

UNIVERSITY OF BAHRAIN

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Department of Physics

Characterization and Heat Generation Ability of Spinel Ferrite MFe_2O_4 Nanoparticles

A Thesis Submitted in Partial Fulfillment of the Requirements for the
Master Degree in Applied Physics

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APPROVAL PAGE

DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at University of Bahrain or other institutions.

Issam Al-Bitar

Signature

Date

DEDICATION

It was so hard to lose a person like you but your soul never left me and it will never do. My father, I dedicate this work to your soul and, hopefully, I could make you proud one day. The faith, the good personality and the patience you had, always inspire me to be a good person and to do the best I can in every single work. You will always be my hero. May your soul rest in peace.

You and my father devoted your lives to raise us. My mother, you have been the source of encouragement throughout my life. I dedicated this work to you because you always believe in me. I love you and I'll always be beside you. May ALLAH bless you.

At the end, being a teacher, a student, a father and a husband at the same time is not simple. However, your presence in my life make it easy going. I know I made many days in our life very hard, but your continuous support and understanding made all of this possible. My wife, Randa, and my son, Fouad, you are everything for me. You are my life. May ALLAH bless both of you.

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ABSTRACT

Four spinel ferrite magnetic nanoparticles (SFMNPs): cobalt ferrite (CoFe_2O_4), nickel ferrite (NiFe_2O_4), copper ferrite (CuFe_2O_4) and zinc ferrite (ZnFe_2O_4) were synthesized by the modified sol-gel technique and then annealed at 1000 °C for 5 h. Their crystallographic, morphological, microstructural, and magnetic properties have been studied. X-ray diffraction (XRD) confirmed the spinel cubic structure with the $Fd\bar{3}m$ space group of all the NPs and the single crystalline phase of two as-prepared NPs: NiFe_2O_4 and CuFe_2O_4 . However, both, CoFe_2O_4 and ZnFe_2O_4 , as-prepared NPs revealed the presence of additional peaks of CoO and ZnO with α - Fe_2O_3 respectively. Moreover, the crystallite size (CS) varied between 16 and 40 nm. Rietveld analysis showed single crystalline phase and an increase in CS for all the annealed samples, where CS ranged between 25 and 73 nm. Characteristic magnetic parameters were determined by vibrating sample magnetometer (VSM). Room temperature ferrimagnetic behavior was confirmed by VSM measurements. The saturation magnetization (M_s) was found to decrease in the order $\text{NiFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 \gg \text{ZnFe}_2\text{O}_4$ under the same synthetic method and annealing temperature. The specific absorption rate (SAR) which is released on the exposure of the ensemble of synthesized particles to an alternating electromagnetic field is calculated using experimental measurements. The highest SAR value was for the annealed CuFe_2O_4 (65.6 W/g) with the least CS (26 nm). It is believed that hysteresis loss is behind the dissipation of heat by the studied SFMNPs. Thus the annealed CuFe_2O_4 can be considered as potential candidates for biomedical applications among the others.

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CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

On December 29, 1959, Richard Feynman said “There is plenty of room at the bottom” (Appenzeller, 1991). Although the American Nobel Laureate physicist at Caltech¹ knew that engineering materials and devices on the very small size scales would have an influence on the technology of the future, he did not realize that this would pave the road to a new technological revolution, the Nano-revolution. Nowadays, nanoscience is a major and central field in science where its technological application, known as Nanotechnology, is spreading rapidly. This is taking place in many fields such as medicine (Shao *et al.*, 2010), material engineering (Bao *et al.*, 2015), industrial chemistry and environmental cleanup applications (Akbarzadeh *et al.*, 2012). But what makes the synthesis of materials and structures on small scales the key to such a revolution?

1.1 Nanotechnology and Magnetic Nanoparticles

Nanotechnology is the ability to manipulate and control materials in the nanoscale regime. It comprises science, engineering and technology conducted at very small scale in the range of 1 to 100 nm. To put this size scale into perspective, we imagine the diameter of the Earth as measuring one meter then a marble would represent a nanometer. When the size of a material structure is reduced to such a small scale, its physicochemical properties will differ from those of the bulk counterpart. The novel

¹ Caltech : California Institute of Technology

phenomena appear leading to new applications and devices (Berry and Curtis, 2003).

Magnetic nanoparticles (MNPs) show enhanced and unique properties such as high surface-to-volume ratio, controllable size and shape, bioactive molecule conjugation capability with no toxicity (Lima *et al.*, 2013), guidance by magnetic fields, and heat dissipation under alternating magnetic field (AMF) gradients (Lin *et al.*, 2010; Tartaj *et al.*, 2003). The higher surface area is, the more reactions can be carried out on the surface. Moreover, small size of tens of nanometers enable MNPs to evade reticuloendothelial (or macrophage) system of the body and penetrate the capillaries within the tissues and other biological molecules such as a virus (20 – 450 nm), a protein (5 – 50 nm) and a cell (10 – 100 μm) (Moghimi *et al.*, 2001; Pankhurst *et al.*, 2003). Thus, after being coated with biocompatible polymers, MNPs can be directed by external AMF toward tumors and locally generate sufficient heat to release the drug, hence destroy the infected cells (Giustini *et al.*, 2010). Such characteristics make MNPs potential candidates for many applications including target drug delivery, hyperthermia agent, magnetic resonance imaging (MRI) contrast enhancement, and magnetic separation (Kashevsky *et al.*, 2015; Yadollahpour and Rashidi, 2015).

1.2 Spinel Ferrites and their Properties

A major class of MNPs is spinel ferrites (SFs) with general molecular formula MFe_2O_4 , where M is a metal cation, often Zn, Cd, Fe, Mn, Ni, Cu, Co, or Mg. Ferrites are ceramic oxide materials composed of two types of positively charged metallic cations, divalent (M^{+2}) or trivalent (Fe^{+3}), and negatively charged nonmetallic anions. Compared to ferromagnetic

materials, ferrites have a reduced net magnetic moment and higher electrical resistivity (Kittel, 2004). This very large resistivity forces the applied AMF not to induce eddy currents in ferrites thereby allowing the latter to be used in high-frequency applications such as telecommunications and radar systems (Callister and Rethwisch, n.d.). Electrochemical sensing properties, such as high surface areas, moderate conductivities, and excellent biocompatibilities, make SFs ideal candidates for fabricating electrochemical sensors for some biological molecules such as hydrogen peroxide (H_2O_2), which is an oxidative stress marker in age-related diseases including Alzheimer's disease, cardiovascular disorders and cancer (Liu *et al.*, 2017; Guo *et al.*, 2013). Some SFs have a high potential capability in the field of photocatalysis. Due to their various properties such as low band gap (1.1 – 2.3 eV), good chemical stability, magnetic recyclability, magento-resistive and magneto-optical properties, cobalt ferrites (CoFe_2O_4) and zinc ferrites (ZnFe_2O_4) can act as magnetic photocatalyst. They facilitate and speed up the decay of organic dyes such as Rhodamine B which is used as a colorant in leather, textile, food and cosmetics industries. The degradation of such dyes in colored wastewater under solar irradiation is of substantial interest, therefore solving many issues regarding energy, sanitation and environment (Sundararajan *et al.*, 2017; Behera *et al.*, 2018). The increasing demand on electrical devices in the fields of electronics and energy storage has attracted the development of supercapacitors that possess high power density and long cycle lifetime, compared to conventional capacitors and rechargeable batteries. Li *et al.* synthesized supercapacitor electrode containing ZnFe_2O_4 NPs loaded on the surface of nitrogen-doped graphene and showed ideal electrical performance (Li *et al.*, 2017). Furthermore, SFMNPs are suitable for biomedical applications such as magnetic hyperthermia for cancer therapy. It is a promising method which is used by itself or as a help to

chemotherapy, radiotherapy and photodynamic therapy (Zélis *et al.*, 2013; Mameli *et al.*, 2016). Magnetite (Fe_3O_4) is one of SFs that has been suggested by many researchers over the past years as a suitable candidate in biomedical applications (Thapa *et al.*, 2004; Rashdan *et al.*, 2013; Hayashi *et al.*, 2014). However, its iron atoms are poorly distinguishable from those of hemoglobin in the blood and its magnetic saturation is reduced by decreasing the size of the NPs (Sharifi *et al.*, 2012). Hence, using MFe_2O_4 is more favorable over using magnetite especially in magnetic hyperthermia. They can be easily coated with hydrophilic and biocompatible biological entities and have posed cytotoxic potential (Alhadlaq *et al.*, 2015; Salunkhe *et al.*, 2016; Ahamed *et al.*, 2016). In addition, they exhibit significant saturation magnetization as well as thermal and colloidal stabilities that make the interest in exploring their role in diagnosis and treatments of many diseases growing rapidly (Gupta and Gupta, 2004; Cullity and Graham, 2009).

1.3 Thesis Outline

Spinel ferrites magnetic nanoparticles (SFMNPs) have received particular attention in nanotechnology due to their significant properties and their use in a variety of applications. For the past few decades, extensive researches were devoted to SFMNPs showing these particles to be promising in the treatment of many problems and diseases especially cancer (Zhang *et al.*, 2017), which is one of the most widespread diseases affecting almost every person either directly or through a loved one. The chemical composition and microstructural features of the SFs, and consequently their synthetic process, affect their properties and heating abilities (Tatarchuk *et al.*, 2017; Yadavalli *et al.*, 2016; Tomitaka *et al.*, 2010). Various synthetic routes for preparing SFMNPs are continuously

reported in the literature including sol-gel (Lemine *et al.*, 2012; Raghavender, 2014; Kareiva *et al.*, 2011), microemulsion (Mathew and Juang, 2007), citrate precursor method (Kumar *et al.*, 2013), hydrothermal process (Nejati and Zabihi, 2012), polymerized complex method (Montemayor *et al.*, 2005), co-precipitation/mechanical milling (Al-Saie *et al.*, 2011; Marinca *et al.*, 2012), mechanochemical method (Ž. Lazarević *et al.*, 2013) and microwave combustion method (Manikandan *et al.*, 2013). The variation of synthetic routes has led to differences in magnetic, thermal and other properties of the same ferrite (Rashdan *et al.*, 2013). Al-Najar *et al.* reported the sensitivity of crystallite size and saturation magnetization of MgFe_2O_4 upon using two different techniques, sol-gel and modified sol-gel methods (Al-Najar *et al.*, 2016). Meanwhile, comparative studies devoted to the characterization and self-heating ability of different SFs under the same conditions including synthetic process, annealing temperature and concentration in distilled water are largely lacking in the literature. Therefore, it is necessity to undertake an in-depth analysis of the characteristics of some SFMNPs under the same conditions.

In this research project, MNPs of four SFs (CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 and ZnFe_2O_4) were prepared using the modified sol-gel method. It has been demonstrated that sol-gel technique is a facile method that offers considerable advantages such as simplicity in preparing NPs, low preparation temperature, high reaction rate and excellent chemical homogeneity in the final product (Al-Najar *et al.*, 2016). Furthermore, arbitrary particle size, appropriate size distribution and strong magnetic properties can be achieved (Sanpo *et al.*, 2013). The synthesized SFMNPs were characterized using various instruments to explore their structural, morphological and magnetic properties. Finally, an assessment of heat generation ability of the SFs under AMF took place by varying the particle concentration (5 and 15 mg MNPs/mL distilled water) and studying the

effect of concentration and annealing on specific absorption rate (SAR), which represents the power for which the magnetic material is heated per gram of that material. The samples studied in the present work represent classes of materials that are being intensively investigated for magnetic hyperthermia and do not represent materials achieving the best SAR values. They could serve the purpose of introducing the comparison between four different SFs under the same synthetic and analytic conditions.

