H_c , (the magnetic field which can reduce the magnetization of the sample to zero) is given in fig.4.20. As it is observed from the figure that, it decreases by the increase of temperature and vanishes above the blocking temperature as expected for superparamagnetic materials. While it is zero above the blocking temperature, it reaches to a value of 5680 Oe at lowest temperature.

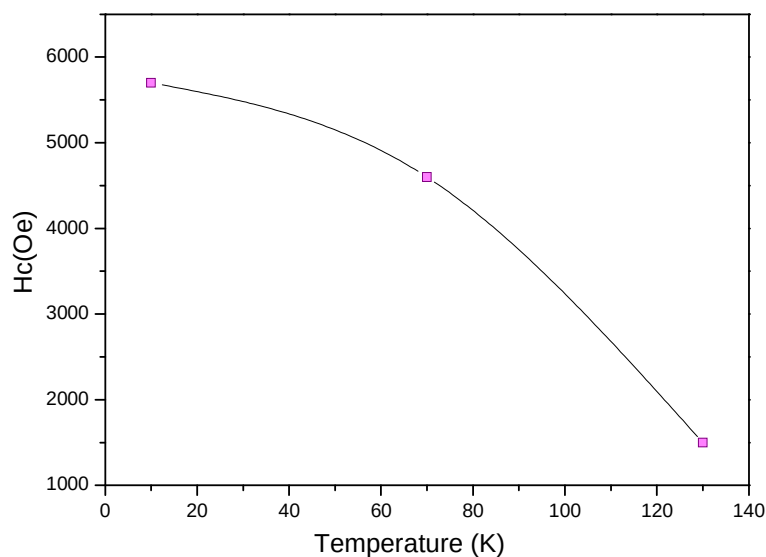


Figure 4.20 Hc values of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

The coercivity (H_c) of a magnetic material is generally a measure of its magnetocrystalline anisotropy [96]. Therefore, the increase in low-temperature coercivity can be attributed to magnetocrystalline anisotropy of the sample. But, it can also originate from exchange anisotropy due to spin disorder at the particles surface at low temperatures. This effect is expected to be larger for smaller particles due to the increase in the surface-to-volume ratio as occurred in the present case.

As can be seen from Figure 4.21, the reduced magnetization (M_r/M_s) value of the sample increases with decreasing temperature.

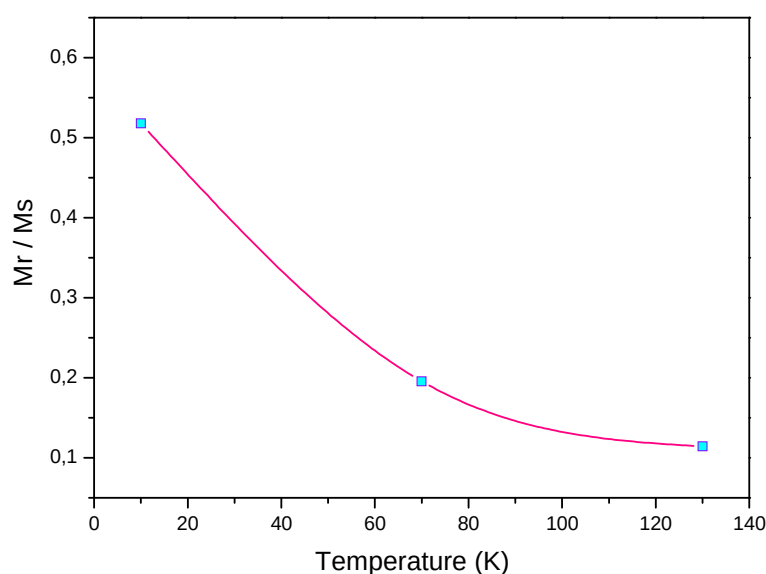


Figure 4.21 Mr/Ms values of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

As a result, we have successfully synthesized $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles by using hydrothermal synthesis. The hysteresis loops of the nanoparticles at different temperatures have indicated the superparamagnetic nature of the particles. The absence of coercivity at high temperature region is attributed to the substitution of Zn atoms in the cobalt ferrite phase, for the presented composition. In the present case, we have observed very slow approach to saturation showing the existence of the disordered spin configuration existing at the surface of magnetic nanoparticles. ZFC M-T curve of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with applied field of 100 Oe has shown the magnetization of the sample increases by decreasing temperature and for high temperature regime, both measurements show the same behaviour.

The temperature variation of the saturation magnetizations of the sample are obtained by extrapolating M vs. $1/H$ plot to $1/H = 0$. It is deduced that the saturation magnetization of the sample is almost linearly decreasing with the temperature and the remnant magnetization of the sample is also decreasing by the temperature and vanishes above the blocking temperature. H_c has observed from the figure that, it decreases by the increase of temperature and vanishes above the blocking temperature as expected for superparamagnetic materials.

4.1.4.3 $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ Nanoparticles

Figure 4.22 shows the temperature dependent hysteresis loops of hydrothermally synthesized $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles. The loops are open at every temperature but they are distorted on the y-axis. However these distortions could be seen only on the loops measured at 10, 20, 40 K temperatures. Such a kind of loop distortion in M-H curve has been also observed for other nanophase materials and these kind of distortions attributed to the freezing of disordered spin states [97]. At room temperature there is no distortion. On the other hand, the magnetization curve for the sample measured at 305 K, exhibit “constricted” hysteretic loops. A magnetic sample that is a mixture of hard and soft magnetic material could give rise to this kind of magnetization curves, for example, the hard magnetic CoFe_2O_4 particles contain some soft magnetic iron oxide associated them [98]. Also this can rise from particle size distribution. While larger particles behave as ferromagnetic, smaller ones behave as superparamagnetic at room temperature. So, overall hysteresis loop can be observed as constricted.

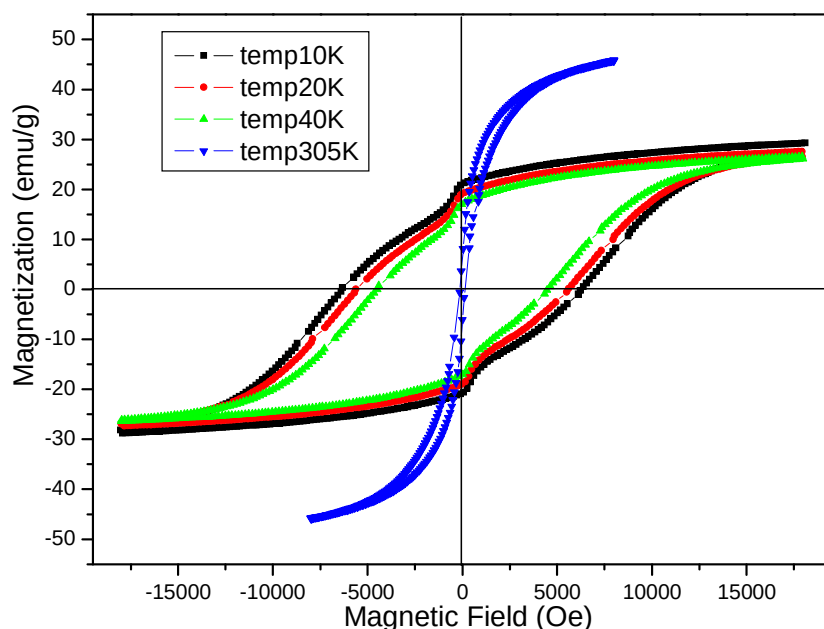


Figure 4.22 M-H curves taken at different temperatures for $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles.

As observed from the magnetization curves, the sample does not reach saturation even at 20 kOe applied field. The saturation magnetization (M_s) of the sample (obtained by extrapolating M vs. $1/H$ plot to $1/H = 0$) is found as 46 emu/g at room temperature and as 30.8 emu/g at 10 K. However, it is found to increase from 27.7 emu/g for the temperature of 40 K to 30.8 emu/g at 10 K. Also, the coercivity of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles increases with decreasing temperature. The coercivity values are 6380, 5580, 4480 and 550 Oe for temperature of 10, 20, 40 and 305 K.

It was reported that the magnetic saturation value is 61.6 emu g^{-1} for the nanoparticles with diameter of 200 nm. Compared with this result, the lower value observed in our work could be attributed to higher value of surface to volume ratio which results the pinning of the surface spins and also to existence of nonmagnetic surfactant (PEG) on the surface of the $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles [49].

The size dependent magnetization results of the nanoparticles are consistent with the size dependence of the magnetocrystalline anisotropy energy (E_A). According to Stoner-Wohlfarth theory, E_A of a single-domain particle is given by

$$E_A = KV \sin^2 \theta \quad (4.1)$$

where K is the anisotropy energy constant, V is the volume of the nanoparticle, and θ is the angle between the nanoparticles easy axis and the applied magnetic field direction [99,100]. E_A serves as an energy barrier to prevent the change in magnetization direction. When the size of a particle is reduced below a critical diameter, E_A becomes comparable with thermal activation energy, $k_B T$ where k_B is the Boltzmann constant. E_A can then be overcome by thermal activation and/or an applied magnetic field, and the nanoparticles magnetization direction can be moved away from its easy axis. The nanoparticles become superparamagnetic with the magnetization direction rapidly changing without any preferred orientation. Although there is still magnetic ordering in each of the nanoparticles, the assembly of nanoparticles collectively shows paramagnetic behaviour.

Zero field cooled (ZFC) temperature dependent magnetization performed by VSM for $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles is presented in Figure 4.23. In ZFC measurements, the nanoparticular sample is cooled from room temperature to 10 K without applying an external magnetic field. After reaching 10 K, 100 Oe field is applied and the magnetization is recorded as the temperature is increased.

As seen in Figure 4.23, upon increasing the measurement temperature, the magnetization increases, nevertheless it has not reached a maximum up to room temperature. This result indicates that the blocking temperature of the sample is higher than the room temperature. Although, at low temperature region, the magnetization increases slowly, at high temperature region the value of magnetization of ZFC curve sharply increases with the temperature.

For field cooling (FC) experiments, the samples are cooled under 100 Oe applied field from room temperature to 10 K temperature. Then the sample magnetization is recorded as temperature is increased. Contrary of ZFC, at FC measurement the curve that is measured low temperature region have increased slowly, then about 80 K the magnetization is decreasing slightly down to the magnetization value of 10 emu/g. At around and/or above room temperature, ZFC and FC curves intersect to each other.

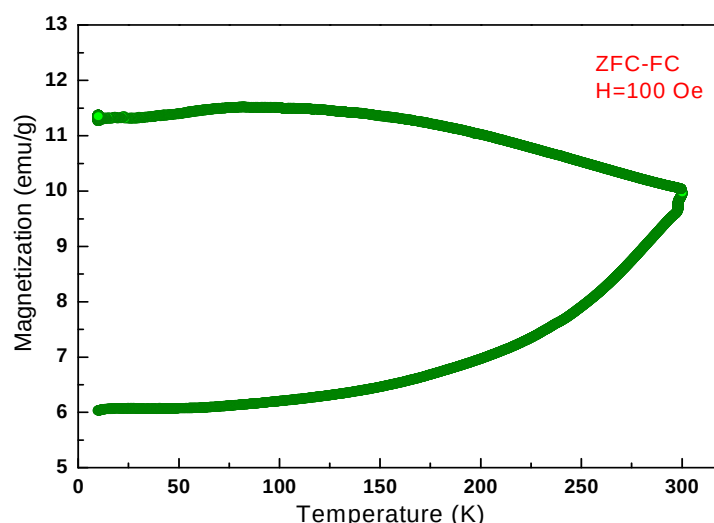


Figure 4.23 ZFC-FC M-T curve of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles with applied field of 100 Oe

When the nanoparticles are cooled without a magnetic field, the magnetization direction of each nanoparticle aligns with its easy axis as the temperature decreases below the blocking temperature. As the measured samples are in powder form, a random orientation of the easy axes among the nanoparticles is observed and the magnetization from each nanoparticle try to cancels each out at 10 K. The weak applied field (100 Oe) alone is not strong enough to overcome the anisotropy energy barrier. Due to the distribution of energy barriers resulting from a distribution of particle sizes, as the temperature is increased, a fraction of the particles gain enough thermal energy to overcome the anisotropy barrier. Their moments are free to move away from their easy axis and align with the applied field direction and an increase in magnetization is observed.

Fig.4.24 and Fig.4.25 shows the changes in the saturation and remnant magnetization of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles at different temperatures. At low temperature region, the saturation magnetization of the nanoparticles slowly decreases with increasing temperature. But, the sample has the largest M_s value at room temperature. However, the remanet magnetization of the sample decreases with the temperature at all regions. The decrease of remanent magnetization (M_r) and saturation magnetization (M_s) suggest the decrease of strongly interacted magnetic state towards a paramagnetic state, as the temperature increases to $T \geq 300$ K.