CHAPTER 2

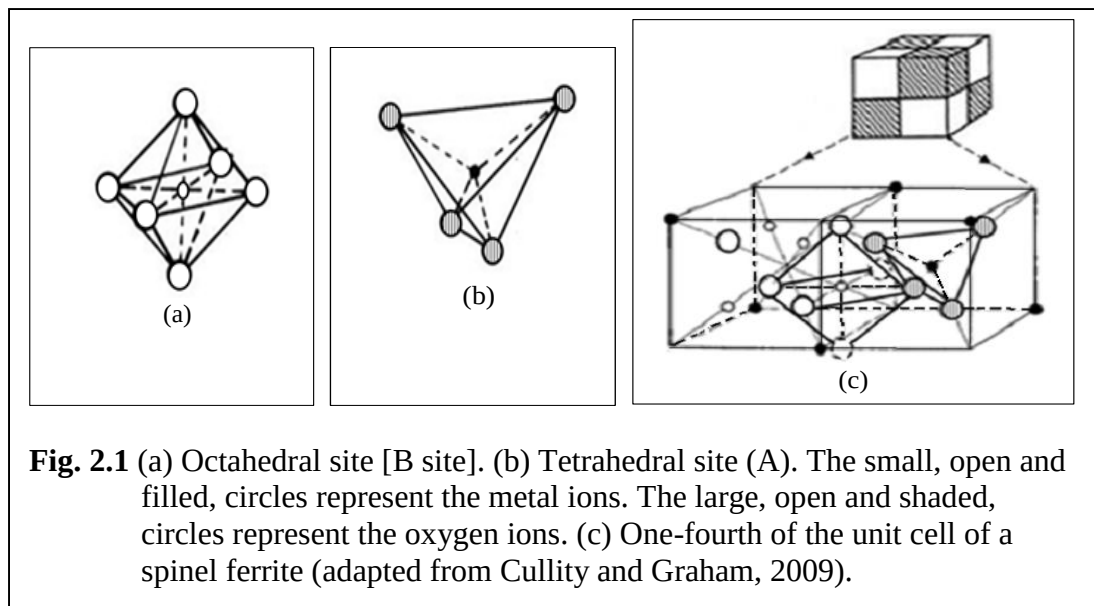
BACKGROUND AND HISTORY

CHAPTER 2

BACKGROUND AND HISTORY

2.1 Crystal Structure of Spinel Ferrites

Spinel ferrites are usually non-conductive ceramic compounds derived from iron oxides as well as oxides of other metals. The origin of the name “spinel” results from 32 divalent oxygen anions (O^{-2}), that crystallize in face-centered cubic (FCC) structures belonging to the space group $Fd\bar{3}m$. SFs can be represented in the following way: $(A)_t[B_2]_o O_4$, where the subscripts ‘t’ and ‘o’ stand for tetrahedral (A sites) and octahedral (B sites) coordination respectively. They are divided into 3 types: normal, inverse, and mixed spinels according to the distribution of the 24 metal cations at 8 out of 64 available tetrahedral (A) sites, and 16 out of 32 available octahedral [B] sites with oxygen coordinating to the central ion (Valenzuela, 2012). Fig. 2.1 shows one fourth of unit cell of the SF in addition to the distribution of oxygen anions around (A) and [B] sites.



The ferrite is normal spinel when (A) and [B] sites are filled with M^{2+} and Fe^{3+} respectively. Bulk $ZnFe_2O_4$ has a normal spinel structure and exhibits mixed spinel structure in nanoregime, where part of zinc ions occupy the [B] sites and part of iron ions occupy the (A) sites (Najafi Birgani *et al.*, 2015). $CoFe_2O_4$, $NiFe_2O_4$, and $CuFe_2O_4$ have partially inverse structure where (A) sites are fully occupied by Fe^{3+} and [B] sites are randomly, but equally, occupied by M^{2+} and Fe^{3+} . In general, $(M_{1-x} Fe_x)_t [M_x Fe_{2-x}]_o O_4$ can be used where 'x' is the degree of inversion (defined as the fraction of (A) sites occupied by Fe^{3+} cations). If $x = 0$ the spinel is normal while $x = 1$ gives purely inverse spinel (Ž. Lazarević *et al.*, 2013; Marinca *et al.*, 2012).

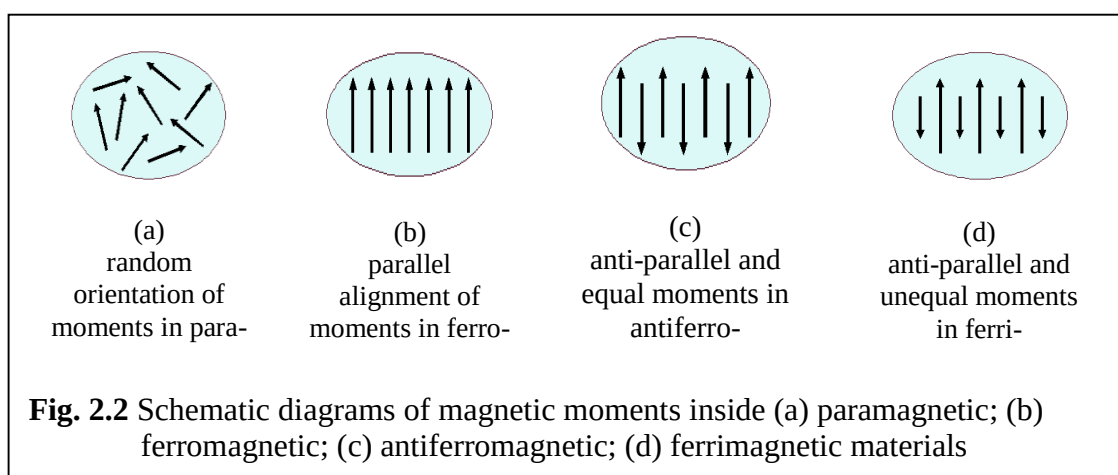
2.2 Magnetism in Matter

The origin of magnetism inside matter comes from atomic magnetic dipoles. Materials can be classified into five basic magnetic categories depending on their response against an external AMF. This can be achieved by examining their magnetic moments that are aligned within domains and are mainly due to the presence of the electrons in atoms because the nucleus has negligible magnetic moment compared to that of electrons. Since the electron orbits the nucleus and possesses its own intrinsic spin, it has two types of magnetic moments. The total magnetic moment of a sample of material is the vector sum of the magnetic moments of all domains (Cullity and Graham, 2009). According to the direction of electronic moments and their sizes, materials can be classified and described briefly herein:

- *Diamagnetic*: Diamagnetism is a quantum mechanical effect that occurs in all materials. It is a weak effect and is only observed when a material does not possess any other magnetic property. The inner atomic

orbital shells are filled and there are no unpaired electrons. The moments of their electrons are directed such that they cancel out, thus the net magnetic moment is zero. In the presence of an applied field, they have negative and small susceptibility, which is independent of temperature, since they create an induced magnetic field opposite to the applied field. When the field is removed, the diamagnetic material loses its magnetism quickly. The magnetization (M) vs. applied magnetic field (H) curve (Fig. 2.3(a)) is linear under normal conditions (e.g., water and calcite CaCO_3). All the other categories of magnetic materials have net magnetic moment due to unpaired electrons in partially filled orbitals, often in the 3d or 4f shells of each atom (Buschow and Boer, 2002).

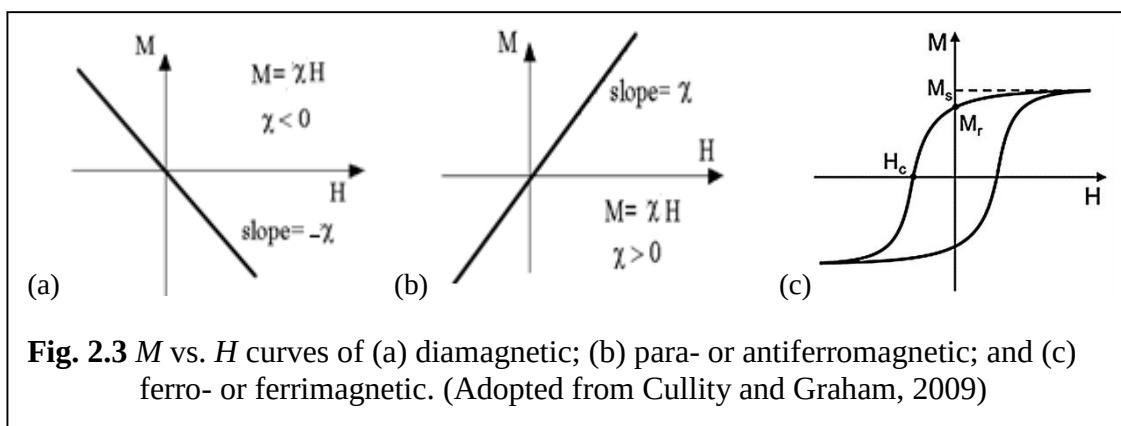
- *Paramagnetic*: At room temperature and in the absence of magnetic field, their moments are oriented randomly (Fig. 2.2(a)). Although there is a net magnetic moment but they still do not interact magnetically. Hence M of the sample as a whole is zero. In the presence of an AMF, the moments align in the same direction as the field so the materials acquires positive and small susceptibility which is independent of H (except for very low temperature or very high field). If the applied field is sufficiently large (order of 100 T; T stands for tesla), the material reaches its maximum saturation magnetization (M_s). But since the largest magnets can provide fields only in the order of 10 T, paramagnets have not



been achieved experimentally. When the field is removed, the material loses its magnetism. The M - H curve is linear under normal conditions (Fig. 2.3 (b)); e.g., pyrite (sulfide) FeS_2 (Buschow and Boer, 2002, Kittel, 2004).

- *Ferromagnetic*: their crystalline structure allows strong coupling interactions between the atomic moments produced by electronic exchange forces. Their moments are aligned in parallel (Fig. 2.2 (b)) resulting in a large net M even in the absence of H . They have high susceptibility (very high compared to paramagnetic materials) and reach M_s , which is the maximum induced magnetic moment that can be obtained in the magnetic field. M_s is an intrinsic property that is independent on particle size but dependent on temperature. The magnetization curve (Fig. 2.3 (c)) is nonlinear and forms a hysteresis loop (e.g., Fe, Co and Ni) (Sorensen, 2001).

- *Antiferromagnetic*: the moments of neighboring atoms are equal and aligned anti-parallel so the net moment is zero (Fig. 2.2 (c)). However the material acquires magnetization when the field is applied. Their susceptibility is positive and small. The M - H curve is linear under normal conditions (Fig. 2.3 (b)). They lose their magnetization when the applied field is removed. We can differentiate between antiferromagnetic and paramagnetic materials only if the magnetic measurements extend over a range of temperature (e.g., ferrous oxide FeO , troilite FeS and ilmenite FeTiO_2) (Cullity and Graham, 2009).



- *Ferrimagnetic*: their domains have opposing and unequal moments which result in a net magnetic moment (Fig. 2.2 (d)). They do not lose their magnetism even if the applied field is removed. Ferrimagnetism exhibits all the characteristics of ferromagnetic behavior: spontaneous magnetization, Curie temperatures, hysteresis and remanence (Fig. 2.3 (c)). At large H , M is constant at its saturation value M_s . After saturation, a decrease in H to zero doesn't reduce M to zero. Instead, M goes to remanent magnetization (M_r). M decreases to zero when the field is reversed and reaches coercivity field (H_C), so H_C is the required field to completely demagnetize the material. However, ferrimagnetic materials have very different magnetic ordering. One can differentiate between ferri- and ferromagnetism if the measurements extend over a range of temperature. At low temperature, below Curie temperature (T_C), ferrimagnetic material shows ferromagnetic behavior. However, it behaves as paramagnets at temperature higher than T_C . Examples: Fe_3O_4 , CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 (Mathew and Juang, 2007; Coey, 2010).

2.2.1 Magnetic Interactions in Spinel Ferrites

SFs acquire their magnetic behavior due to the crystal structure and cation distribution. Néel postulated the existence of exchange interactions between electrons of ions in (A) and [B] sites in the crystal lattice. These interactions are mediated by the oxygen ions. Three probable superexchange interactions are suggested in the ferrites as follows: A–A, B–B, and A–B interactions. The interactions between the cations of sublattices (A) and [B] are much stronger than the intra-sublattice interactions A–A. The B–B interaction is the weakest (Prévoit and Dunlop, 2001). On one hand, the magnetic moments of cations in (A) sites, as well

as in [B] sites, are aligned parallel with respect to each other. On the other hand, the magnetic moments in (A) sites are directed antiparallel to the ones in [B] sites. Since the number of occupied [B] sites is double than that of (A) sites then there is net magnetic moments and SFs exhibit ferrimagnetic behavior. These interactions may cause aggregation and agglomeration that stand as a major obstacle to overcome during synthesis because MNPs have high tendency to reduce the energy associated with the high surface-to-volume ratio (Noor *et al.*, 2013). To overcome aggregation, a broad size particle distribution of superparamagnetic and ferrimagnetic NPs can be considered and thus reducing their dipole-dipole interactions (Hergt *et al.*, 2009). In addition, the use of some specific agents can reduce the effect of agglomeration and hence single phase nanoparticles are obtained. Özdiñer *et al.* reported the use of monoethylene glycol (MEG) as a capping agent for this purpose (Özdiñer *et al.*, 2017).

2.2.2 Single Domain Particles and Magnetic Anisotropy

In bulk ferrimagnetic materials, there exist magnetic domains separated by walls which have characteristic width and energy associated with their formation. Each domain contains magnetic moments oriented in the same direction but with magnetization randomly oriented with respect to its neighbor domains. Thus, the net magnetization of the material is zero. In the presence of an external AMF, the magnetization is a function of domain wall movement and size (Giustini *et al.*, 2010). As particle size in a material decreases below 100 nm, a large fraction of the constituent atoms are found on the surface of the nanocrystals initiating significant changes in the physical properties at nanometer scale as compared to their bulk counterparts. Single domain particles are formed below a critical diameter

where domain wall formation is not energetically favored anymore. The magnetization of these particles can result from coherent rotation of magnetic moments about preferable orientation (easy axis). The energy required to do rotation in non-easy direction is dominated by anisotropy energy, the dependence of the magnetic properties on the direction of the applied field with respect to the crystal lattice. This energy is expressed in terms of certain anisotropy constants and the direction to which the magnetization is rotated (Chen *et al.*, 2013).

Generally, four different mechanisms control the heat generation of a material under an external AMF: (1) dielectric losses in a material of low electrical conductivity; (2) generation of eddy currents in a material of high electrical conductivity; (3) relaxation losses due to the physical rotation of anisotropic magnetic particle and; (4) hysteresis losses in a magnetic material (Giustini *et al.*, 2010). Particularly, the third and the fourth mechanisms account for SFMNPs because such particles are too small and the AC field frequencies, used in biomedical applications, are much low to generate eddy currents and dielectric losses (Pankhurst *et al.*, 2003). This generated heat can make SFMNPs powerful agents in many applications in biomedicine such as hyperthermia. The best choice for hyperthermia is a magnetic material which possesses high M_S and T_C while being bio-compatible at the same time. T_C is the temperature above which the material loses its magnetism and thus its ability to generate heat. It has been considered that a MNP used in hyperthermia has only one magnetic moment $\mu = M_S \cdot V$, where $V = 4\pi R^3/3$ is the volume of the magnetic core of the NP, assuming nearly spherical particles. The fluctuation of μ in the presence of applied field causes heat dissipation. Mamiya reported an overview discussing the heating mechanisms of superparamagnetic and ferrimagnetic NPs (Mamiya, 2014).

2.2.3 Heating Mechanisms of Magnetic Nanoparticles

The function of MNPs as heat generators is parameterized by the SAR value, usually measured for a stable fluid suspension of MNPs. SAR must be maximized to optimize the heating efficiency. It is calculated by direct calorimetric measurement according to equation (1) (Reyes-Rodríguez *et al.*, 2017)

$$SAR = \frac{c}{m} \times \frac{\Delta T}{\Delta t} \quad (1)$$

Where m is the ferrite mass in the fluid per unit mass of fluid, $\Delta T/\Delta t$ is the slope of the temperature vs. time curve and c is the specific heat capacity of the distilled water (4.18 J.g^{-1}). When they are exposed to an AMF, these particles become powerful heat sources where their magnetic moments overcome an anisotropy energy barrier to realign with the AMF. This self-heating can occur by hysteresis and relaxation losses due to the physical rotation of anisotropic magnetic particles (Singh *et al.*, 2009). So when MNPs are guided by magnetic field gradient or injected into the tumor, it is warmed up to 42°C and is consequently destroyed. Continuous investigations have reported the ability of SFMNPs to generate heat at a temperature within the appropriate range for hyperthermia ($42 - 47^\circ\text{C}$), therefore, cancer cells are killed while the healthy ones remain unaffected (Jasso-Terán *et al.*, 2017). Additionally, MNPs act like a switch to “turn off” the heat once they reach T_c . Hence, and in the presence of the external magnetic field, they cannot generate heat anymore which is harmful for the human body (Zargar and Kermanpur, 2017).

The magnetization of MNPs can be plotted against the applied field, as shown in Fig. 2.2 (c). The area enclosed by the hysteresis loop is related

to the amount of energy dissipation upon reversal of the field from $H(M_S)$ to $H(-M_S)$ and back. It is determined by M_S , coercivity (H_C) and remnant magnetization (M_r) (Cullity and Graham, 2009). Relaxation loss includes the Brownian relaxation (BR) loss where the magnetic moments rotate with the entire particles and the Néel relaxation (NR) loss where the magnetic moments rotate without the motion of the particle (Yelenich *et al.*, 2014). Tomitaka *et al.* reported that at high frequency and when NiFe_2O_4 MNPs showed superparamagnetic behavior (superpara-magnetism is characterized by relatively high net magnetic moment and absence of interaction between single domain particles), the generated heat is due to relaxation loss and mainly NR loss since they used dried powder. However, the generated heat was due to hysteresis loss for the samples that exhibited ferrimagnetic behavior (Tomitaka *et al.*, 2010).

The total power loss to heat is given by the product of frequency of the AMF and the area of the hysteresis loop. The general equation is given by equation (2) (Pankhurst *et al.*, 2003):

$$P = \mu_0 f \int_{-H_{max}}^{H_{max}} M(H) dH \quad (2)$$

Where μ_0 is the permeability of the free space and equals to $4\pi \times 10^{-7} \text{ H.m}^{-1}$, M is the magnetization and H is the applied magnetic field. For the used SFMNPs, there is no implicit frequency dependence in the integral of equation (2), so P can be readily determined from the measurements of the hysteresis loop using VSM apparatus. The NR time (τ_N) can be expressed by equation (3) (Mamiya, 2014) as:

$$\tau_N = \tau_0 e^{KV/k_B T} \quad (3)$$

And the BR time (τ_B) is given by equation (4) (Mamiya, 2014) as:

$$\tau_B = 3\eta V_H / k_B T \quad (4)$$

Where τ_0 is the average relaxation time in response to a thermal fluctuation and approximately equals to $10^{-9}s$, K is the effective magnetic anisotropy constant, V is the magnetic volume of the particle, k_B is the Boltzmann constant, T is the absolute temperature, η is the dynamic viscosity of carrier liquid and V_H is the hydrodynamic volume of the nanoparticles. As it can be seen from equations (3) and (4), both NR and BR times are highly sensitive to the particle size. While τ_N increases exponentially, τ_B grows linearly with the particle dimension. If both times take place then we define an effective relaxation time τ_{eff} using equation (5) (Mamiya, 2014)

$$\tau_{eff}^{-1} = \tau_N^{-1} + \tau_B^{-1} \quad (5)$$

The power dissipated in the MNPs due to the application of AMF of maximum strength H and frequency f depends on the magnetic spin relaxations of the MNPs and is given by equation (6) (Mamiya, 2014) as

$$P = \mu_0 \chi H^2 \frac{2\pi^2 f^2 \tau_{eff}}{1 + (2\pi f \tau_{eff})^2} \quad (6)$$

where χ is the magnetic susceptibility.

2.3 Previous Studies

The investigations of MNPs have shown promising improvements in treating some types of cancer via hyperthermia. The story has started in

1957 with Gilchrist *et al.* who used AMF to heat iron oxides dispersed in lymph nodes and kill lymphatic metastases (Gilchrist *et al.*, 1957). However, the reported temperature rise was due to the high frequency of the magnetic field being used (1.2 MHz) rather than the heat given by the MNPs. Experiments were carried on and Jordan *et al.* injected ferromagnetic NPs into tumors and heat was generated by the NPs using AMF (Jordan *et al.*, 1993). Further progress has been made in studying the response of MNPs to magnetic fields and the way their properties are controlled and used in magnetic separation, drug delivery, hyperthermia treatments and MRI contrast enhancement (Pankhurst *et al.*, 2003). Recent studies have shown the potential capability of SFMNPs in magnetic fluid hyperthermia. Kim *et al.* showed that CoFe_2O_4 could be used to achieve the desired heating necessary for drug delivery and hyperthermia. They reported a hyperthermia temperature range of 42 – 45 °C that can kill the tumor cells using a field strength range of 101 – 157 Oe and frequency range of 0.15 – 1.1 MHz (Kim *et al.*, 2008). Tomitaka *et al.* reported the self-heating of NiFe_2O_4 NPs by hysteresis loss where the ones of size 130.7 nm had shown the highest temperature rise and heat generation ability, within the excitation conditions considering human safety, among the range of 7.7 – 242.0 nm (Tomitaka *et al.*, 2010). Sharifi *et al.* presented literature survey on the synthetic method, magnetic properties and heat generation mechanism of some ferrites. They listed a summary of SAR values of three spinel ferrites (CoFe_2O_4 , manganese ferrite and magnetite) with different initial conditions like synthetic route (so different particle size), applied field and frequency. The highest SAR value was reported for CoFe_2O_4 (396 W g⁻¹) prepared by thermal decomposition method (Sharifi *et al.*, 2012). Esmaeili and Alizadeh Hadad synthesized superparamagnetic ZnFe_2O_4 NPs coated with chitosan and loaded with drug doxorubicin hydrochloride. The heating mechanism of the NPs was Brownian

relaxation and the reported SAR value was 80.66 W g^{-1} (Esmaeili and Alizadeh Hadad, 2015). Salunkhe *et al.* investigated the effect of magnetic field intensity and particle concentration of superparamagnetic NPs of CoFe_2O_4 . They showed that SAR values decreased with increasing particle concentration, whereas they increased with increase in the magnetic field intensity. The reported SAR value was 91.84 W g^{-1} for 5 mg mL^{-1} (Salunkhe *et al.*, 2016). In addition to all the foregoing, Kombaiah *et al.* prepared CuFe_2O_4 NPs by conventional and microwave combustion methods. The average particle size was in the range of 50 – 200 nm and the particles exhibited ferromagnetic behavior. SAR value was 14.63 W g^{-1} (Kombaiah *et al.*, 2018).

CHAPTER 3

EXPERIMENTAL PROCEDURE

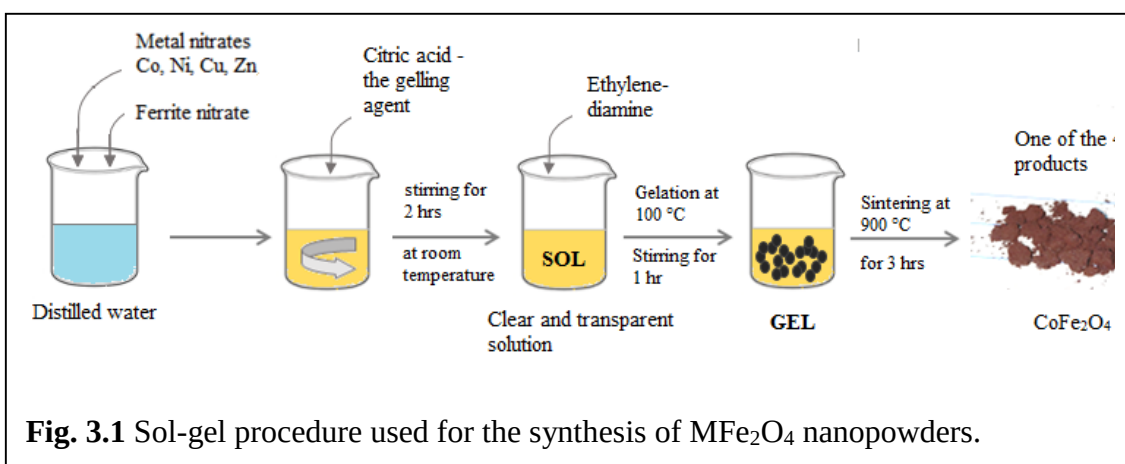
CHAPTER 3

EXPERIMENTAL PROCEDURE

In the present investigation, work was conducted over four spinel ferrites: CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 and ZnFe_2O_4 . The powders were synthesized using the modified sol-gel method. Some amount of each SF powder was annealed; therefore, obtaining four as-prepared and four annealed samples. Their structures and microstructure (size and shape) as well as morphology were characterized using X-ray diffractometer (XRD) and field emission scanning electron microscope (FE-SEM) respectively. Next, magnetic properties of the samples were studied using vibrating sample magnetometer (VSM). Finally, the magnetic hyperthermia measurements were performed using MagneTherm system in order to optimize the heating properties depending on various parameters such as frequency and magnetic field as well as MNPs/Solution mass ratio.