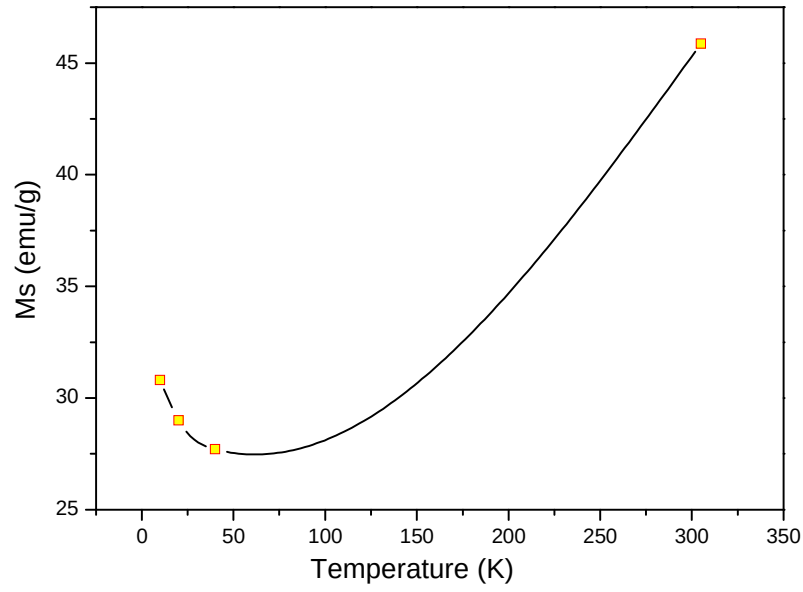


Figure 4.24 Ms values of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

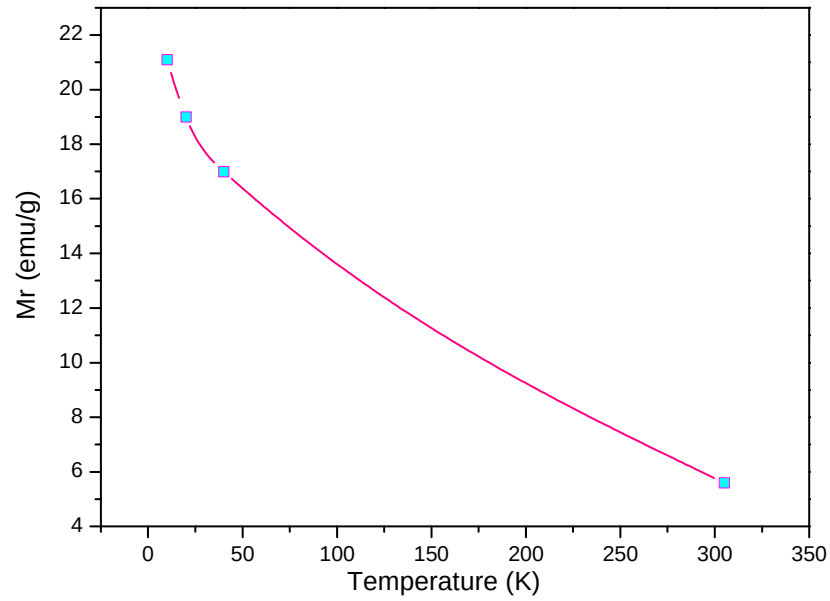


Figure 4.25 Mr values of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

Coercive field (H_C), increases with lowering temperature as seen in Fig.4.26. The large values of coercive field (H_C) below $T \leq 100\text{K}$ is associated with the increase of effective anisotropy field (K_{eff}), where $K_{\text{eff}} = 4\pi M_S H_C$. This may be attributed to the

random freezing of clusters in locally canted states, for which the random anisotropy energy will act as pinning potential [101, 102].

For assemblies of single domain nanoparticles, H_C is widely acknowledged to decrease with nanoparticle size due to the reduction in magnitude of E_A resulting from decreasing nanoparticles size [103]. In most of the nanoparticle systems, this trend of decreasing H_C with decreasing particle size is observed recent theoretical investigations predict that the coercivity should increase with decreasing nanoparticle size when the surface anisotropy is considered [104]. The surface anisotropy, K_S , contributes to the anisotropy K by

$$K_{net} = K + (6/d)K_S \quad (4.2)$$

As the particle size decreases, K_{net} increases and by the equation above, E_A should therefore increase [104]. A larger coercive force is needed for magnetization reversal as nanoparticle size decreases.

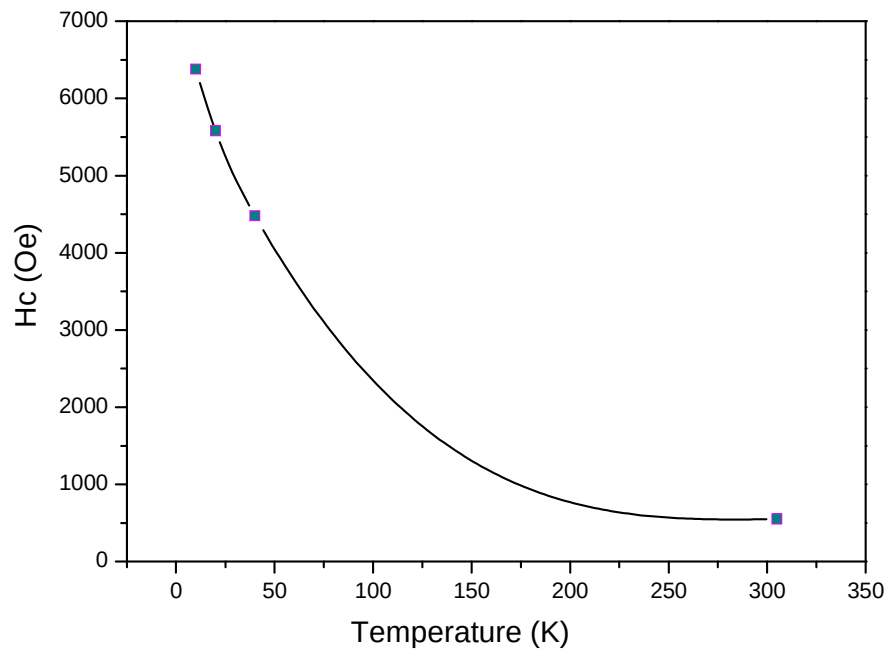


Figure 4.26 Hc values of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles at various temperatures.

Figure 4.27 shows the variation of the normalized magnetization (M_r/M_s) with temperature. As can be seen from the figure, M_r/M_s value of the sample increases with the decrease in temperature. Increase of M_r/M_s value indicates that the M-H curve is getting square shape which is important for magnetic recording.

As a result, the changes in the magnetic properties, i.e. M_s , H_c , M_r , from the bulk values can be due to the formation of a dead layer on the surface, the existence of random canting of particle surface spins, non-saturation effects due to random distributions of particle size, deviation from the normal cation distribution, presence of adsorbed water, etc. All these factors may reduce the magnetic properties of nanoparticles. The deviation of cation distribution in nanoparticles from the bulk also influences the temperature dependence of magnetization [79,102]. In the cubic system of ferrimagnetic spinels, the magnetic order is mainly due to a super-exchange interaction mechanism occurring between the metal ions in the A and B sublattices.

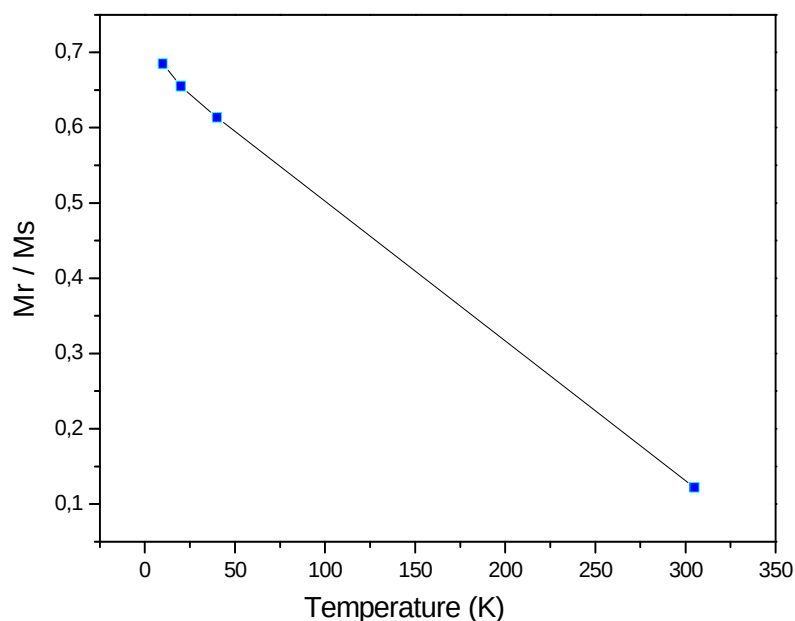


Figure 4.27 M_r/M_s values of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles with various temperatures.

4.1.4.4 CoFe₂O₄ Nanoparticles

Figure 4.28 displays the hysteresis loops of the CoFe₂O₄ nanoparticles at different temperatures. The loops that were measured at 10, 20, 30, 40, 80 K temperatures are distorted on the y-axis. Above 80 K, distortions have been disappeared. So we could attribute these distortions to the freezing of disordered spin states. Such a loop distortion in M-H curve has been observed earlier in the nanophase materials [97].

As it is seen from the figure, the coercivity of the nanoparticles increases with decreasing temperature. At room temperature, the figure shows that the CoFe₂O₄ has a coercivity (H_c) of 215 Oe while at the lowest (10 K) and medium (80 K) temperature have coercivities of 7750 Oe and 4500 Oe, respectively. The saturation magnetization is found to increase from 45 emu/g for the room temperature to 67,8 emu/g for 10 K. The saturation magnetization value (45 emu/g) measured at room temperature for the nanocrystalline cobalt ferrite is found lower than its bulk value (86 emu/g), which can be attributed to the surface spin canting due to large surface to volume ratio [98,78]. While the room temperature coercivity value (215 Oe) of the CoFe₂O₄ nanoparticles is less than that of bulk material (5300 Oe), the coercivity value (7750 Oe) at the lowest temperature is much larger than that of bulk [78,105].

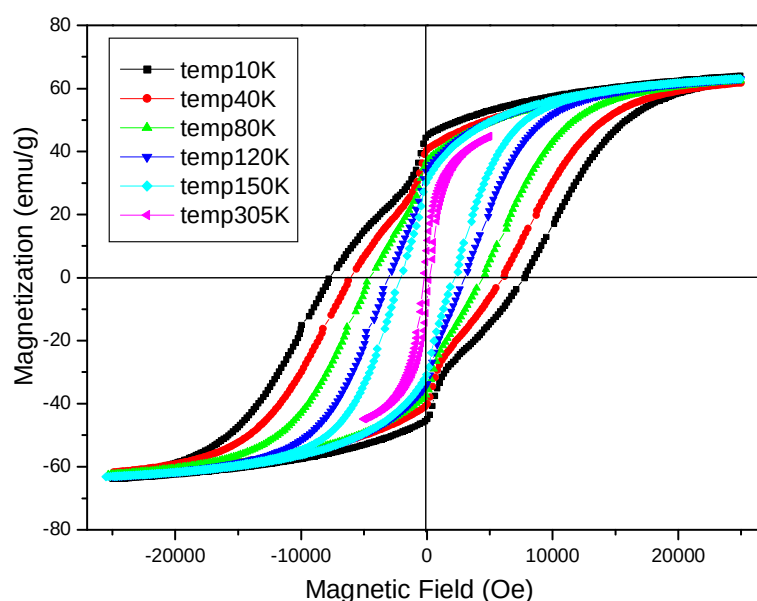


Figure 4.28 M-H curves taken at different temperatures for CoFe₂O₄ nanoparticles.

Since CoFe_2O_4 usually forms an inverse spinel structure and has very high anisotropy energy constants, K_1 and K_2 , and is sensitive to temperature in the lower temperature region, the increase in the coercive field of CoFe_2O_4 is much greater than other ferrites. The large values of the coercive field is associated with the increase in the effective anisotropy field (K_{eff}), where $K_{\text{eff}} = 4\pi M_s H_{\text{irr}}$. This can be attributed to random freezing of nanoparticles in locally canted states, for which the random anisotropy energy will act as a pinning potential [73,78].

Changes in the magnetic properties, i.e. M_s , H_c , M_r , can be attributed to the formation of a dead layer on the surface, the existence of random canting of particle surface spins, non-saturation effects due to random distributions of particle size, deviation from the normal cation distribution, presence of adsorbed water, etc. All these factors may reduce the magnetic properties of nanoparticles. The deviation of cation distribution in nanoparticles from the bulk influences the temperature dependence of magnetization [79,102].

Zero field cooled (ZFC) temperature dependent magnetization performed on a VSM for CoFe_2O_4 nanoparticles is shown in Figure 4.29. In ZFC measurements, the nanoparticle sample is cooled from room temperature to 10 K without applying an external magnetic field. After reaching 10 K, 100 Oe field is applied and the magnetization is recorded as the temperature is increased. As seen in Figure 4.29, at the ZFC upon increasing the measurement temperature, the magnetization increases, nevertheless it has not reached a maximum. Although at the low temperature region, the magnetization increases slowly, at the high temperature regions the value of magnetization of ZFC increases faster with the temperature.

For FC experiments, the samples are cooled from room temperature under 100 Oe applied field to 10 K. Then the sample magnetization is recorded as temperature is increased. Contrary of ZFC, at FC measurement the curve that is measured at low temperature region have increased slowly, then about 150 K the magnetization is decreasing slightly until the magnetization value of 9.6 emu/g. ZFC and FC curves do not intersect to each other at 300 K, this means that the blocking temperature of the sample is above room temperature.

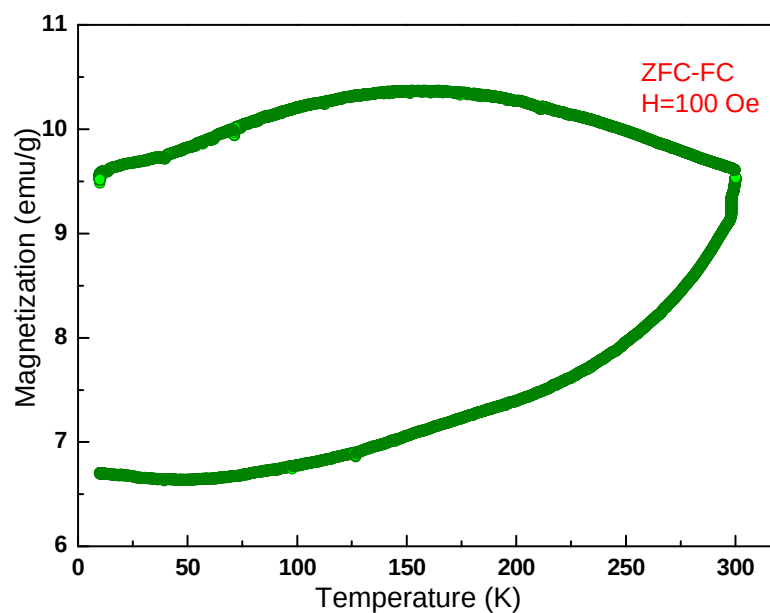


Figure 4.29 ZFC M-T curve of CoFe_2O_4 nanoparticles with applied field of 100 Oe.

Figure 4.30 shows the changes in the saturation magnetization of CoFe_2O_4 nanoparticles at different temperatures. As it is observed from the figure, the saturation magnetization of the sample decreases slowly at low temperature region. However, it decreases sharply above 150 K. This decrease in saturation magnetization is due to the decrease of magnetic anisotropy of the particle by increasing temperature. At high temperature region thermal energy overcomes the magnetic energy. Therefore magnetization at high temperatures is less than that of low temperatures.

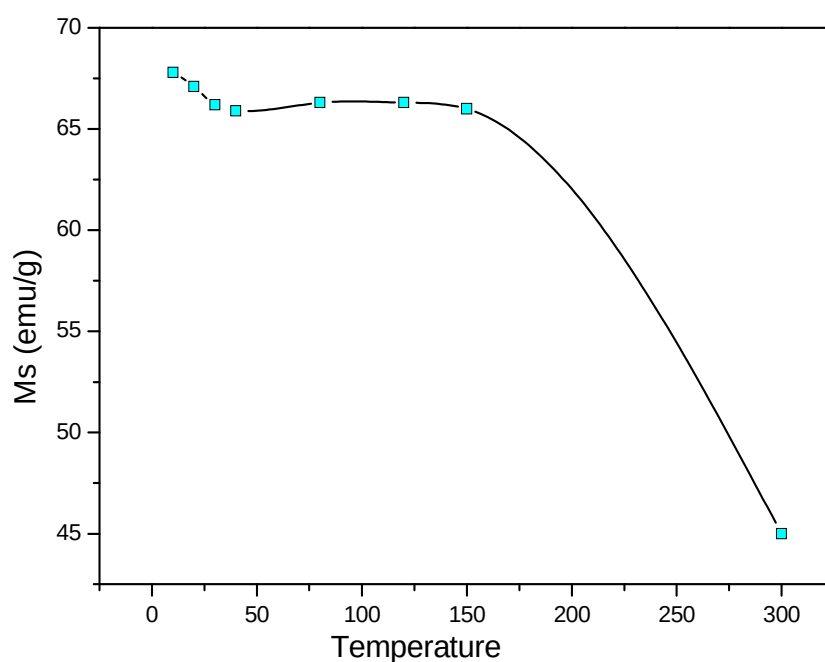


Figure 4.30 Ms values of CoFe_2O_4 nanoparticles at various temperatures.

Temperature dependence of the coercive field of CoFe_2O_4 nanoparticles is shown in Figure 4.31. As can be seen, the coercive field is strongly temperature dependent. The most important observation is the dramatic increase of coercivity for Co-ferrite at low temperatures. The coercivity (H_c) of a magnetic material is generally a measure of its magnetocrystalline anisotropy [96,100]. However, the dramatic increase in coercivity at low temperatures cannot be attributed only to magnetocrystalline anisotropy. It seems to originate from exchange anisotropy due to spin disorder at the particle surface at low temperatures. This effect is expected to be larger for smaller particles due to the increase in the surface-to volume ratio as occurred in the present case. While the coercive force is less at high temperatures, it reaches very high values at the lowest temperature.

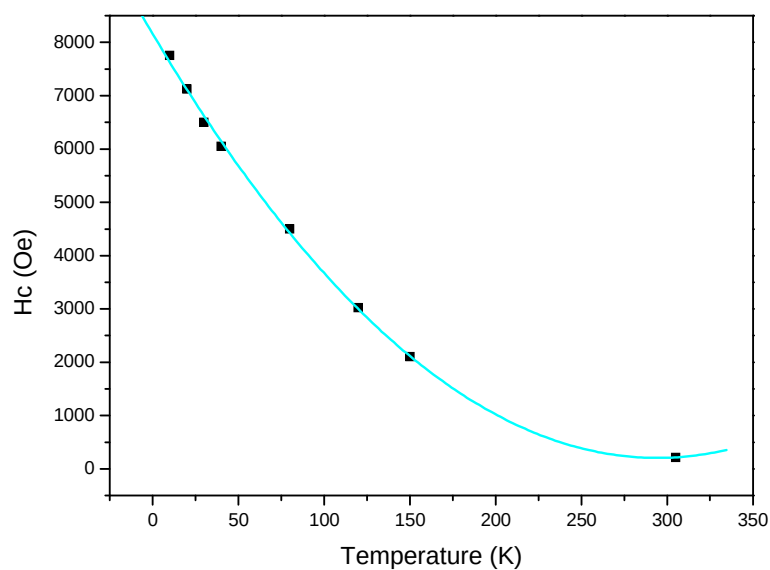


Figure 4.31 H_c values of CoFe₂O₄ nanoparticles at various temperatures.

Linear temperature dependence of the remanent magnetization is observed in Figure 4.32. While the temperature is decreasing, the remanent magnetization is increasing. This behavior is due to the increase in coercivity by decreasing the temperature.

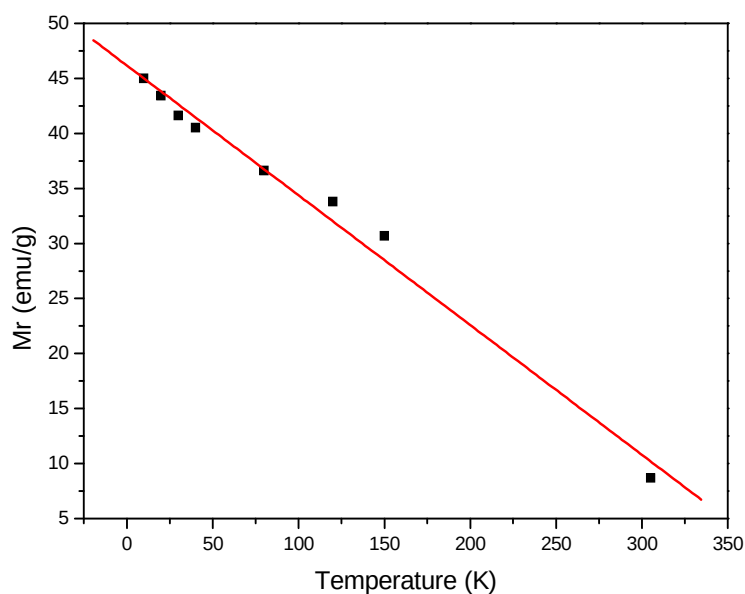


Figure 4.32 Mr values of CoFe₂O₄ nanoparticles at various temperatures.

Figure 4.33 shows the temperature dependence of the normalized magnetization (M_r/M_s). It has almost linear temperature dependence. M_r/M_s value increases by decreasing temperature. The increase in M_r/M_s value indicates that the hysteresis loop is getting squareness which is important for magnetic recording.

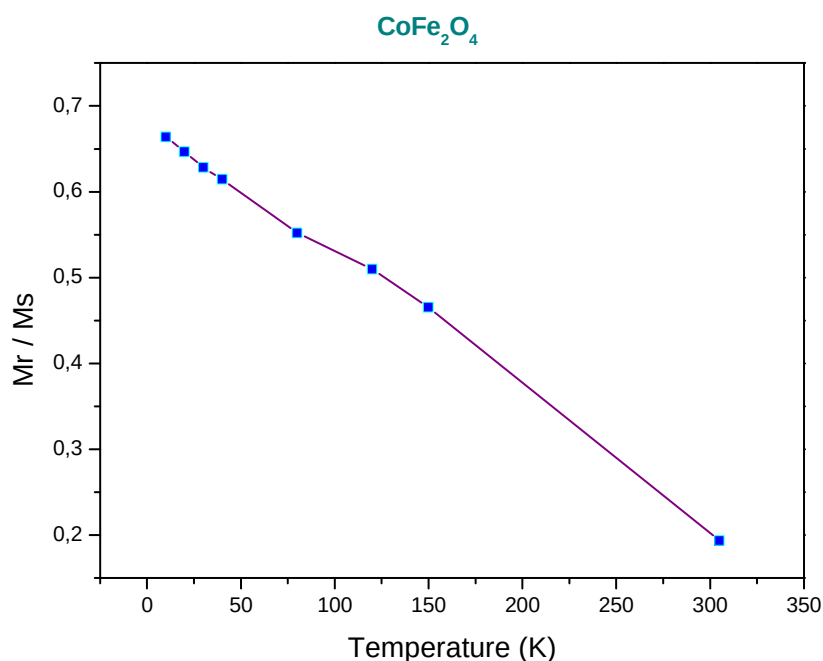


Figure 4.33 M_r/M_s values of CoFe_2O_4 nanoparticles at various temperatures.

In conclusion, using cobalt and ferric salts as the starting materials, fine CoFe_2O_4 powder has been successfully synthesized by hydrothermal method. Magnetic measurements have shown that the coercivity of CoFe_2O_4 nanoparticles increases drastically at low temperatures. The lowest temperature coercivity of the CoFe_2O_4 is much larger than that of bulk and this is attributed to the exchange anisotropy due to spin disorder at the particle surface caused by the increase in the surface-to-volume ratio.

The temperature variation of the saturation magnetizations of the sample are obtained by extrapolating M vs. $1/H$ plot to $1/H = 0$. It is deduced that the saturation magnetization of the sample is decreasing with the temperature and the remnant magnetization of the sample is also decreasing by the temperature. H_c has observed from the figure that, it decreases by the increase of temperature.

4.2. $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) NANOPARTICLES SYNTHESIZED BY MICROWAVE METHOD

4.2.1. FTIR Measurements

With a view to study the effect of the substitution of Co^{2+} ions in Zn ferrite, FTIR frequency data was analyzed using the observed FTIR spectra shown in Fig. 4.34. The higher frequency band (ν_1) ($555\text{--}565\text{ cm}^{-1}$) and lower frequency band (ν_2) ($420\text{--}430\text{ cm}^{-1}$) are assigned to the tetrahedral and octahedral complexes [106-109]. It explains that the normal mode of vibration of tetrahedral cluster is higher than that of octahedral cluster. It should be attributed to the shorter bond length of tetrahedral cluster and longer bond length of octahedral cluster.