3.1 Synthesis of MFe_2O_4 Nanoparticles

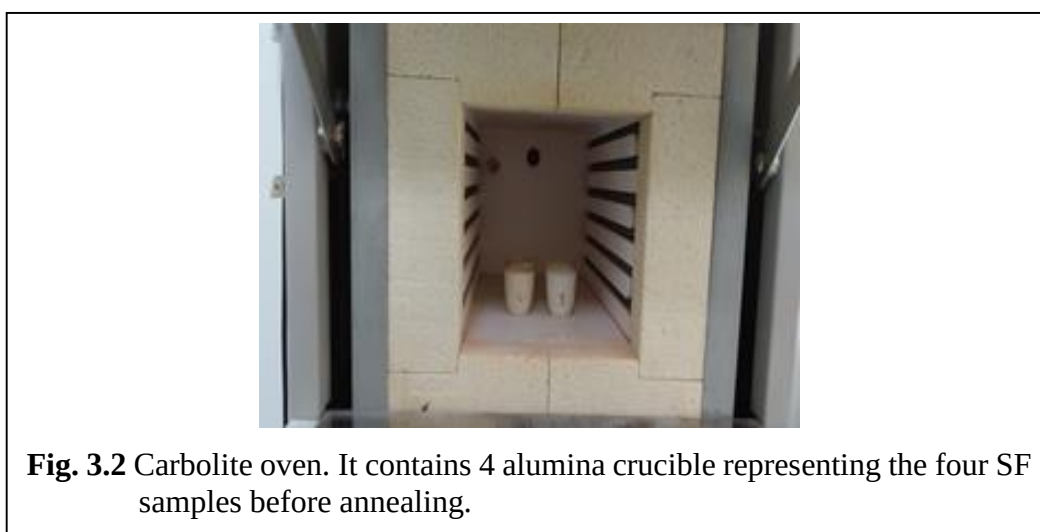
MFe_2O_4 (M= Zn, Cu, Ni, Co) NPs were prepared by the modified sol-gel technique. All the used reagents were of analytical grade obtained from Merck, India. Calculated amount of these metal nitrates ($\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in double distilled water and citric acid was added as the gelling agent. The resulting solution was stirred at room temperature for 2 hours to get clear, transparent and homogenous solution. Its pH was adjusted to 9 by adding ethylenediamine. The resultant solution was kept for gelation at 100 °C with constant stirring



for approximately 1 hour from which the catalysts in the form of powder was obtained. Later, these powders were annealed at 900 °C at a heating rate of 5 °C min⁻¹ for 3 h in an air atmosphere. The sample code was M-AP, where AP stands for as-prepared.

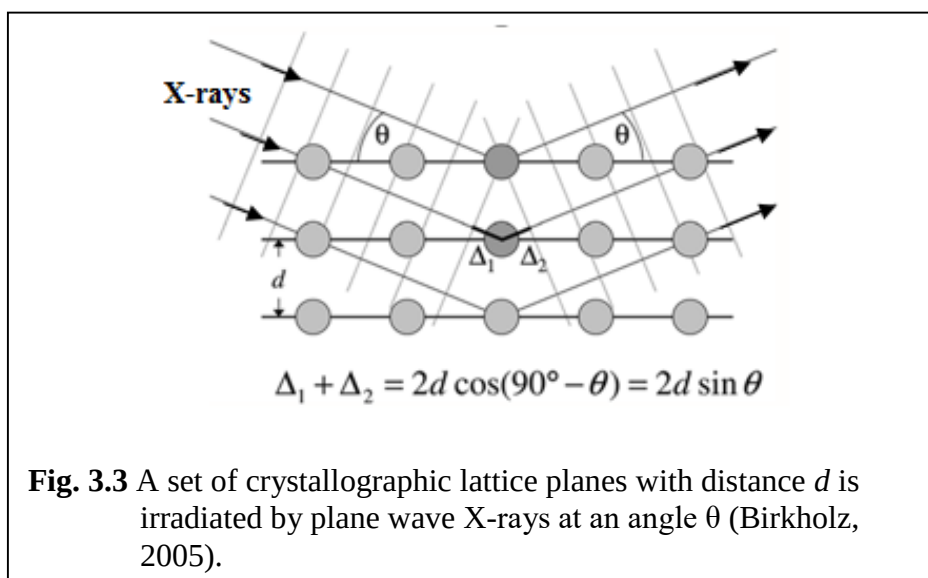
3.2 Annealing

Amounts of each sample of MFe_2O_4 – AP were subjected to annealing under air in a Carbolite oven as shown in Fig. 3.2. The nanopowders were put in alumina crucible then introduced into the oven. The annealing conditions are: T=1000 °C for 5 h using a heating/cooling rate of 10 °C min⁻¹. The sample code was M-A, where A stands for annealed.



3.3 X-ray Powder Diffraction

XRD is a useful structural characterization technique used to determine the crystalline phase of a sample. The crystal is modeled as a set of discrete parallel planes separated by a constant parameter d (Fig. 3.3). The incident X-rays of wavelength λ would produce very strong intensities, known as Bragg peaks, if their reflections off the various planes interfered constructively. The interference is constructive when the phase shift, comprised of Δ_1 and Δ_2 , is a multiple of 2π . This condition can be explained by Bragg's law $n\lambda = 2d\sin\theta$, where n represents the the reflection order and θ is the angle between the incident rays and the scattering planes. Bragg peaks are located in a diffraction pattern, obtained by measuring the intensity of scattered waves as a function of scattering angle, at the points where the scattering angles satisfy the Bragg condition. By comparing the diffraction pattern from a sample to the pattern reported in the powder diffraction file provided by the Joint Committee on Powder Diffraction Standards (JCPDS), which is nowadays called the International Centre for Diffraction Data (ICDD), the lattice planes of the sample and the crystalline structure can be determined (Birkholz, 2005).

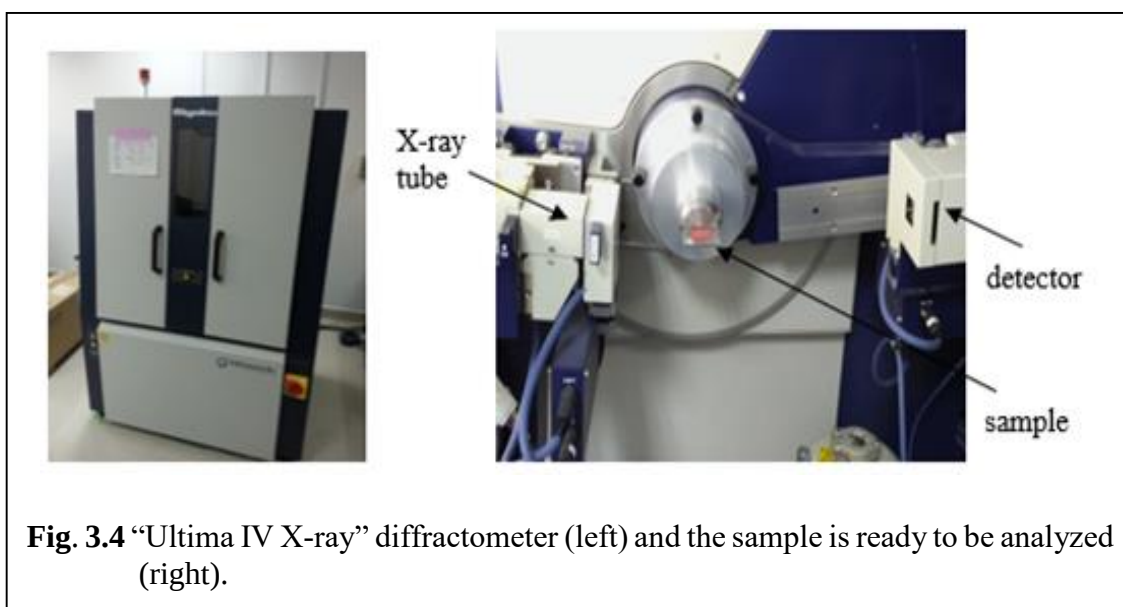


In this study, XRD measurements were performed using “Ultima IV X-ray” diffractometer (Fig. 3.4) which is an advanced XRD instrument equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The data were collected in the 2θ range of $20^\circ - 80^\circ$ using step size of 0.04° and a counting time of 1 second.

3.4 Rietveld Analysis

The refinements of XRD patterns were carried out based on the Rietveld method which is using PDXL program provided with the diffractometer by Rigaku Company. The program is a powerful tool that automatically carries out smoothing, background subtraction and peak decomposition.

Rietveld analysis has been adopted to determine the microstructural parameters of nanocrystalline SFs. The analysis aims at studying the phase composition of the samples before and after annealing and characterizing the as-prepared and annealed samples in terms of crystallite size, microstrain and lattice parameters. The detailed analytical method



implemented in Rietveld analysis has been reported elsewhere (Pradhan *et al.*, 2005).

3.5 Field Emission Scanning Electron Microscopy

FE-SEM is an advanced microscope that produces high resolution images of a sample by scanning it with a beam of electrons. High energy electron beam is projected on a sample where its electrons become excited and have sufficient energy to escape the sample's surface. The topography of the sample is influenced by the number of electrons being detected by a secondary electron detector from any point on the scanned surface. This local variation in electron intensity creates the image contrast that reveals the surface morphology. Thus, FE-SEM gives details about the sample microstructure, particle's size and particle's shape (Zhong-Lin, 2013). The investigation of microstructural and surface characteristics has been carried out by using FEI Sirion 200 FE-SEM operating at 5 and 10 kV.

3.6 Vibrating Sample Magnetometer

VSM is one of the most sensitive ($0.5 \mu\text{emu}$ at 1 second per point) instruments with the ability to determine the magnetic behavior as well as the magnetic properties of a wide range of sample materials (Fig. 3.5). Its principle of operation is quite simple. The sample is suspended by a non-magnetic rod which is connected to a vibrating drive head. A magnetic moment is induced in the sample in the presence of a uniform magnetic field produced by a small high-performance electromagnet. This sample is made to undergo vertical sinusoidal vibration resulting a change in the magnetic flux through a set of 4 pickup coils located in the proximity of

the samples, hence, a voltage is induced in the coils. The magnitude of this voltage is proportional to the magnetic response of the vibrating sample. Fig. 3.6 shows the sample attached to the rod and suspended in the space between the coils and the electromagnet.

Magnetic measurements were measured by VSM at room temperature, with step field 50 Oe in the magnetic field cycling between -10 and 10 kOe, using powder samples. The magnetic parameters of saturation magnetization (M_s), remnant magnetization (M_r), and coercive field (H_c) were determined from the $M-H$ curves.

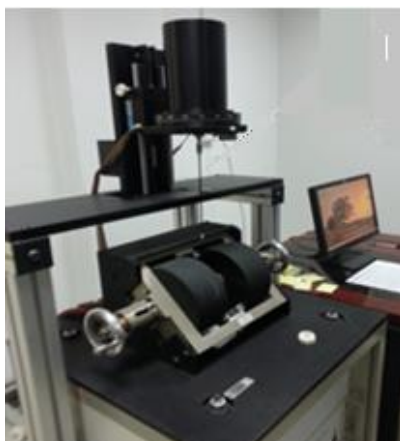


Fig. 3.5 Vibrating sample magnetometer.

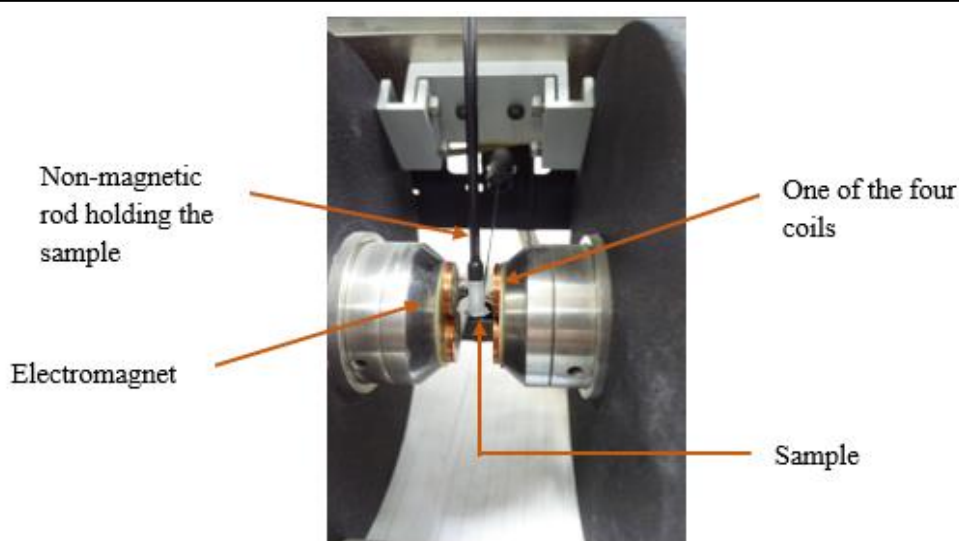


Fig. 3.6 Part of VSM. The sample is made to vibrate in between the 4 coils and the electromagnet.

3.7 Self-heating Measurements

The hyperthermia properties of MNPs can be investigated using a MagneTherm system from nanoTherics (Fig. 3.7). Hyperthermia is based on the transformation of magnetic energy into heat, governed by thermal fluctuations that occur in magnetic nanoparticles in an AC magnetic field. Practically, nano-ferrofluids can be placed in nano-centrifuge tube in the center of a circular coil inside the MagneTherm and is exposed to AMF. The thermocouple is inserted inside the tube and connected to a data processing system to record the temperature and its variations over time (dT/dt). Thermal equilibrium and a saturation temperature are reached after a certain period of time. The desirable case is to achieve this saturation between 42 °C and 47 °C because MNPs are capable to burn cancerous cells within this range (Hedayatnasab *et al.*, 2017).

The heating capacity in the present investigation was conducted on suspensions of 5 and 15 mg of SFMNPs per millilitre of distilled water by solid state magnetic induction at ambient room temperature for 20 min (strength of magnetic field = 13.56 kA m⁻¹, 329.77 kHz). The samples were

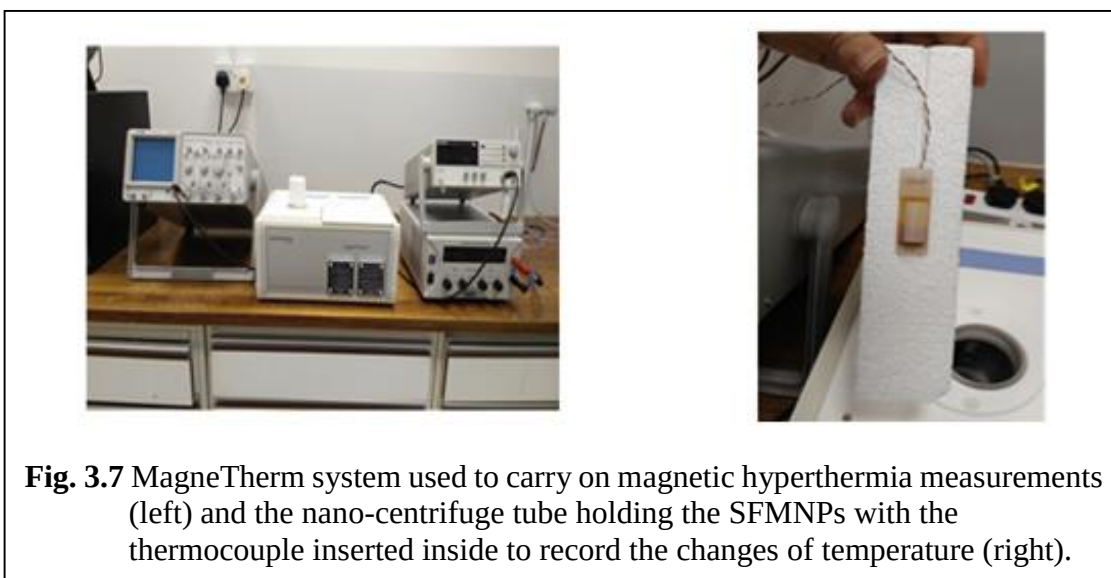


Fig. 3.7 MagneTherm system used to carry on magnetic hyperthermia measurements (left) and the nano-centrifuge tube holding the SFMNPs with the thermocouple inserted inside to record the changes of temperature (right).

subjected to 10 minutes of ultrasonication before magnetic hyperthermia readings were recorded. SAR values were calculated by direct measurement according to equation 1.

CHAPTER 4

RESULTS AND DISCUSSION

CHAPTER 4

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4.1 Crystal Structure Analysis

XRD was performed to determine the structural characteristics of SFMNPs synthesized using the modified sol-gel method. XRD patterns of M-AP samples (Fig. 4.1) display well-defined and relatively broad peaks. This is an indication that the samples are nanocrystalline in nature. Peak broadening originates from mainly finite crystallite size and strain effect within the crystal lattice. The patterns also show a slight displacement of the reflections when it is observed from the bottom to the top due to the larger ionic radius of Zn^{+2} (0.60 Å) in comparison to those of Co^{+2} (0.58 Å), Cu^{+2} (0.57 Å) and Ni^{+2} (0.55 Å) ions. These ionic radii were considered for a coordination number of 4 where the latter is defined as the number of anion nearest neighbors for a cation to attain stability (Callister and Rethwisch, n.d.; Shannon, 1976). The formation of spinel cubic structure with the $Fd\bar{3}m$ space group was confirmed by the presence of the (220), (311), (400), (422), (511), (440) and (533) major lattice planes in the XRD patterns (Fig. 4.1). It can be noticed that both Ni-AP and Cu-AP were single phase in agreement with the powder diffraction file of JCPDS cards No. 01-086-2267 and 01-074-8585 respectively (Table 4.1). For Co-AP and Zn-AP, both spinel phases were consistent with JCPDS cards No. 00-022-1086 and 01-082-1049 respectively, but with the presence of additional peaks identified as CoO and ZnO with α - Fe_2O_3 phases (Fig. 4.1 and Table 4.1). The presence of CoO and ZnO might be due to oxidation that occurred

by oxygen ions in water during synthesis process. Also, it might be suggested that low amount of Fe^{2+} ions in the reaction medium causes the appearance of hematite alongside with ZnFe_2O_4 phase, because electrons are not transferred to the Fe^{3+} ions neighboring the inner structure of the precursor material to convert them into the spinel structure (Jolivet *et al.*, 1992). Moreover, Behdadfar *et al.* showed that a specific amount of citric acid in the sol-gel preparation was required to obtain single phase of zinc ferrite and this suggests the formation of unsuitable hematite phase in the present work where the amount of citric acid used might not have been in the optimized level (Behdadfar *et al.*, 2012).

The effect of annealing on the structure of the M-AP samples is shown in Fig. 4.2 and Table 4.1 where some important changes took place in the SFMNPs:

- (i) NiFe_2O_4 remained single phase.
- (ii) Interestingly, CuFe_2O_4 underwent a phase transformation from cubic into tetragonal.
- (iii) CoFe_2O_4 and ZnFe_2O_4 became single phases which means that annealing favors the dissolution of additional CoO phase within CoFe_2O_4 main phase and further solid state reaction between ZnO and $\alpha\text{-Fe}_2\text{O}_3$ ($\text{ZnO} + \text{Fe}_2\text{O}_3 \rightarrow \text{ZnFe}_2\text{O}_4$).

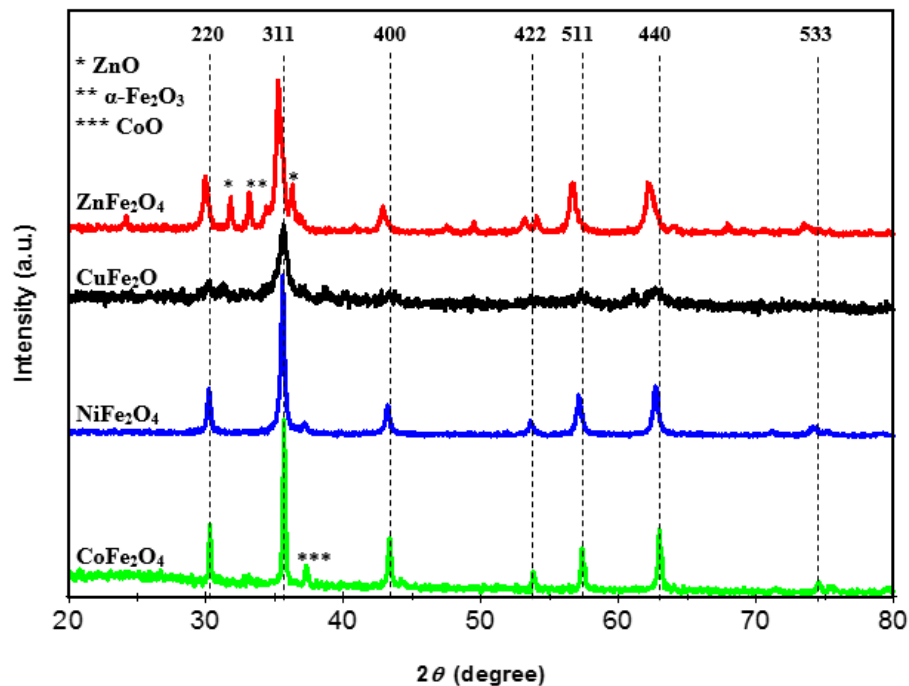


Fig. 4.1 X-ray diffraction patterns of as-prepared $M\text{Fe}_2\text{O}_4$ nanoparticles synthesized using modified sol-gel method

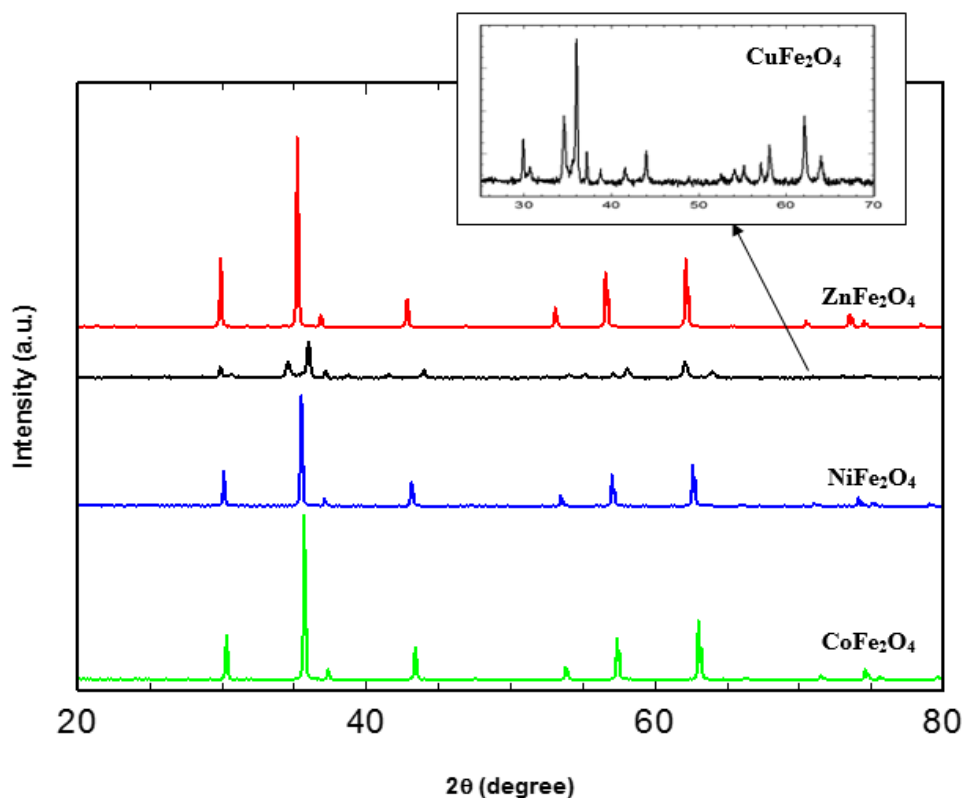


Fig. 4.2 X-ray diffraction patterns of annealed $M\text{Fe}_2\text{O}_4$ nanoparticles synthesized using modified sol-gel method. Annealing temperature is 1000 °C for 5 hrs.

Table 4.1 Quantitative XRD analysis of MFe₂O₄: crystal structure, space group, lattice parameter and JCPDS number

Samples	Type of crystal structure	Space group	Lattice parameters (Å)	JCPDS card number
CoFe₂O₄	cubic	Fd $\bar{3}$ m(227)	8.3919	00-022-1086
CoO	cubic	Fm $\bar{3}$ m(225)	4.2400	01-071-4749
NiFe₂O₄	cubic	Fd $\bar{3}$ m(227)	8.3370	01-086-2267
Cu-AP	cubic	Fd $\bar{3}$ m(227)	8.3730	01-074-8585
Cu-A	tetragonal	I4 ₁ amd(141)	a=5.8100 c=8.7100	01-072-1174
ZnFe₂O₄	cubic	Fd $\bar{3}$ m(227)	8.4409	01-082-1049
ZnO	hexagonal	P6 ₃ mc(186)	a=3.2533 c=5.2072	01-0738765
α- Fe₂O₃	trigonal	R $\bar{3}$ c(167)	a=5.0390 c=13.7700	01-089-0596

The formation of spinel cubic structure of SFMNPs is also confirmed by the ICDD database provided with the diffractometer where qualitative phase analysis was performed. Figures 4.3 and 4.4 show the phase identification of each sample. Comparing both figures, it is observed that annealing causes the half-width of the diffraction peaks to decrease, whereas the peak relative intensities significantly increased. This increase can be attributed to the increase in the crystallites size as annealing favors grain growth as well as a better crystallinity and homogeneity of the chemical composition. This is in agreement with the results reported by Yelenich *et al.* (Yelenich *et al.*, 2014).

The recorded XRD patterns of M-AP and M-A are refined in comparison to theoretical patterns by using Rietveld method. The results are reported in Fig.4.5, Fig. 4.6 and Table 4.2. During refinements, the goodness of fit is calculated by the reliability factors S and χ^2 , where the closer these quantities are to unity, the better the matching between the theoretical and the experimental XRD patterns (Patange *et al.*, 2010). Rietveld analysis, as well as XRD analysis, confirmed the formation of single phase of Ni-AP, Cu-AP, Co-A, Ni-A, Cu-A and Zn-A samples (100%). The results indicate that 6% of CoO and 13% of ZnO with 14% of α -Fe₂O₃ precipitate are present in Co-AP and Zn-AP samples respectively. The values of the lattice parameters of M-AP obtained by the Rietveld analysis (Table 4.2) are comparable to the ones reported in JCPDS file (Table 4.1) and elsewhere (Swatsitang *et al.*, 2016 for CoFe₂O₄; Nogueira *et al.*, 2015 for NiFe₂O₄; Kombaiah *et al.*, 2018 for CuFe₂O₄; Yadav *et al.*, 2017 for ZiFe₂O₄). In addition, annealing slightly reduced these values for all the samples (Table 4.2). This behavior can be explained by the redistribution of M⁺² and Fe⁺³ ions within the interstitial sites, which in turn reduces the interatomic interactions that leads to the decrease of the lattice parameters.