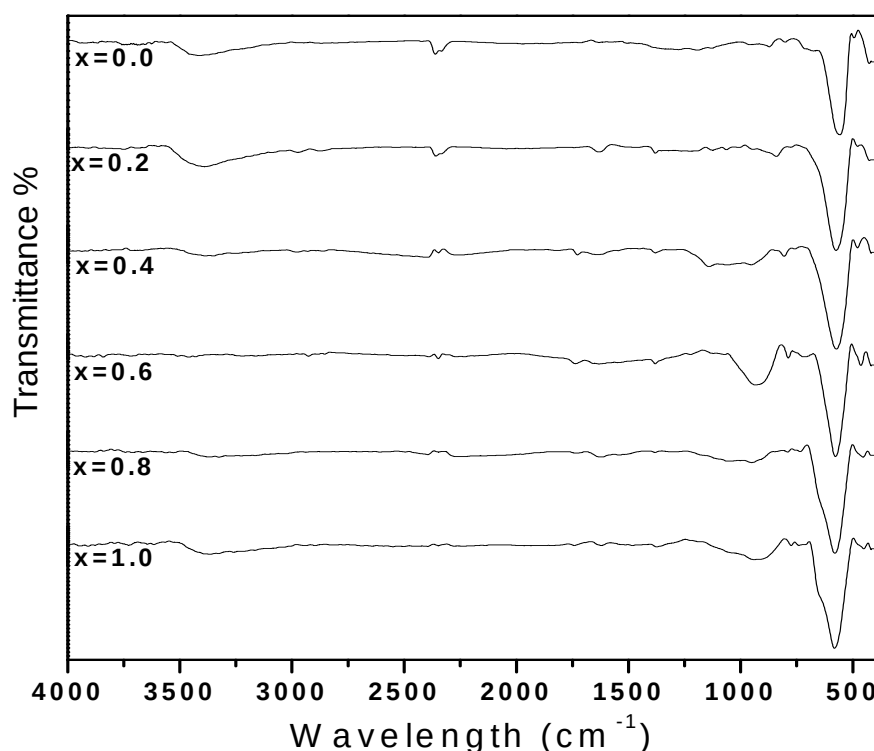


Figure 4.34 FTIR spectra of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$), synthesized by Microwave Method.

In the IR spectra (Fig. 4.34) traces of adsorbed or atmospheric CO_2 are evidenced by very light band around 2350 cm^{-1} [110]. Bands assigned to uncoordinated NO_3^- are also identified at $\approx 830\text{ cm}^{-1}$ [111]. The absorption band at around 1380 and 1720 cm^{-1} in the as-prepared material may be assigned to the unreacted metallic salts and carbonyl (from urea), respectively. It is evident that the presence of residual water in the spectra as-prepared sample small peak at about 1620 cm^{-1} [112] .

In the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles, Co^{2+} is stabilized in the octahedral crystal field whereas Zn^{2+} prefers tetrahedral sites. Consequently, the ν_1 band, observed at 561 cm^{-1} for ZnFe_2O_4 (see Fig. 4.35) can be assigned to tetrahedral Zn^{2+} stretching and the ν_2 band, observed at 425 cm^{-1} , involves the Fe^{3+} vibration at the octahedral site. In the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ sample, when Zn^{2+} are replaced by smaller Co^{2+} ions with lower atomic weight, the ν_1 vibration shifts to higher wavenumber, as shown in Fig. 4.35 and Table 4.4 . On the other hand, the ν_2 -octahedral band displacement is so light that it is only noticed when comparing the end members, ZnFe_2O_4 and CoFe_2O_4 .

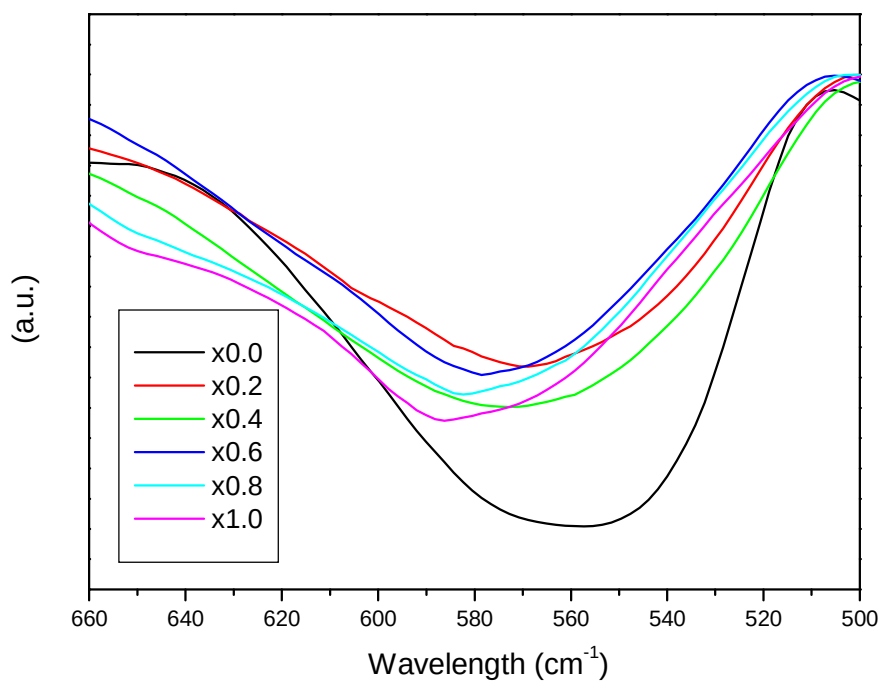


Figure 4.35 FTIR spectra of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$), synthesized by Microwave Method.

Table 4.4 Variation ν_1 vibration with x (Co content).

Compound	ν_1 (cm^{-1})
ZnFe_2O_4	557
$\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	568
$\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	572
$\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$	578
$\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$	582
CoFe_2O_4	586

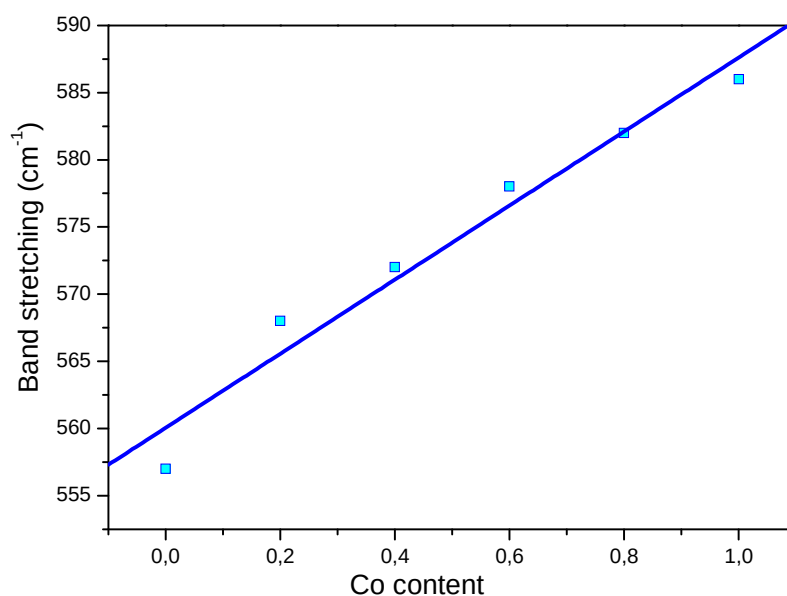


Figure 4.36 Variation of the band ν_1 of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) synthesized by Microwave Method.

4.2.2 X-ray Measurements

Fig. 4.37 shows that the diffraction patterns of the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) shift towards higher 2θ values when x increases. The decreasing of the lattice parameter from $8.4341 \text{ \AA}$ to $8.3902 \text{ \AA}$ as x varies from 0.0 to 1.0 (Table 4.6) is attributed to the smaller ionic radius of Co^{2+} (Tet: $0.58 \text{ \AA}$, Oct: $0.745 \text{ \AA}$) in comparison to that of Zn^{2+} ($0.74 \text{ \AA}$).

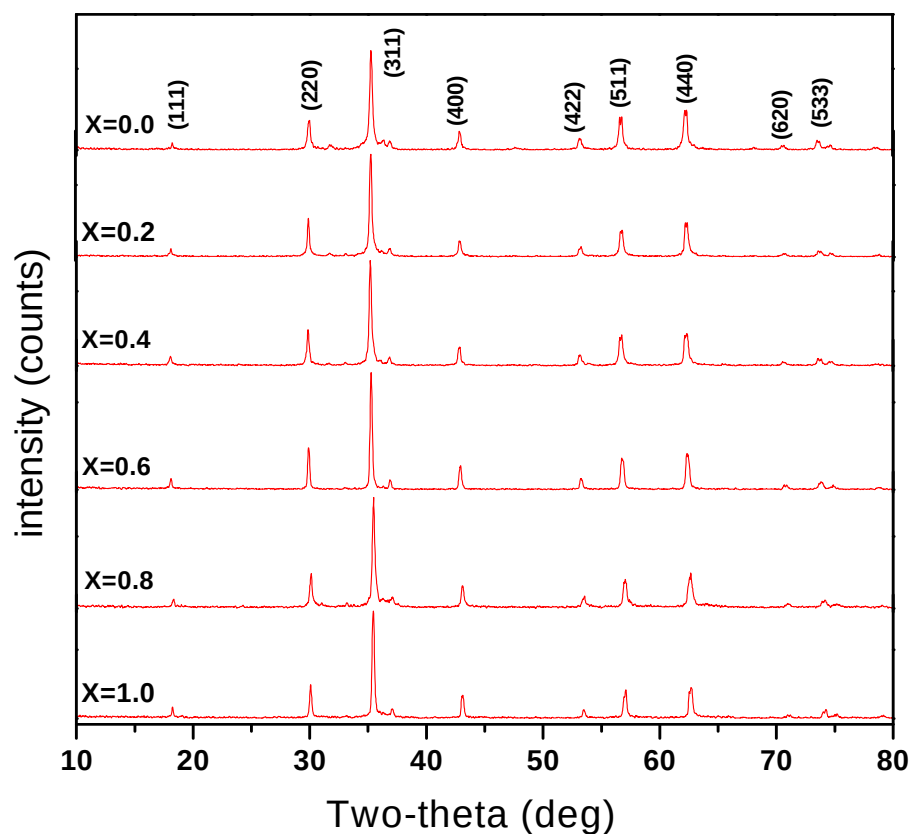


Figure 4.37 XRD powder patterns of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles, synthesized by Microwave Method.

As seen in Table 4.5, the particle size of the sample is found as 41.0 nm for $x = 0.0$ and as 36.7 nm for $x = 1.0$ Co.

Table 4.5 Particle size of samples, synthesized by Microwave Method, at different compositions.

Sample	Particle Size (nm)
ZnFe_2O_4	41.0
$\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	41.0
$\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	35.0
$\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$	40.1
$\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$	36.4
CoFe_2O_4	36.7

Table 4.6 Lattice Constant ($\text{\AA}$) of samples, synthesized by Microwave Method, at different compositions.

Sample	Lattice Constant ($\text{\AA}$)
ZnFe_2O_4	8.4341
$\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	8.4263
$\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	8.4125
$\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$	8.4125
$\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$	8.3968
CoFe_2O_4	8.3902

The lattice parameters were computed using the d-spacing values and the respective (*hkl*) parameters. The values of the lattice parameter, *a*, exhibit a linear dependence, thus obeying Vegard's law as shown in Fig. 4.38. Since, the ionic radius of Zn^{2+} (0.74 $\text{\AA}$), smaller than that of Co^{2+} (Tet: 0.58 $\text{\AA}$, Oct: 0.745 $\text{\AA}$), the replacement of Zn by Co ions leads to a decrease of the lattice parameter [113].

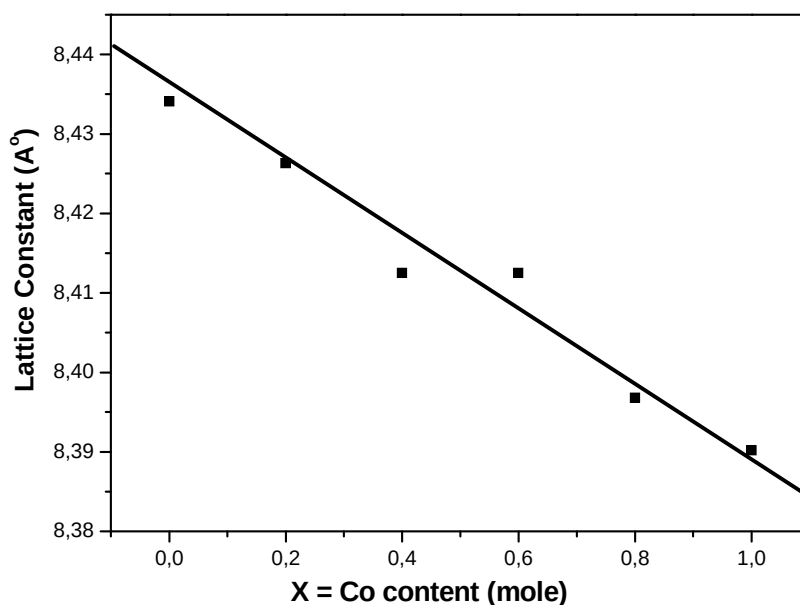


Figure 4.38 Variation of Lattice constant of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by Microwave Method.