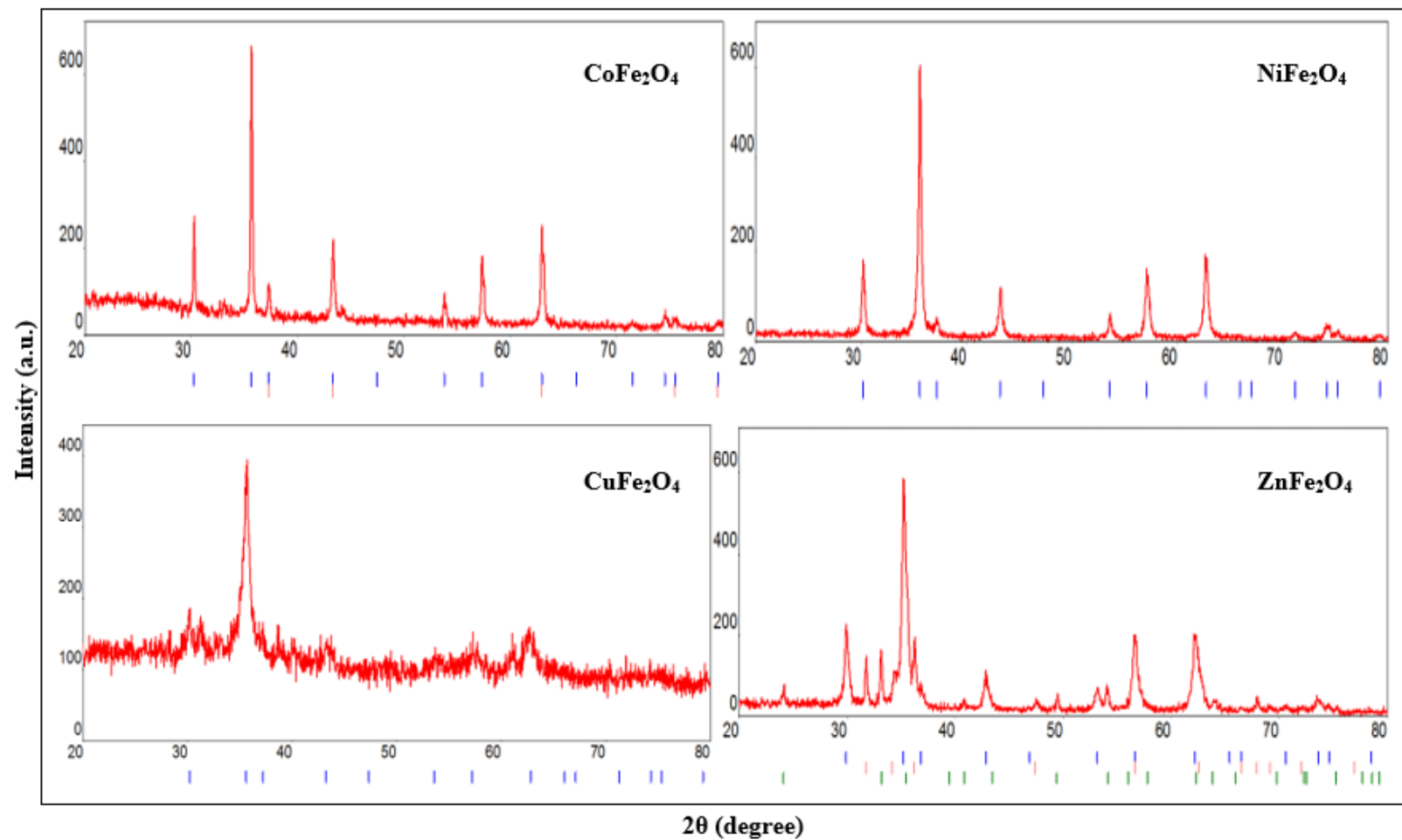


Fig. 4.3 Phase identification of MFe_2O_4 – AP, showing intensity (a.u.) vs. 2θ (degrees) with Bragg reflections

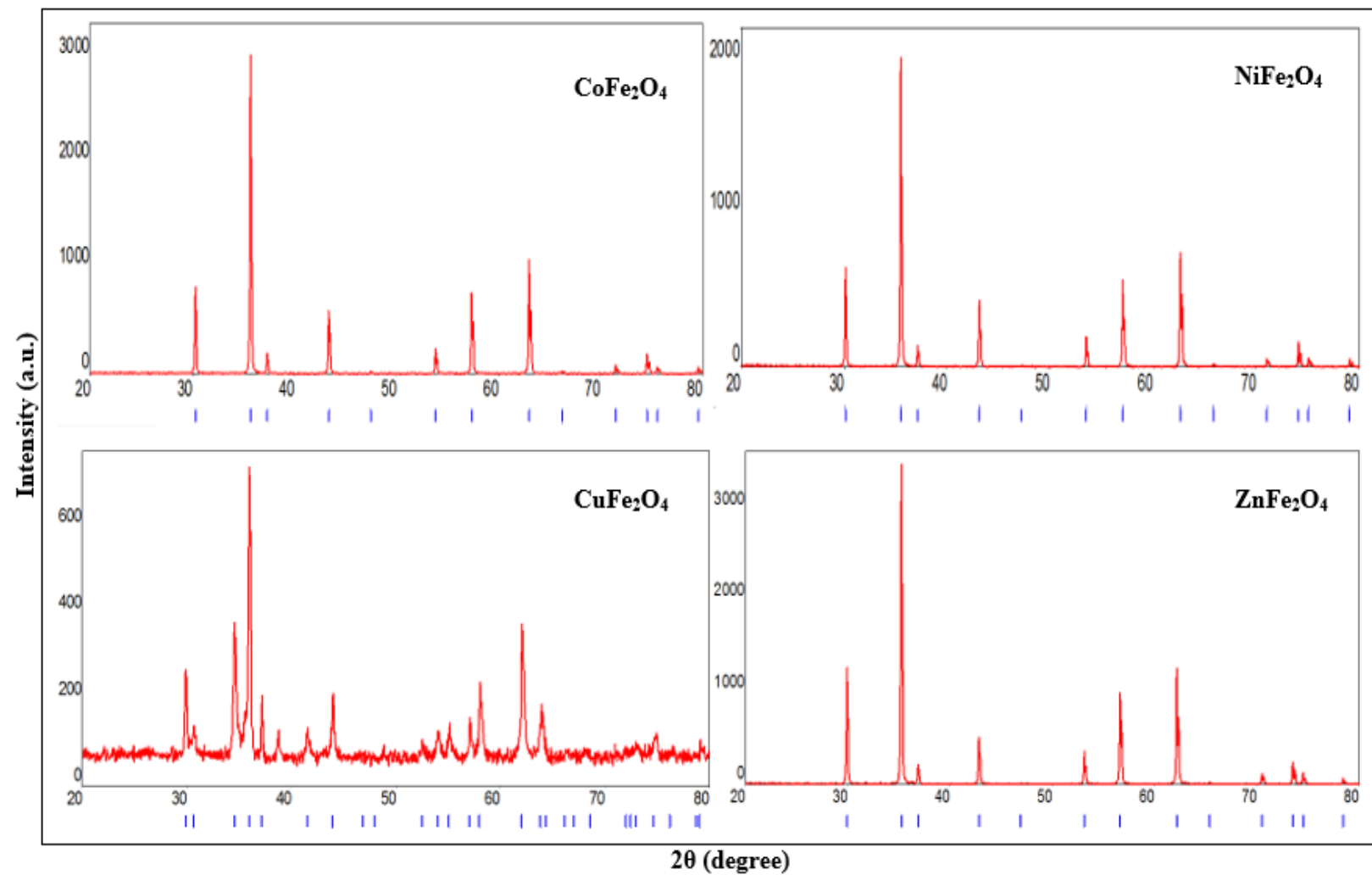


Fig. 4.4 Phase identification of $\text{MFe}_2\text{O}_4 - \text{A}$, showing intensity (a.u.) vs. 2θ (degrees) with Bragg reflections

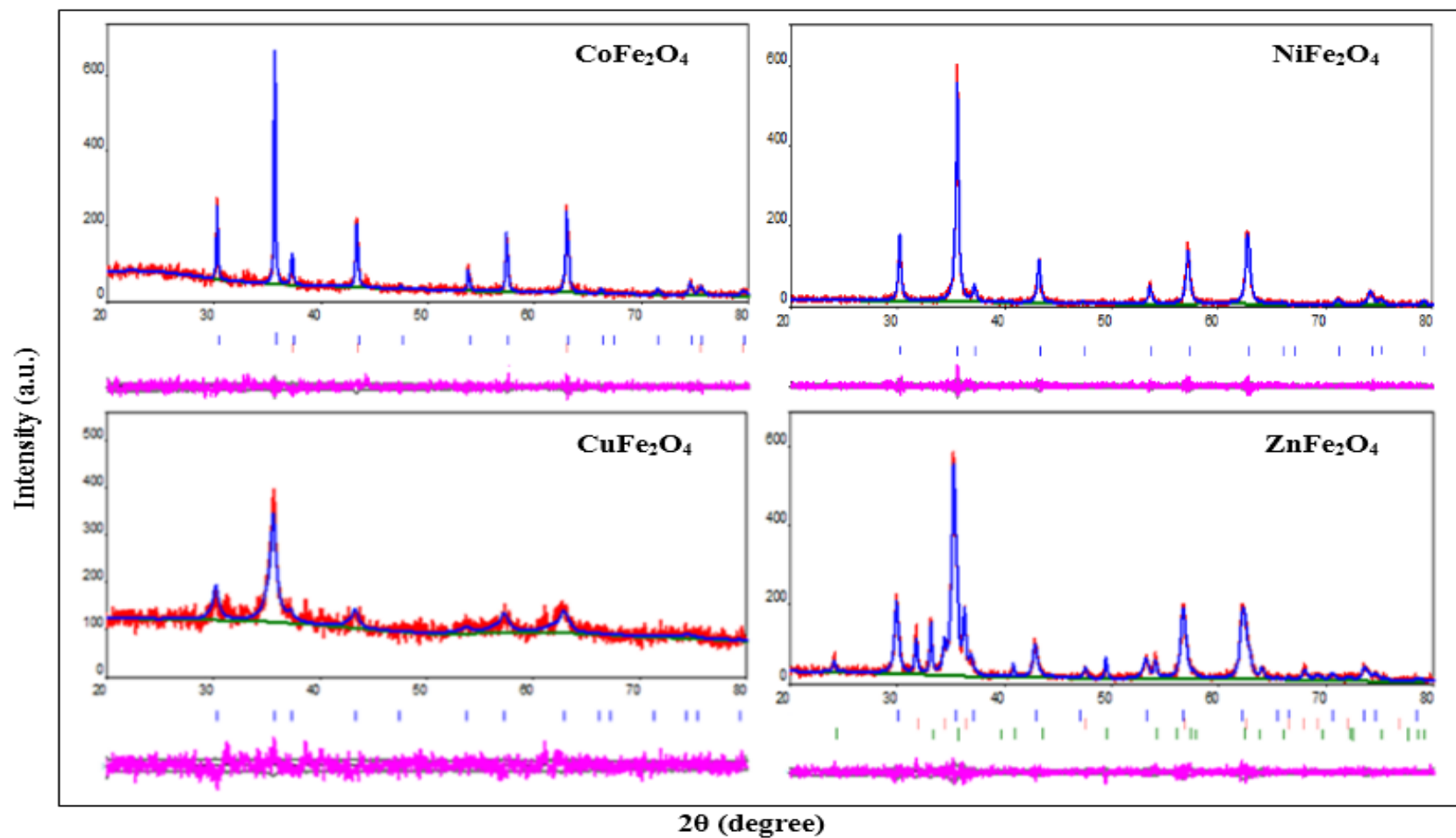


Fig. 4.5 XRD pattern refinements using the Rietveld method MFe_2O_4 – AP. Red line: experimental data; blue upper solid line: calculated pattern; purple lower solid line: intensity difference; | : Bragg reflections positions