The values of lattice parameter found for ZnFe_2O_4 ($a = 8.4341 \text{ \AA}$) and CoFe_2O_4 ($a = 8.3902 \text{ \AA}$) agree with those reported in JCPDS card numbers 89-1012 and 22-1086, respectively.

4.2.3 Magnetic Measurements

All magnetic measurements have been carried out by using Quantum Design Vibrating Sample Magnetometer (QD-VSM). The samples were cooled either in the presence of an external magnetic field (Field cooling case-FC) or in zero field (Zero field cooling case-ZFC) and, the magnetic hysteresis curves were recorded by sweeping the external field between $\pm 10 \text{ kOe}$ at different temperatures. Also, temperature variation of the magnetization were recorded between room temperature and 10 K.

4.2.3.1 ZnFe_2O_4 Nanoparticles

Figure 4.39 shows the hysteresis loops of the ZnFe_2O_4 nanoparticles synthesized by microwave combustion method at different temperatures. In the M-H graphs of ZnFe_2O_4 nanoparticles while the coercive field of 420 Oe could be observed at 10 K, it has been disappeared at 305 K. At the same time, remenant magnetization also hasn't been observed at highest temperatures, although a little remenant of 1,95 emu/g magnetization could be seen at the lowest temperature.

As can be seen from M-H curves, magnetization of the sample sharply increases with the external magnetic field at low field region. However, it can not reach a saturation state yet in the presence of a relatively strong magnetic field of 10 kOe, which is consistent with the earlier works [71, 72]. Also the magnetization of the sample increases by decreasing temperature as seen in the figure.

The M-H curve obtained at 305 K is almost linear with the external field has an s-shape at the origin. Saturation values at 10 K and 305 K are 12.8 emu/g and 2.2 emu/g. The measured value of saturation magnetization decreases with increasing temperature and coercive field was also observed at lowest temperature. This behavior implies the co-existence of ferromagnetic and antiferromagnetic interactions. The non-saturated magnetization suggests the existence of strong antiferromagnetic inter-cluster interactions mixed with ferromagnetic interactions [73, 74] inside the clusters. This (co-existence of ferromagnetic and antiferromagnetic) can also cause the canted spin structures inside the clusters.

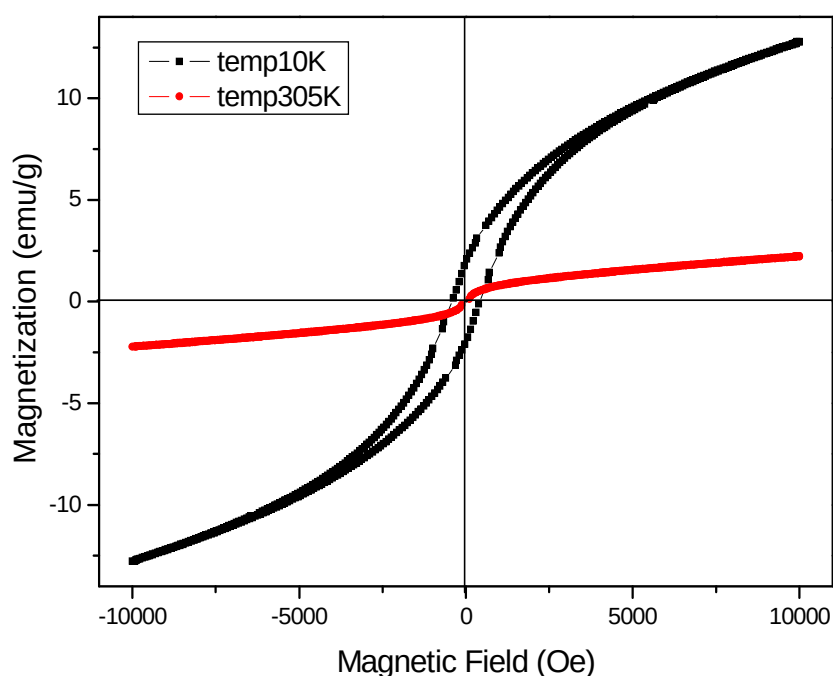


Figure 4.39 M-H curves taken at different temperatures for ZnFe_2O_4 nanoparticles.

It is well known that the physical and magnetic properties of materials are different from their ‘bulk’ values when the size of the particle is sufficiently reduced. The interparticle spacing and surface-to-volume ratio in particles play a predominant role in influencing the materials magnetic properties. Normally bulk ZnFe_2O_4 is a well-known normal spinel with tetrahedral A-sites almost exclusively occupied by Zn^{2+} ions and exhibiting antiferromagnetic behaviour with a Neel temperature of 10 K. In this study, the size of the ZnFe_2O_4 nanoparticle is approximately 40 nm. Small particles

structurally differ from bulk solids, in that a large fraction of atoms resides at the surface [114-116].

This can be explained by the redistribution of cations in the nanocrystalline ZnFe_2O_4 . In bulk form, ZnFe_2O_4 is a normal spinel with Zn^{2+} ions in the A-sites and Fe^{3+} ions in the B-sites and it is antiferromagnetic below 10 K and paramagnetic above this temperature. The large value of magnetization observed in the present study may indicate that the cation distribution has changed from normal to mixed spinel type. Hence, some percentage of Fe^{3+} ions occupies the tetrahedral sites which switches on the A–B super-exchange interaction and gives rise to a large magnetization. Nanocrystalline ZnFe_2O_4 prepared by various other methods also shows a larger magnetisation when compared with that of the bulk [117-130].

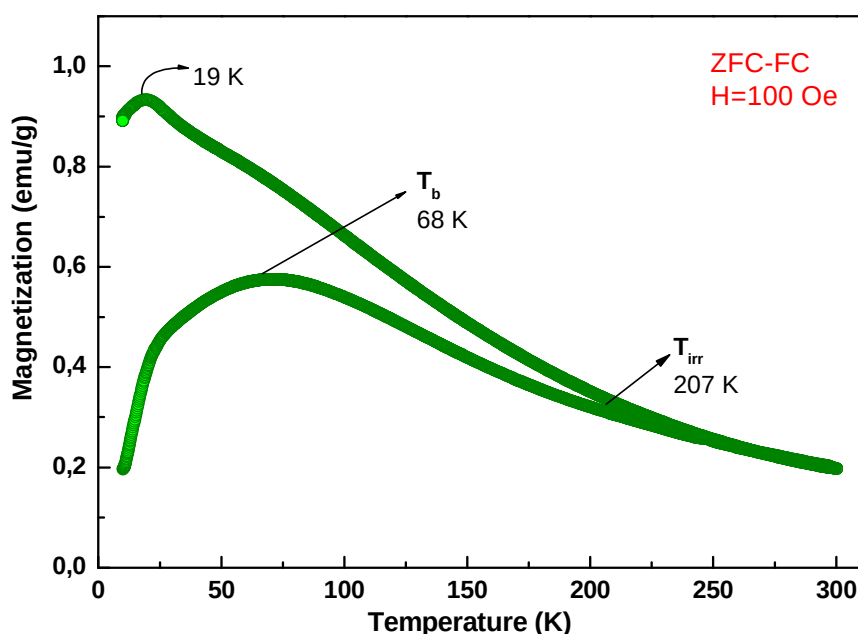


Figure 4.40 ZFC M-T curve of ZnFe_2O_4 nanoparticles with applied field of 100 Oe.

Temperature dependence of magnetization for zero field cooling (ZFC) and field cooling (FC) cases are represented in Figure 4.40. The magnetization of the sample increases by decreasing temperature and at high temperature regime, both curves follow the same line. By decreasing the temperature further, while FC curve continuous to

increase, ZFC curve reaches to a maximum magnetization of 0,6 emu/g at 68 K and then starts to decrease by further decreasing the temperature. The temperature at which the magnetization is maximum for ZFC case is called as blocking temperature. Also FC curve reaches to a maximum magnetization of 0,93 emu/g at 19 K and then starts to decrease by decreasing temperature. The magnetic transition temperature is found to be higher for nanocrystalline ZnFe_2O_4 compared to 10 K for the bulk ZnFe_2O_4 . This may be caused by the superexchange interaction between the Fe^{3+} ions at the octahedral sites and the Fe^{3+} ions which have occupied the tetrahedral sites.

The separation between the ZFC and the FC curves gives an indication that there is a non-equilibrium magnetization below 207 K for the ZFC case, and represents the irreversibility temperature, T_{irr} . In general, T_{irr} indicates the blocking temperature of particles with the highest energy barrier and T_{max} is related to the average blocking temperature, T_B . The difference between T_{max} and T_{irr} corresponds to the width of the blocking temperature distribution [131].

4.2.3.2 $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ Nanoparticles

Fig. 4.41 represents the magnetic hysteresis of the $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles over the field range -10 kOe to 10 kOe. It has been observed that the magnetization level decreases with increasing temperature. It should be noted that the magnetization is not fully saturated up to ± 10 kOe at 10K and 305K. The wide hysteresis loop at 10 K with a coercive field (H_c) of 2.5 kOe and remanent magnetization (M_r) of 32 emu/g confirm the presence of large ferromagnetic order at low temperatures. At room temperature, non hysteric behavior and nonsaturated magnetization indicates the presence of superparamagnetic behavior at high temperatures. This can easily be seen in temperature dependence of magnetization.

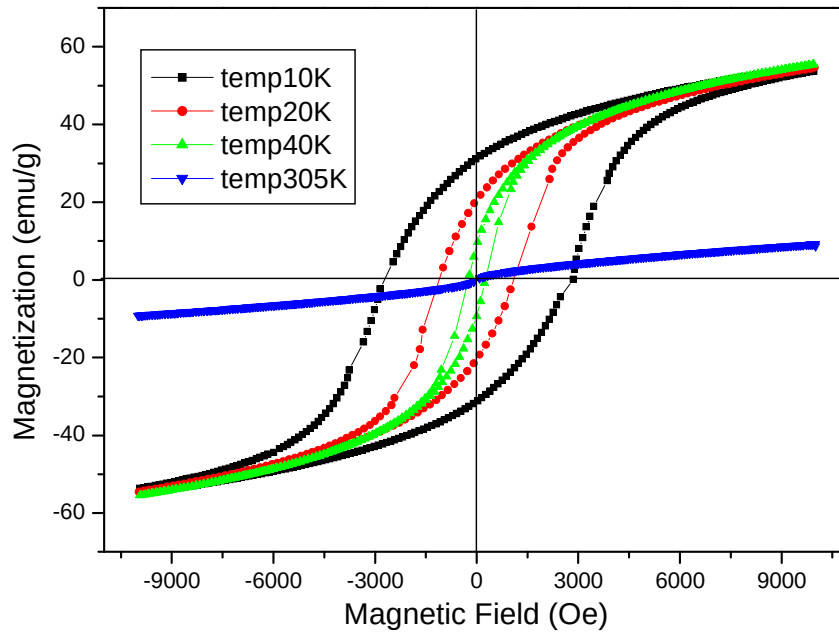


Figure 4.41 M-H curves taken at different temperatures for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles.

The increase of magnetic hardness, associated with the sharp increase of H_c , below 40 K may arise from the random freezing of ferrimagnetic clusters in spin glass state. The coexistence of ferrimagnetic order with spin glass state at low temperature is also revealed by the observation of metamagnetic transition with S shape behaviour in $M(H)$ data on decreasing temperature to 10 K. The hysteresis loop area drastically reduces on increase of temperature with H_c and M_r becoming small above 40 K and no hysteresis at $T = 305$ K. The non-saturation of magnetization and linear temperature dependence at high temperature regime suggest the existence of strong antiferromagnetic intercluster interactions mixed with ferrimagnetic interactions inside the clusters [74]. This also reflects the canted spin structure inside the clusters [132]. By increasing the applied field, the ferrimagnetic part tends to saturate, whereas the antiferromagnetic part increases linearly, resulting in lack of saturation of magnetization. The remanent magnetization (M_r), coercive field (H_c) and irreversibility field (H_{irr}) where the hysteresis loop closes, increases with lowering temperature. The large values of coercive field (H_c) and irreversibility field (H_{irr}) below the blocking temperature is associated with the increase of effective anisotropy field (K_{eff}), where $K_{eff} = 4\pi M_S H_{irr}$.