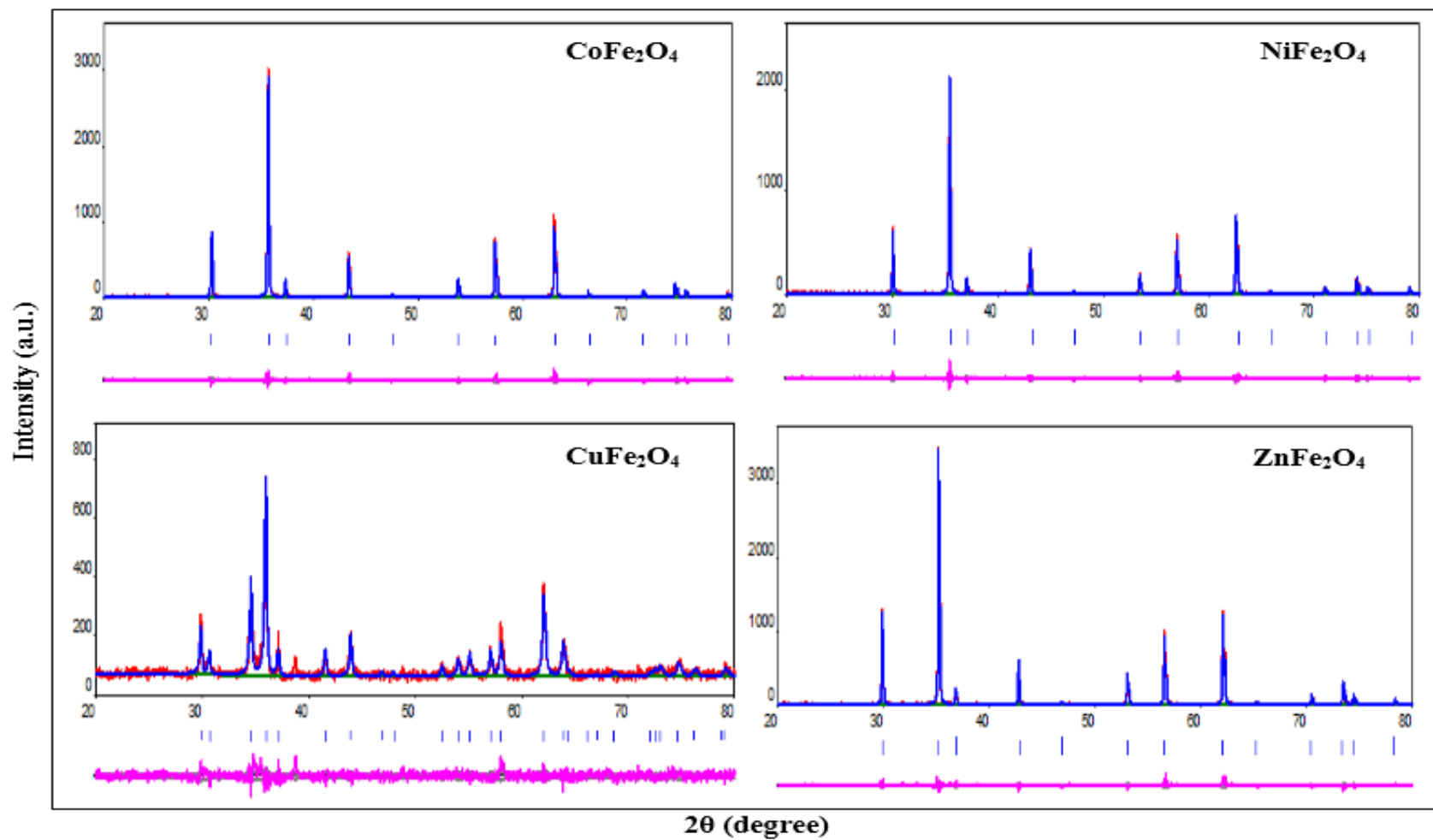


Fig. 4.6 XRD pattern refinements using the Rietveld method MFe_2O_4 – A. Red line: experimental data; blue upper solid line: calculated pattern; purple lower solid line: intensity difference; | : Bragg reflections positions

Table 4.2 Quantitative Rietveld parameters before and after annealing: phase composition, crystallite size, microstrain, lattice parameter, and fit parameters: S (R_{wp}/R_e) and χ^2

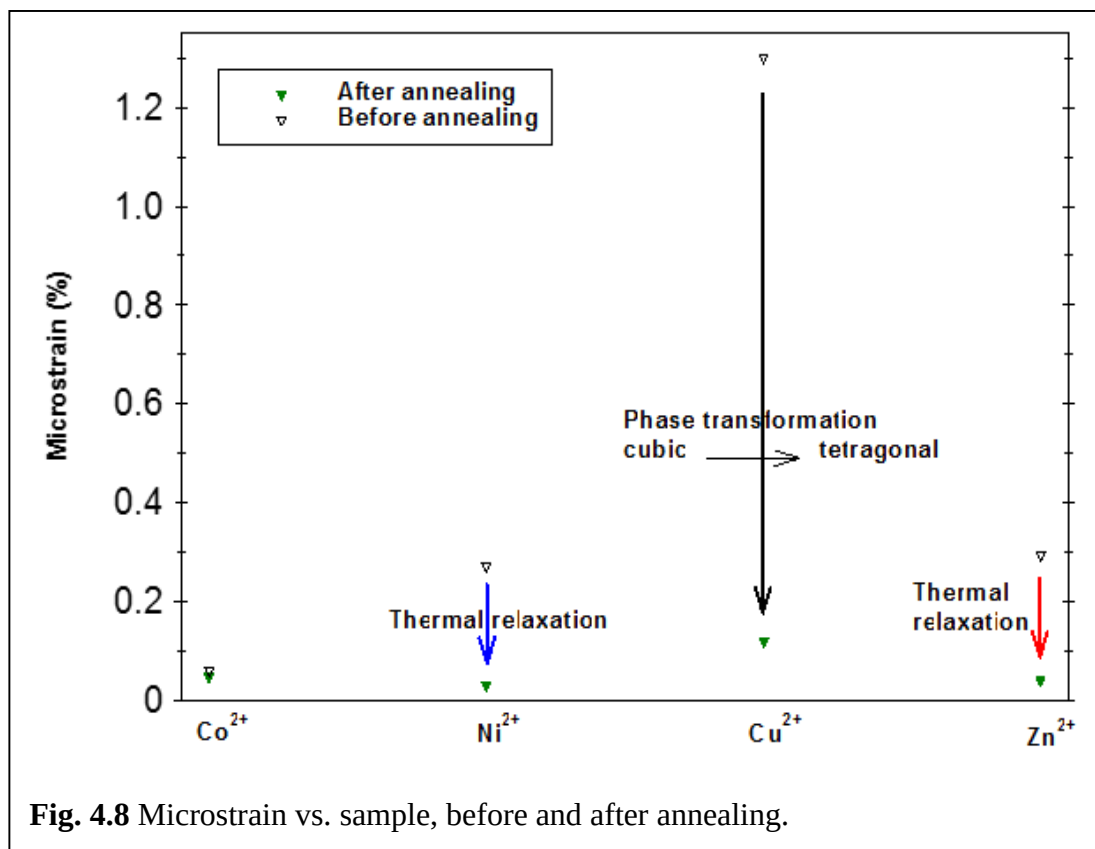
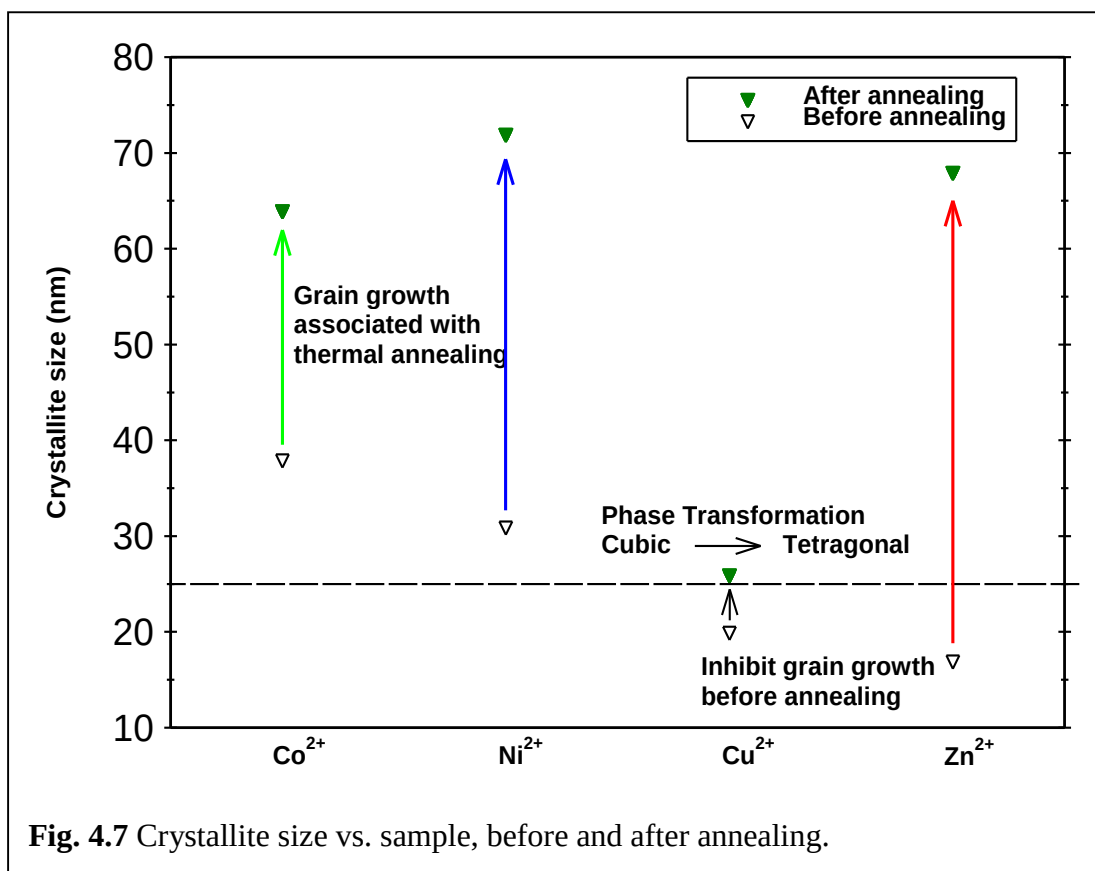
Rietveld analysis before annealing										
	Phase composition (%)		Crystallite size (nm)	Microstrain (%)	Lattice parameters (Å)	Fit Parameters				
						R_{wp} (%)	R_p (%)	R_e (%)	S	χ^2
Co-AP	CoFe ₂ O ₄	94	38	0.060	8.344(3)	15.29	11.31	14.33	1.0637	1.1314
	CoO	6	23	0.170	4.181(3)					
Ni-AP	NiFe ₂ O ₄	100	31	0.272	8.390(5)	22.87	15.86	21.33	1.0709	1.1469
Cu-AP	CuFe ₂ O ₄	100	20	1.30	8.368(6)	10.34	8.18	9.35	1.1041	1.2191
Zn-AP	ZnFe ₂ O ₄	73	17	0.295	8.444(4)	16.59	11.89	15.60	1.0603	1.1243
	ZnO	13	43	0.327	a=3.249(2) c=5.212(3)					
	α -Fe ₂ O ₃	14	22	0.200	a=5.040(2) c=13.756(7)					

Table 4.2 - continued

Rietveld analysis after annealing										
	Phase composition (%)		Crystallite size (nm)	Microstrain (%)	Lattice parameters (Å)	Fit Parameters				
						R_{wp} (%)	R_p (%)	R_e (%)	S	χ^2
Co-A	CoFe ₂ O ₄	100	64	0.047	8.3396(5)	23.78	14.13	18.42	1.2896	1.6630
Ni-A	NiFe ₂ O ₄	100	72	0.030	8.3833(8)	26.33	15.58	21.45	1.2257	1.5024
Cu-A	CuFe ₂ O ₄	100	26	0.12	a=5.8249(19) c=8.689(3)	13.36	10.44	10.80	1.2358	1.5271
Zn-A	ZnFe ₂ O ₄	100	68	0.040	8.4431(6)	22.64	13.32	16.90	1.3372	1.7882

From the data obtained in Table 4.2, further analysis was carried out. During the preparation by the modified sol-gel method, both Cu-AP and Zn-AP seem to inhibit grain growth, while Co-AP and Ni-AP favor grain growth. The variation of the crystallite size (CS) of the samples due to annealing can be observed in Fig. 4.7. All the annealed samples exhibit an increase in CS. This is supported by Al-Saie *et al.* where they reported a significant increase in the CS of the annealed CoFe_2O_4 (Al-Saie *et al.*, 2011). This dramatic increase in CS for Co-A, Ni-A and Zn-A is due to grain growth and lattice relaxation associated with the thermal energy provided during annealing. This means that higher temperature or longer annealing time provokes grain growth. However, there was no significant effect on grain growth of CuFe_2O_4 which might be due to the fact that the provided thermal energy was directed to the phase transformation from cubic to tetragonal phase.