This can be attributed due to the random freezing of clusters in locally canted states, for which the random anisotropy energy will act as pinning potential. The decrease of remanent magnetization (M_r) and saturation magnetization (M_s) suggest the decrease of strongly interacted magnetic state towards a paramagnetic state, as the temperature increases to $T \geq 300$ K [133].

$\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ is a such a system where B site Fe^{3+} moments grouped into finite clusters as a result of frustration and strong antiferromagnetic short range interactions. We have taken $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ as a basic system for the following reasons. This sample is a mixture of CoFe_2O_4 with long range ferrimagnetic transition temperature at 790 K and ZnFe_2O_4 with antiferromagnetic Neel temperature at 9 K with molar ratio 2:8 [134]. It has been reported that CoFe_2O_4 has the highest anisotropy constant K_1 among the ferrite spinels due to the presence of Co^{2+} ions on B sites [135-137]. It is a good candidate for magnetic recording media and magnetic fluids whereas, ZnFe_2O_4 is used as a catalyst. In an earlier work, the experimental data for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ suggest a cluster freezing behaviour at 125 K with a possible short range ferrimagnetic ordering temperature at 260 K [138].

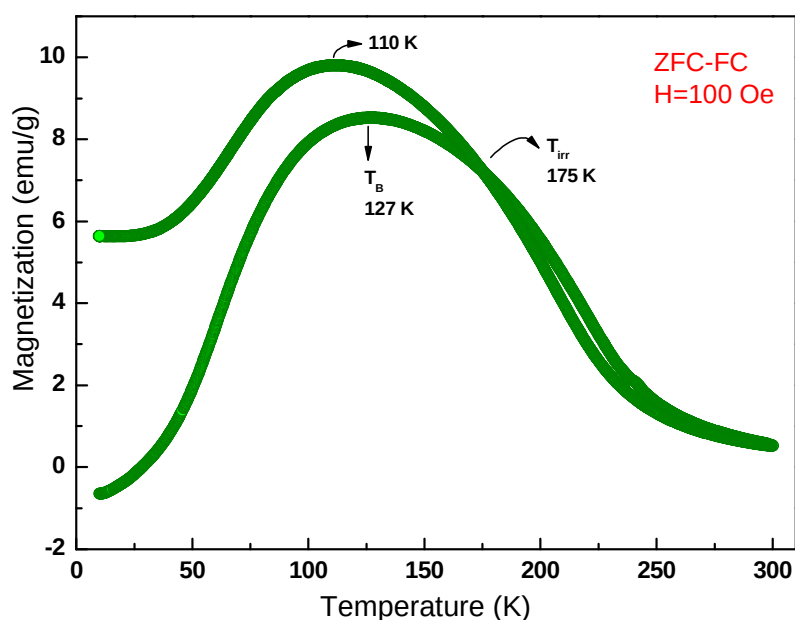


Figure 4.42 M-T curve of $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles with applied field of 100 Oe.

Zero field cooled (ZFC) and field cooling (FC) temperature dependent magnetizations performed on a VSM device for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles are presented in Figure 4.42. In ZFC measurements, the nanoparticle sample is cooled from room temperature to 5 K without applying an external magnetic field. After reaching 5 K, a 100 Oe field is applied (FC) and the magnetization is recorded as the temperature is increased. As seen in Fig.4.42, for the ZFC case upon increasing the measurement temperature, the magnetization increases and reaches a maximum at the blocking temperature (127 K), T_B , of the nanoparticle. At the blocking temperature, measured maximum magnetization is 8.5 emu/g. Above the blocking temperature, the magnetization starts to decrease and display typical paramagnetic behaviour. FC curve measured under 100 Oe field also follows the same way, but it unsticks from ZFC curve at 175 K. The separation between the ZFC and the FC curves gives an indication that there is a non-equilibrium magnetization and represents the irreversibility temperature, T_{irr} [131]. And the FC curve reaches to maximum magnetization of 9.8 emu/g at 110 K then starts to decrease by decreasing temperature.

4.2.3.3 $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ Nanoparticles

The magnetic properties of $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ ferrite nanoparticles are shown in Fig. 4.43 and Fig. 4.44. And Fig. 4.43 shows the M-H loops measured at two different temperatures. In the M-H curve measured at room temperature, typical superparamagnetic S'-like shape of hysteresis curves without open loops and no coercivity were observed. While the magnetization sharply increases with the applied field at low field region, it is approximately linear at high field region. It does not reach the saturation even at relatively high field of 20 kOe. This means that the sample shows superparamagnetic behavior at room temperature.

The magnetization value of the M-H curve measured at 10 K does not attain saturation at the highest applied magnetic field of 20 kOe. At the same time, a remanent magnetization of 46 emu/g and a coercivity of 1280 Oe are observed at 10 K. At the applied magnetic field of 20 kOe, the saturation magnetization is found to increase from

34,5 emu/g for the room temperature to 78,6 emu/g for the temperature of 10 K. Also the corecivity first increases from 0 Oe at room temperature to 1280 Oe at 10 K.

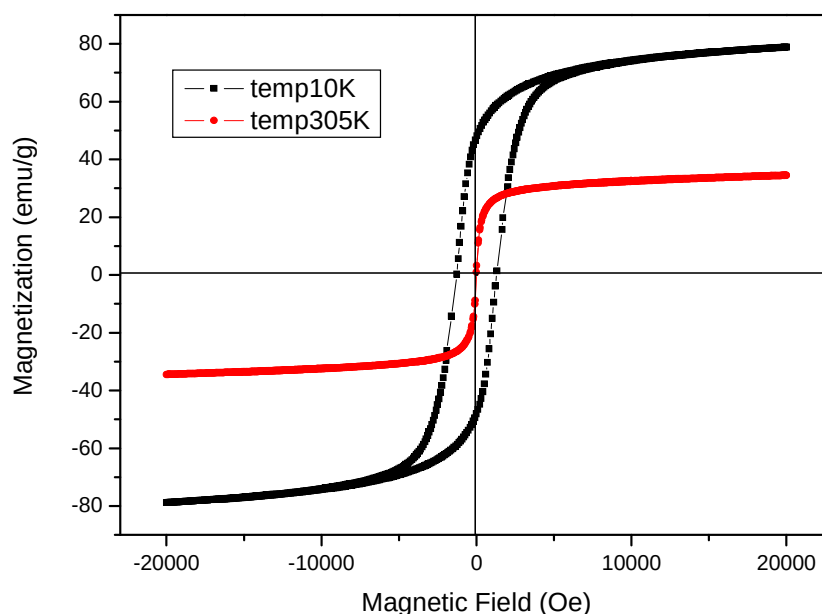


Figure 4.43 M-H curves taken at different temperatures for $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles.

Fig. 4.44 displays the M–T curves of the sample at the applied magnetic field of 100 Oe, respectively. In the case of the FC curve with 100 Oe magnetic field applied, the magnetization increases to a value of 16.5 emu/g down to 50 K, which is due to the decrease of the interactions among the particles with decreasing applied field [130]. Below this temperature, it slightly decreases.

For the ZFC curve with 100 Oe magnetic field applied, the magnetization slowly increases down to 270 K. At around 275 K it has a wide peak which indicates the spin-glass behavior. This is compatible with the heat capacity results obtained by Hamdeh et al. [139]. In detail, the magnetization increases slowly with the rise of the temperature up to 100 K. While the temperature exceeds 100 K, as a result of the uncompensated spins in the two sublattices, magnetization increases rapidly with the rise of the temperature, and reaches a peak at about 265 K. At this temperature, the relaxation time

of spins are equal to the measurement time of VSM, the magnetization decreases, indicating the spins become disordered, namely superparamagnetic.

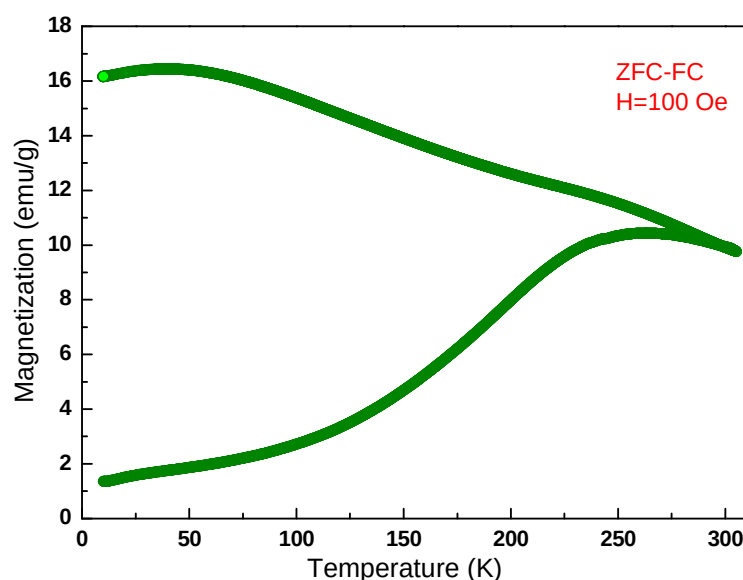


Figure 4.44 M-T curve of $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles with applied field of 100 Oe.

4.2.3.4 $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ Nanoparticles

Magnetization versus applied field (M-H curves) measurements are plotted in figure 4.45. M-H curve at room temperature has a small coercivity of 117 Oe and remanence of 9.7 emu/g. Also, the magnetization does not reach to saturation. The value of magnetization at an applied field of 10 kOe is 55.6 emu/g.

The magnetization value of the M-H curve measured at 10 K does not also attain saturation at the highest applied magnetic field of 20 kOe. The M-H curve at 10 K has a coercivity of 1282 Oe and a remanence of 67 emu/g. At 10 K, the sample has a saturation value of 106 emu/g. From these results, we can conclude that the sample does not show superparamagnetic behavior, it shows ferromagnetic behavior at all measuring temperatures.

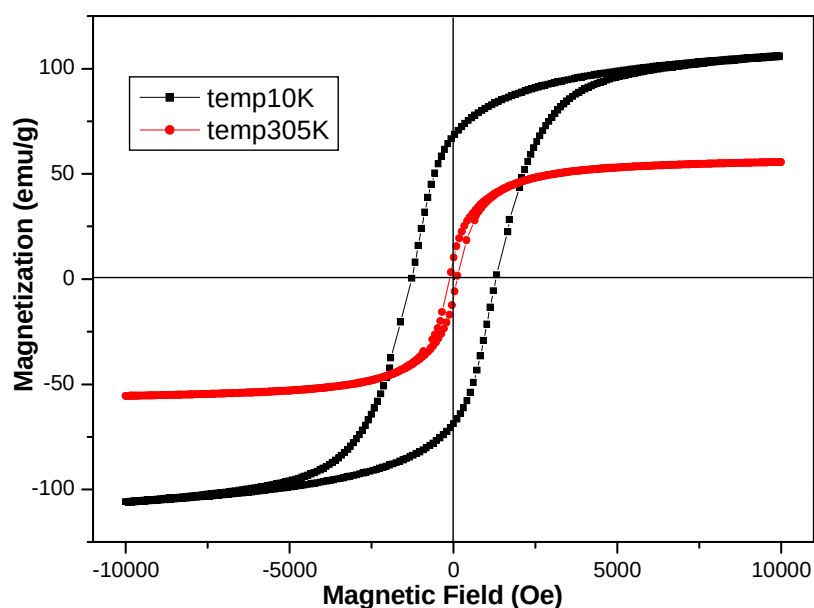


Figure 4.45 M-H curves taken at different temperatures for $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles.

The magnetic properties of $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles have been studied by measuring the magnetization as a function of temperature; ZFC and FC (with field of 200 Oe) M-T curves are shown in Fig. 4.46. It reveals that the magnetization increases by increasing the temperature up to room temperature. While the FC curve slightly increasing with the temperature, ZFC curve slightly increases up to 150 K and rapidly above 150 K. Both curves do not come together up to room temperature. This means that the blocking temperature of the sample is higher than room temperature.

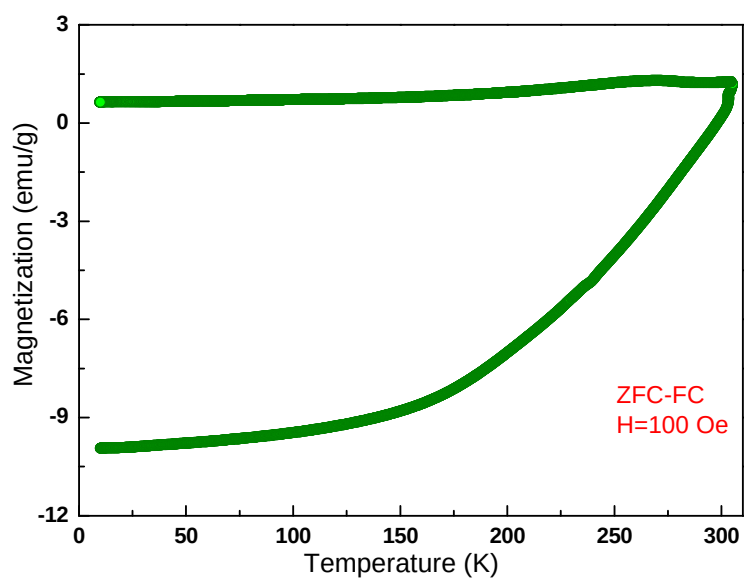


Figure 4.46 M-T curve of $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles with applied field of 100 Oe.

CHAPTER 5

CONCLUSION

$\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ where $x = 0, 0.3, 0.5, 0.7, 1.0$ nanoparticles with PEG as a surfactant were successfully synthesized by using Hydrothermal Method. At the same time, $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ mole content are used to obtain $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles by using microwave method with urea as a fuel. At the end of each synthesis method, single-phase well-crystallized nanosized ferrites of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ were successfully obtained. For the structural, morphological, spectroscopic and magnetic investigations of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles XRD, TEM, FTIR and VSM were used respectively.

The X-ray diffraction patterns (XRD) of the samples corresponds to spinel phase which was identified as an intermediate composition between CoFe_2O_4 and ZnFe_2O_4 . Average particle size was obtained from the XRD. The mean crystallite sizes for the nanoparticles synthesized by hydrothermal route and microwave combustion method are about 8-12 nm and 36-41 nm.

The FTIR spectra show two fundamental bands, ν_1 and ν_2 , in the frequency range of $400\text{-}4000\text{ cm}^{-1}$ that correspond to the tetrahedral and octahedral complexes, respectively. The band ν_1 , shifts towards the higher frequency site with increasing Co content.

Transmission electron microscopy (TEM) analysis revealed that all $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticle samples are spherical with a narrow size distribution.

The magnetization of the samples were characterized by Quantum Design Vibrating Sample Magnetometer (VSM). For hydrothermally synthesized sample, the magnetization measurements of ZnFe_2O_4 and $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles have shown that the particles are superparamagnetic at room temperature and typical superparamagnetic 'S'-like shape of hysteresis curves (without open loops- coercive forces are zero) were observed at high temperature region. The nanoparticles have also shown spin-glass like behavior. The absence of coercivity at high temperature region is attributed to the substitution of Zn atoms in the cobalt ferrite phase, for the presented composition. We have observed very slow approach to saturation showing the existence of the disordered spin configuration at the surface of the magnetic nanoparticles.

The magnetic characterization of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ and CoFe_2O_4 nanoparticles synthesized by hydrothermal method have shown that they are ferromagnetic at room temperature (not superparamagnetic). They show hysteresis and the coercivity increases drastically at low temperatures. The lowest temperature coercivity of the CoFe_2O_4 is much larger than that of bulk and this was attributed to the exchange anisotropy due to spin disorder at the particle surface caused by the increase in the surface-to-volume ratio. Some distortions have been seen on the M-H loops of the samples measured at low temperatures. Such a kind of loop distortion in M-H curve has been also observed for other nanophase materials and these kind of distortions attributed to the freezing of disordered spin states. From ZFC curves, upon increasing the measurement temperature, the magnetization increases, nevertheless it has not reached a maximum up to room temperature. This result indicates that the blocking temperature of the samples is higher than the room temperature. From these results, we have concluded that the samples do not show superparamagnetic behavior, they show ferromagnetic behavior at all measuring temperatures.

Changes in the magnetic properties, i.e. M_s , H_c , M_r , were attributed to the formation of a dead layer on the surface, the existence of random canting of particle surface spins, non-saturation effects due to random distributions of particle size, deviation from the normal cation distribution, presence of adsorbed water, etc.

The temperature variations of the saturation magnetizations of the samples are obtained by extrapolating M vs. $1/H$ plot to $1/H = 0$. It is deduced that the saturation magnetizations of the samples are almost linearly decreasing with the temperature and the remnant magnetization of the samples are also decreasing by the temperature and vanishes above the blocking temperature. The coercivity, H_c , of the decreases by the increase of temperature and vanishes above the blocking temperature as expected for superparamagnetic materials.

The hysteresis loops of the ZnFe_2O_4 , $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ and $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by microwave combustion method shows that the M - H curves obtained at high temperatures are almost linear with the external field and has an s-shape at the origin. At room temperature, non-hysteric behavior and nonsaturated magnetization indicated the presence of superparamagnetic behavior at high temperatures. The measured value of saturation magnetization decreases with increasing temperature and coercive field was also observed at low temperatures. This behavior implies the co-existence of ferromagnetic and antiferromagnetic interactions. The non-saturated magnetization suggests the existence of strong antiferromagnetic inter-cluster interactions mixed with ferromagnetic interactions inside the clusters.

Temperature dependence of magnetization for zero field cooling (ZFC) curves indicated that the magnetization of the samples increases by decreasing temperature and at high temperature regim ZFC curve reaches to a maximum magnetization, then starts to decrease by further decreasing the temperature. The temperature at which the magnetization is maximum for ZFC case was called as blocking temperature of the sample.

The magnetic properties of $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by microwave combustion method displays M - H curve at room temperature that has a small coercivity and the magnetization does not reach to saturation. These results showed that the sample does not show superparamagnetic behavior, it shows ferromagnetic behavior at all measuring temperatures. The ZFC magnetization curve increases by increasing the temperature up to room temperature. This means that the blocking temperature of the sample is higher than room temperature.

As a result, the sizes and all the magnetic properties of the samples synthesized by two methods differ from each other. The samples showing superparamagnetic behavior can be used for hypothermia, cancer treatment and as a drug carrier. The samples showing ferromagnetic behavior can be used for high density recording, read-write heads, microwave absorption, etc.

As a further study, microwave absorption properties and dielectric properties of these samples will be studied.

REFERENCES

- [1] D. S. Mathew, R. S. Juang. Chemical Engineering Journal, 129 (1-3) (2007) 51.
- [2] C.N.R. Rao and A.K. Cheetam J. Mater. Chem., 11 (2001) 2887.
- [3] G.A. Ozin. Adv. Mater., 4 (1992) 612.
- [4] C. Kittel, Phys. Rev., 70 (1946) 965.
- [5] L. Neel, Compt. Rend. 252 (1961) 4075.
- [6] A.H. Morrish. The Physical Principles of Magnetism, Wiley, New York (1965).
- [7] S. Sun , C.B. Murray, D. Weller, L. Folks and A. Moser. Science, 287 (2000) 1989.
- [8] R.D. McMichael, R.D. Shull, L.J. Swaertzendruber and L.H. Bennett. J. Magn.Magn. Mater., 111 (1992) 29.
- [9] U. Häfeil, W. Schütt, J. Teller and M. Zborowski (Eds.) Scientific and Clinical Applications of Magnetic Carriers, Plenum Press, New York, (1997).
- [10] D.G. Mitchell. J. Magn. Reson. Imaging, 7 (1997) 1.
- [11] C. R. Vestal and Z. J. Zhang. Int. J. of Nanotechnology, 1 (1/2) (2004) 240.
- [12] C. Liu, B. Zou, A.J. Rondinone and Z.J. Zhang J. Am. Chem. Soc., 122 (2000) 6263.
- [13] A. Goldman, Modern Ferrite Tech, Nostrand Reinhold, New York, 1990.
- [14] B.M. Berskovsky, V.F. Mcdvdcv, M.S. Krakov, Magnetic Fluids: Engineering Applications, Oxford University Press, Oxford, 1993.
- [15] R. Morineau, M. Paulus. IEEE Trans. Magn. 28 (5) (1992) 2441.
- [16] K. Janghorban, H. Shokrollahi. Journal of Magnetism and Magnetic Materials 308 (2007) 238
- [17] M.F. Yan, D.W. Johnson, J. Am. Ceram. Soc. 61 (7–8) (1978) 342.
- [18] M. Drofenik, A. Znidarsic, D. Markovec, J. Am. Ceram. Soc. 81 (11) (1998) 2841.

- [19] C.R. Hendricks, D. Sullivan, *Ceram. Bull.* 70 (5) (1991) 817.
- [20] R.E. Ayala, D.W. Marsh, *Ind. Eng. Chem. Res.* 30 (1991) 55.
- [21] L.A. Bissett, L.D. Strickland, *Ind. Eng. Chem. Res.* 30 (1991) 170.
- [22] T.M. Clark, B.J. Evans, *IEEE Trans. Magn.* 33 (1997) 3745.
- [23] S. Krupicka, P. Novak. In: Wohlfarth EP, editor. *Oxide spinels in ferromagnetic materials*,. Amsterdam: North Holland; 3 (1982).
- [24] R.E. Vandenberghe, E. De Grave. In: Long GJ, Grandjean F, editors. *Meossbauer effect studies of oxidic spinels in muossbauer spectroscopy. Applied to inorganic chemistry*,. New York: Plenum Press; 3 (1989) .
- [25] C.R. Vestal, J.Z. Zhang. *Int. J. Nanotechnol.* 1 (2004) 240.
- [26] H. Ehrhardt, S.J. Campbell , M. Hofmann. *Scripta Materialia* 48 (2003) 1141
- [27] H.S.C. O'Neill, *Eur. J. Mineral.* 4 (1992) 571.
- [28] J.C. Waerenborgh, M.O. Figueiredo, J.M.P. Cabral, L.C.J. Pereira, *J. Solid State Chem.* 111 (1994) 300.
- [29] A. Pavese, D. Levy, A. Hoser, *Am. Miner.* 85 (2000) 1497.
- [30] N.L. Pakhomova, V.N. Belogurov, V.A. Bylinkin, A.M. Vinnik, L.M. Kassimenko, P.E. Senkov, *Sov. Phys. Solid State* 19 (1977) 1060.
- [31] R.K. Puri, U. Varshney. *J. Phys. Chem. Solids* 44 (1983) 655.
- [32] C.N. Chinnasamy, A. Narayanasamy N. Ponpandian¹, K. Chattopadhyay, H. Gue´rault and J-M. Greneche. *Scripta mater.* 44 (2001) 1407.
- [33] L. Neel, *Magnetic properties of ferrites: ferrimagnetism and antiferromagnetism*, *Ann. Phys. Paris* 3 (1948) 137.
- [34] D.C. Jiles, *Introduction to Magnetism and Magnetic Materials*, second ed., Chapman & Hall, London, 1991.
- [35] E.C. Snelling, *Soft Ferrites: Properties and Applications*, second ed., Butterworths Publishing, 1989.
- [36] Q. Song, *Size and Shape Controlled Synthesis and Superparamagnetic Properties of Spinel Ferrites Nanocrystals*, Ph.D. Thesis, Georgia Institute of Technology, December 2005
- [37] <http://www.ndt-ed.org/EducationResources/CommunityCollege/MagParticle/Introduction/history.htm>.
- [38] http://www.irm.umn.edu/hg2m/hg2m_index.html (Hitchhiker's Guide to Magnetism Bruce M. Moskowitz).

- [39] http://www.vectorsite.net/tpqm_04.html.
- [40] <http://www.aacg.bham.ac.uk>.
- [41] D. S. Mathew, Ruey-Shin Juang, Chemical Engineering Journal, 129 (1-3), (2007) 51.
- [42] D. Zins, R. Massart, E. Auzans, E. Blums, Journal of Material Science, 34 (1999) 1253.
- [43] L.J Love, J.F. Jansen, T.E. Mcknight, Y. Roh, T.J.A Phelps, A Magnetocaloric Pump for Microfluid Applications IEEE Transactions on Nanobioscience, 3 (2004) 2.
- [44] E. O. Bermudez Torres , Design and Mechanical Characterization of a Magnetocaloric Pump, Ph.D. Thesis, University of Puerto Rico Mayagüez Campus, 2007.
- [45] M.Atif, S.K. Hasanain, M.Nadeem, Sol. Stat. Com. 138 (2006) 416.
- [46] A.H. Morrish, The Physical Principles of Magnetism, Wiley, New York,1965.
- [47] <http://www.mritutor.org/mritutor/superpar.htm>.
- [48] L Neel. Journal de Physique et le Radium, 15 (1954) 225.
- [49] R. H. Kodama, A. E. Berkowitz, E. J.McNiff, Jr. S. Foner. Phys. Rev. Lett. 77 (1996) 394.
- [50] R. H. Kodama, A. E. Berkowitz, E. J. McNiff, Jr. S. Foner. Mater. Sci., 643 (1997) 235.
- [51] R. H. Kodama, A. E. Berkowitz. Physical Review B: Condensed Matter and Materials Physics, 59 (1999) 6321.
- [52] <http://wikis.lib.ncsu.edu/index.php/Spinel>
- [53] L. Neel. Ann. Phys. Paris 3 (1948) 137.
- [54] D. Weller, A. Moser, L.Folks, M. E. Best, W. Lee, M. F. Toney, M. Schwickert, J. U. Thiele, M. F. Doerner. IEEE Trans. Magn. 36 (2000)10.
- [55] <http://mmrc.caltech.edu/FTIR/FTIRintro.pdf>.
- [56] B. D. Cullity, Elements of X-Ray Diffraction; 2 ed.; Department of Metallurgical Engineering and Materials Science, University of Notre Dame, 1978.
- [57] C. Giacovazzo. Ed. Fundamentals of Crystallography; 2 ed.; Oxford University Press: Oxford, 2002.

- [58] V. K. Pecharsky, Z. Y. Peter. Fundamentals of Powder Diffraction and Structural Characterization of Materials; Kluwer Academic Publishers: Boston, 2003.
- [59] [<http://www.dms-magnetics.com/pdf/vsmmost.pdf>.].
- [60] S.Hafner, Z.Krist., 115 (1961) 331.
- [61] R.D.Waldron, Phys.Rev. 99 (1955)1727.
- [62] F.A. Lopez, A. Lopez-Delgado, J.L.M. de Vidales, E. Vila, J. Alloys Compd. 265 (1998) 291.
- [63] G. Zhang, C. Li, F. Cheng, J. Chen, Sens. Actuators B 120 (2007) 403.
- [64] M.M.Bahout, S.Bertrand, O.Pena, J.SolidState Chemistry 178 (2005) 1080.
- [65] Z. Chen, L. Gao, Mater. Sci. Eng. B 141 (2007) 82.
- [66] Z.Q. Li, Y.J. Xiong, Y. Xie, Inorg. Chem. 42 (2003) 8105.
- [67] H.H. Huang, X.P. N'I, G.L. Loy, C.H. Chew, K.L. Tan, F.C. Loh, J.F. Deng, G.Q. Xu, Langmuir 12 (1996) 909.
- [68] Y.G. Sun, Y.N. Xia, Adv. Mater. 14 (2002) 833.
- [69] Y.I. Kim, D. Kim, C.S. Lee, Physica B 337 (2003) 42.
- [70] C. K. Kim, J. H. Lee, S. Katoh, R. Murakami, Mater. Res. Bull. 36 (2001) 2241.
- [71] J.G. Yu, X.J. Zhao, Q.N. Zhao, G. Wang, Mater. Chem. Phys. 68 (2001) 253.
- [72] a) H. Xue, Z. Li, X. Wang, X. Fu, Mater. Lett. 61 (2007) 347.
b) F. Li, H.Wang, L.Wang, J.Wang, J. Magn. Magn. Mater. 309 (2007) 295.
- [73] Y. Köseoğlu, A. Baykal, M. S. Toprak, F. Gözüak, A. C. Başaran, B. Aktaş, Journal of Alloys and Compounds, 462 (2008) 209.
- [74] a) R.N. Bhowmik, R. Ranganathan, J. Magn. Magn. Mater. 248 (2002) 101.
b) D.Fiorani, S. Vitiocoli, J.L. Dorman, J.L. Tholence, A.P. Murani, Phys. Rev. B 30 (1984) 2776; D. Fiorani, S. Vitiocoli, J. Magn. Magn. Mater. 49 (1985) 83.
- [75] T. Song, R.M. Roshko, IEEE Trans. Magn. 36 (2000) 223.
- [76] C.N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, H. Guerault, J. M. Gereneche, J. Phys.: Condens. Matter 12 (2000) 7795.
- [77] G.F.Goya, IEEE Trans. Magn. 38 (5) (2002) 2610.

- [78] N. Kasapoğlu, A. Baykal, Y. Köseoğlu, M.S. Toprak, Scripta Materialia 57 (2007) 441.
- [79] G. Vaidyanathan, S. Sendhilnathan, R. Arulmurugan, J. Magn. Magn. Mater. 313 (2007) 293.
- [80] V. Kumar, A. Rana, M.S. Yadav, R.P. Pant, Journal of Magnetism and Magnetic Materials 320 (2008) 1729.
- [81] M.S. Tomar, S.P. Singh, O. Perales-Perez, R.P. Guzman, E. Calderon, C. Rinaldi-Ramos. Microelectronics Journal, 36, (3-6), (2005), 475.
- [82] R.H. Kodama, A.E. Berkowitz, E.J. McNiff Jr., S. Foner, J. Appl. Phys. 81 (1997) 5552.
- [83] H. Nathani, R.D.K. Misra, Mater. Scie. And Eng. B 113 (2004) 228.
- [84] R.D. Sanchez, J. Rivas, P. Vaquerio, M.A. Lopez-Quintela, D. Caeiro, J. Magn. Magn. Mater. 247 (2002) 92.
- [85] H. Nathani, R.D.K. Misra, Mater. Sci. & Eng. B. 113 (2004) 228.
- [86] Zhigao Huang, Qian Feng, Zhigao Chen, Shuiyuan Chen, Youwei Du, Microelectronics Engineering 66 (2003) 128.
- [87] H. Kachkachi, M. Nogues, E. Tronc, and D.A. Garanin, J. Magn. Magn. Mater. 221 (2000) 158.
- [88] O. Iglesias and A. Labarta, Phys. Rev. B 63 (2001) 184416.
- [89] E. De Biasi, C.A. Ramos, R.D. Zysler, and H. Romero, Phys. Rev. B. 65 (2002) 144416.
- [90] R.D. Zysler, H. Romero, C.A. Ramos, E. De Biasi and D. Fiorani, J. Magn. Magn. Mater. 266 (2003) 233.
- [91] C. Liu, A. J. Rondinone, Z. J. Zhang, Pure Appl. Chem. 72(1-2)(2000) 37.
- [92] Y. Köseoğlu and H. Kavas. Journal of Nanoscience and Nanotechnology, 8 (2) (2008) 584
- [93] Y. Köseoğlu, H. Kavas, and B. Aktaş, Phys. Stat. Solid. (a) 203 (2006) 1595.
- [94] J.P. Chen, C. M. Sorensen, K. J. Klabunde, G.C. Hadjipanayis, E. Devlin, A. Kostas, Phys. Rev. B 54 (13) (1996) 9285.
- [95] M. Goerge, A. M. John, S. S. Nair, P.A. Joy, M.R. Anantharaman, J. Magn. Magn. Mater. 302 (2006) 190.
- [96] P.A. Joy, S.K. Date, J. Magn. Magn. Mater. 222 (2000) 33.

- [97] R.H. Kodama, A.E. Berkowitz, E.J. McNiff Jr., S. Foner, Appl. Phys. 75 (1994) 5639.
- [98] L. Zhao, H. Zhang, Y. Xing, S. Song, S. Yu, W. Shi, X. Guo, J. Yang, Y. Lei, F. Cao, Journal of Solid State Chemistry, 181 (2) (2008) 245
- [99] E.C. Stoner and E.P. Wohlfarth. Philos. Trans. R. Soc. A. 240 (1948) 599.
- [100] T. Ozkaya, A. Baykal, H. Kavas, Y. Köseoğlu, M.S. Toprak, Physica B: Condensed Matter, In Press, (2008), doi:10.1016/j.physb.2008.07.002.
- [101] S. Mukherjee, R. Ranganathan, S. B. Roy, Solid State Comm. 98 (1996) 321.
- [102] A. Baykal, N. Kasapoğlu, Y. Köseoğlu, M. S. Toprak, H. Bayrakdar, Journal of Alloys and Compounds. 464 (2008) 514.
- [103] G. Bertotti. Hysteresis in Magnetism: For Physicists, Materials Scientist, and Engineers. Academic Press: San Diego, (1998) 375.
- [104] D.A. Dimitrov and G.M. Wysin. Phys. Rev. B. 50 (1994) 3077.
- [105] X. Huang, Z. Chen, J. Magn. Mater. 280 (2004) 37.
- [106] S.A. Patil, V.C. Mahajan, A.K. Ghatage, S.D. Lotke, Mater. Chem. Phys. 57 (1998) 86.
- [107] B.K. Labde, C. Madan Sable, N.R. Shamkuwar, Mater. Lett. 57 (2003) 1651.
- [108] S.S. Bellad, R.B. Pujar, B.K. Chougule, Indian J. Pure Appl. Phys. 36 (1998) 598.
- [109] G.M. Bhongale, D.K. Kulkarni, V.B. Sapre, Bull. Mater. Sci. 15 (1992) 121.
- [110] M. Mouallem-Bahout, S. Bertrand and O. Pena, J. Sol. Stat. Chem. 178 (2005) 1080.
- [111] O. Carp, L. Patron and A. Reller, Mater. Chem. Phys., 101 (1) (2006) 142.
- [112] A. F. Junior, E. Celma de O. Lima, M. A. Novak, P. R. Wells Jr, Journal of Magnetism and Magnetic Materials 308 (2007) 198.
- [113] M.A. Gabal and S.S. Ata-Allah, Mater. Chem. Phys., 85 (2004) 104.
- [114] K. Tkacovba, V. Sepelak, N. Sterklora, V.V. Noldyrev, J. Solid State Chem. 123 (1996) 100.
- [115] V. Sepelak, U. Steinike, D. Chr. Uecker, S. Wißman, K.D. Becker, J. Solid State Chem. 135 (1998) 52.
- [116] T. Sato, K. Haneda, M. Seki, T. Iijima, Appl. Phys. A 50 (1990) 13
- [117] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, Materials Science and Engineering A, (304) (2001) 983

- [118] T.M. Clark, B.J. Evans, IEEE Trans. Magnetics 33 (1997) 3745.
- [119] J. Battle, T. Clark and B.J. Evans J. Phys. Coll. IV (7C1) (1997) 257.
- [120] V. Sepelak, M. Zatroch, K. Tkacova, P. Petrovic, S. Wißmann, K.D. Becker, Mater. Sci. Eng. A, Proc. RQ9 (Suppl.) (1997) 22.
- [121] J.Z. Jiang, P. Hymn, S. Morup, T. Okada, F.J. Berry, Nanostruct. Mater. 12 (1999) 737.
- [122] D.D. Awschalom, D.P. Divicenz, Phys. Today, 48 (1995) 43.
- [123] I.M.L. Bills, A. Chatselain, W.A. De Heer, Science 265 (1994) 1682.
- [124] K. Tkacovba, V. Sepelak, N. Sterklora, V.V. Noldyrev, J. Solid State Chem. 123 (1996) 100.
- [125] V. Sepelak, U. Steinike, D.Chr. Uecker, S. Wißman, K.D. Becker, J. Solid State Chem. 135 (1998) 52.
- [126] T. Sato, K. Haneda, M. Seki, T. Iijima, Appl. Phys. A 50 (1990) 13.
- [127] H.H. Hamedh, J.C. Ho, S.A. Oliver, R.J. Wiley, G. Oliveri, G. Busca, J. Appl. Phys. 81 (1997) 1851.
- [128] V. Sepelak, K. Tkacova, A.I. Rykov, Crystal. Res. Technol. 28 (1993) 53.
- [129] H.H. Hamedh, J.C. Ho, S.A. Oliver, R.J. Wiley, J. Kramer, Y.Y. Chen, S.H. Lin, Y.D. Yao, M. Daturi, G. Busca, IEEE Trans. Mag. 31 (1995) 3808.
- [130] M.R. Anantharaman, S. Jagatheesan, K.A. Malini, S. Sindhu, A. Narayanasamy, C.N. Chinnasamy, J.P. Jacobs, S. Reijne, H. Seshan, R.H.H. Brongersma, J. Magn. Magn. Mater. 189 (1998) 83.
- [131] H. Nathani, R.D.K. Misra, Mater. Scie. And Eng. B 113 (2004) 228.
- [132] D.N.H. Nam, K. Jonason, P. Nordblad, N.V. Kheim, N.X. Phuc, Phys. Rev. B 59 (1999) 4189.
- [133] S.Mukherjee, R.Ranganathan, S.B.Roy, Solid State Comm. 98 (1996) 321.
- [134] G.A. Pettit, D.W. Forester, Phys. Rev. B 4 (1971) 3912.
- [135] J.L. Dorman, M. Nogues, J. Phys.: Condens. Matter 2 (1990) 1223.
- [136] D. Fiorani, S. Vitticoli, Solid State Commun. 29 (1979) 239.
- [137] K.P. Belov, A.N. Goryaga, A.N. Lymzin, Sov. Phys. Solid State 30 (1988) 715.
- [138] R.N. Bhowmik, R. Ranganathan, Journal of Magnetism and Magnetic Materials 237 (2001) 27.
- [139] H.H. Hamdeh, J.C. Ho, S.A. Oliver, R.J. Willey, J. Kramer, Y.Y. Chen, S.H. Lin, Y.D. Yao, M. Daturi, G. Busca, IEEE Trans. Magn. 31 (1995) 3808.