As can be observed from Fig. 4.8, the microstrain of CoFe_2O_4 was very small (0.060%) so that there was no significant change after annealing (22% of drop). However, NiFe_2O_4 , CuFe_2O_4 and ZnFe_2O_4 all showed dramatic reduction of microstrain (was 89%, 91% and 86% drop respectively). Microstrain exists due to crystal imperfection and distortion. CuFe_2O_4 witnessed dramatic effect due to the phase transformation (cubic to tetragonal) occurring during annealing. This reduction is expected due to the crystal relaxation, and it usually accompanies the thermal energy provided during annealing and might strengthen the mechanical properties of the SFs due to the dislocation motion that occurs along specific directions in the preferred plane (Callister and Rethwisch, n.d).



4.2 Morphological Observations

Morphological observations of the SFMNPs were checked by FE-SEM. The images of M-AP and M-A are shown in Fig.'s 4.9 and 4.10 respectively. M-AP samples show very high tendency for agglomeration compared to M-A, so their NPs are indistinguishable due to the presence of strong magnetic interactions. Annealing reduces agglomeration and Fig. 4.10 for M-A reveals non-uniform grain growth by aggregation of a number of nanocrystals. The NPs have varying sizes and rounded shapes, with a fraction of distorted ones in some cases. The average particle size for M-A was found to be in the range of 100 – 300 nm. There is also a broad distribution of particle sizes as well as shapes for M-A. The particle size obtained by SEM analysis is in good agreement with the crystallite size estimated by XRD analysis. The particle size values are higher than the crystallite size, which means that the particles are formed by few crystals.

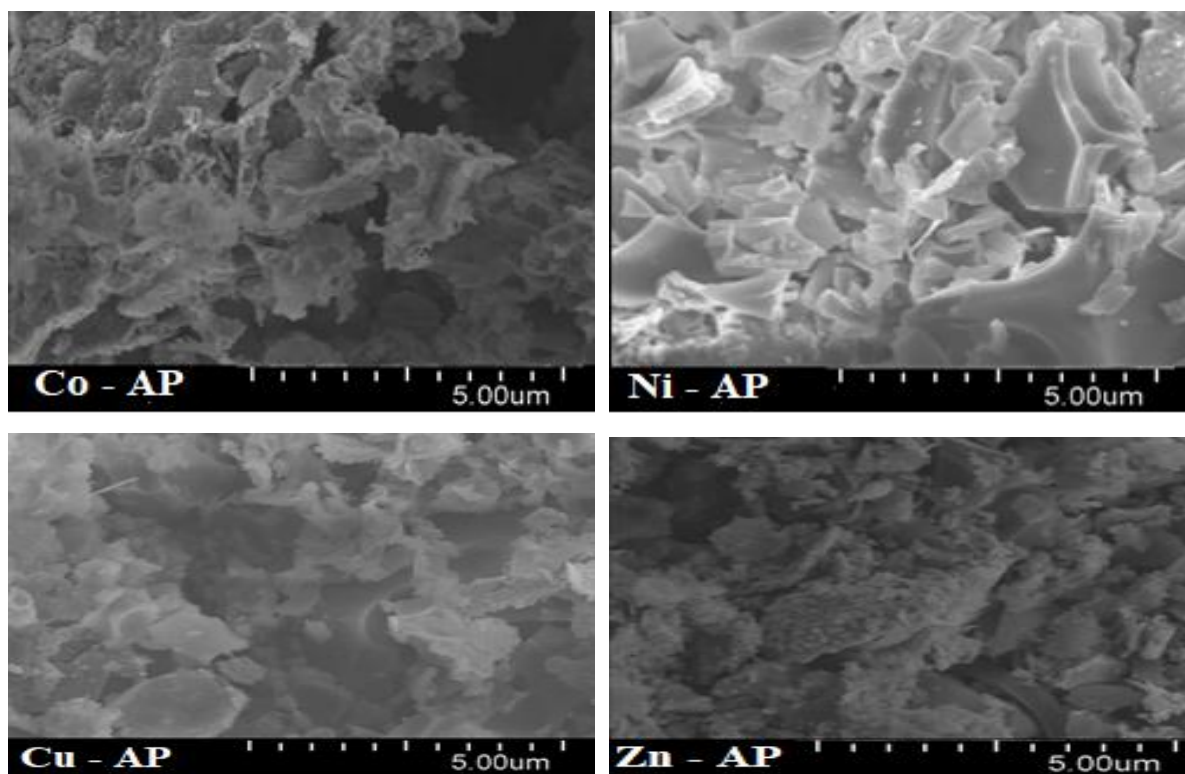


Fig. 4.9 SEM micrographs of M-AP NPs synthesized by modified sol-gel method

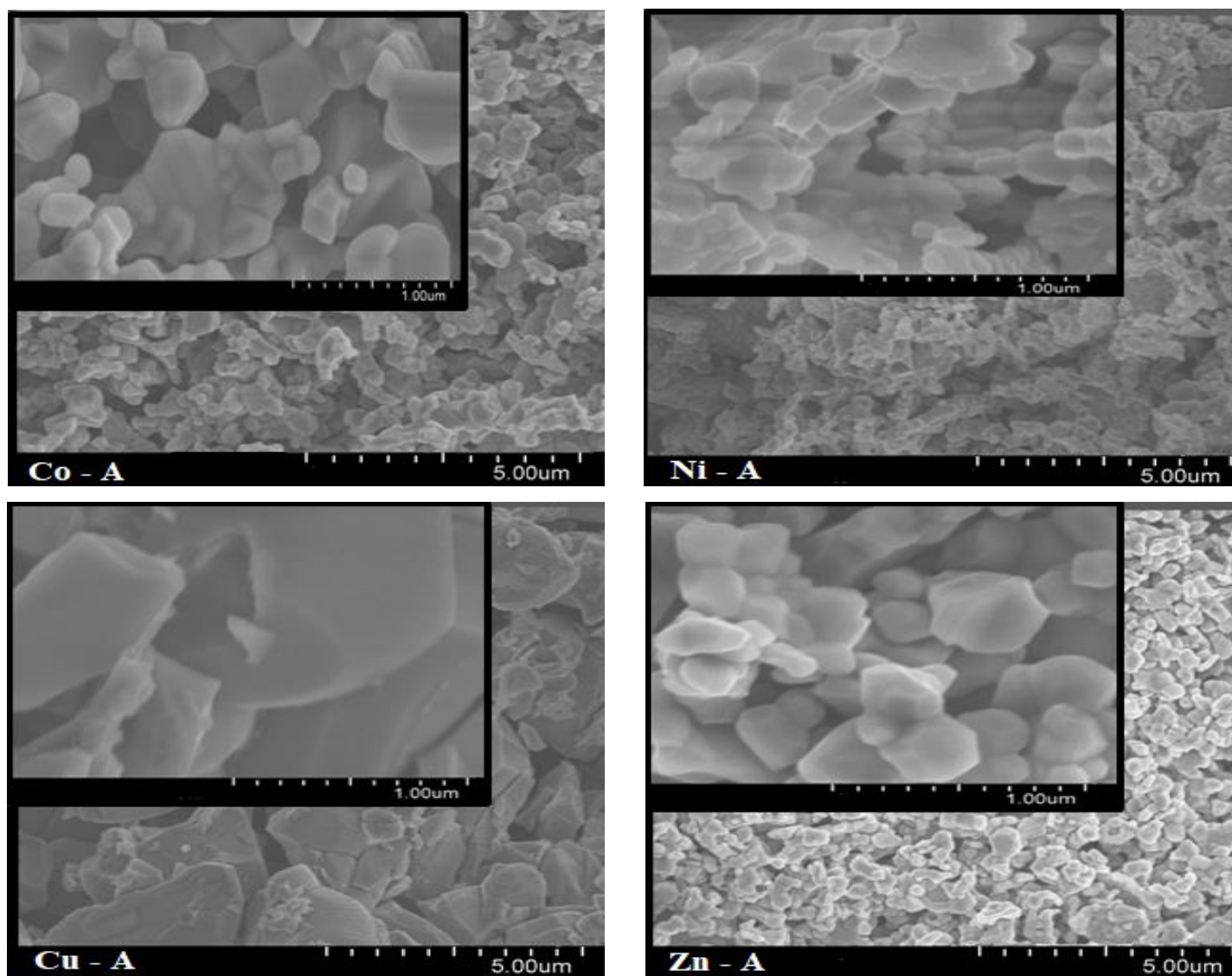


Fig. 4.10 SEM micrographs of M-A NPs synthesized by modified sol-gel method. The inset shows 1 µm resolution

4.3 Magnetic Properties

Figures 4.11 and 4.12 show the measured M - H curves, measured by VSM at room temperature, for M-AP and annealed M-A samples respectively. In both cases, magnetization tends to saturate at high fields. M - H curves show hysteresis loops for all samples with NiFe_2O_4 , as-prepared and annealed, exhibiting the largest loop compared to the others. Thus the samples revealed ferrimagnetic behavior. The magnetic properties obtained from the M - H curves are summarised in Table 4.3. The saturation magnetization (M_s) at room temperature was found to decrease in the order $\text{NiFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 \gg \text{ZnFe}_2\text{O}_4$ under the same synthetic method and annealing temperature. The values of M_s for NiFe_2O_4 and ZnFe_2O_4 agree with the values reported by some researchers while they disagree with those of others. They are comparable to the ones reported by Yadav *et al.* for Ni and Esmaeili and Alizadeh Hadad, for Zn (Yadav *et al.*, 2017; Esmaeili and Alizadeh Hadad, 2015); but smaller than the one reported for ZnFe_2O_4 (Guo *et al.*, 2013) and bigger than the one reported for NiFe_2O_4 (Nogueira *et al.*, 2015). On the other hand, M_s of CoFe_2O_4 is smaller than M_s reported elsewhere (Lee *et al.*, 2007). Similarly CuFe_2O_4 has lower M_s (Anandan *et al.*, 2017). This variation of M_s in literature is due to several factors: the synthesis method, annealing temperature and time, particle size distribution, and particle size, etc. The low M_s of Zn-AP (5.629 emu/g) could be due to the presence of hematite having a very small magnetic moment ($0.002 \mu_B$), the bulk value is the contribution of both ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ phases with respect to their corresponding amounts.

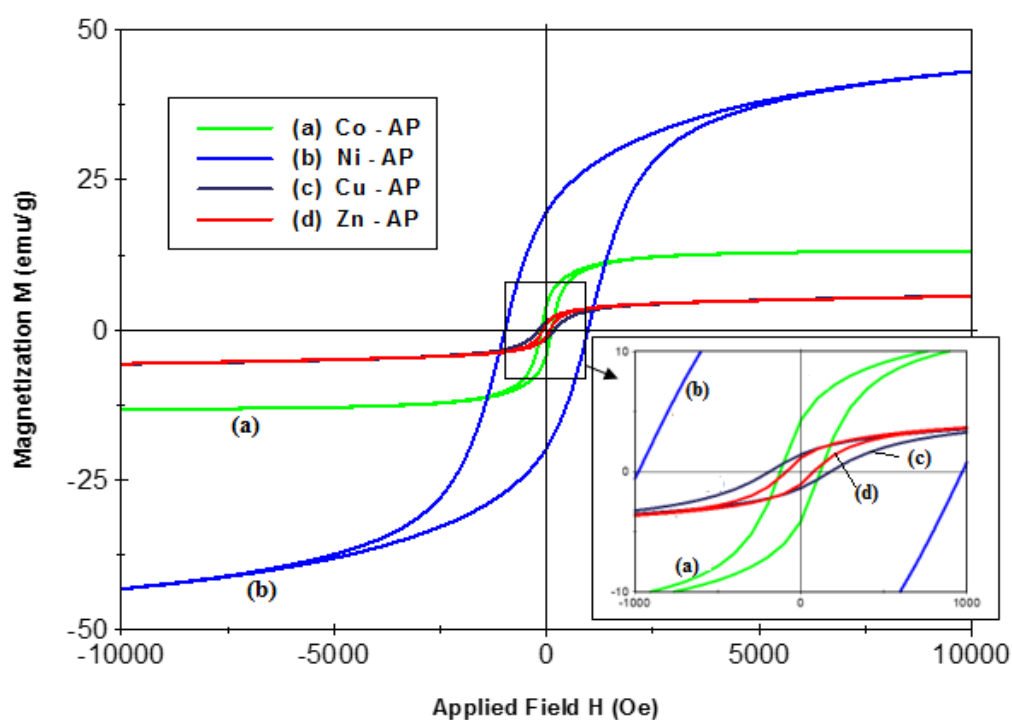


Fig.4.11 M - H curves measured at room temperature for as-prepared $M\text{Fe}_2\text{O}_4$ samples. The inset shows low field parts

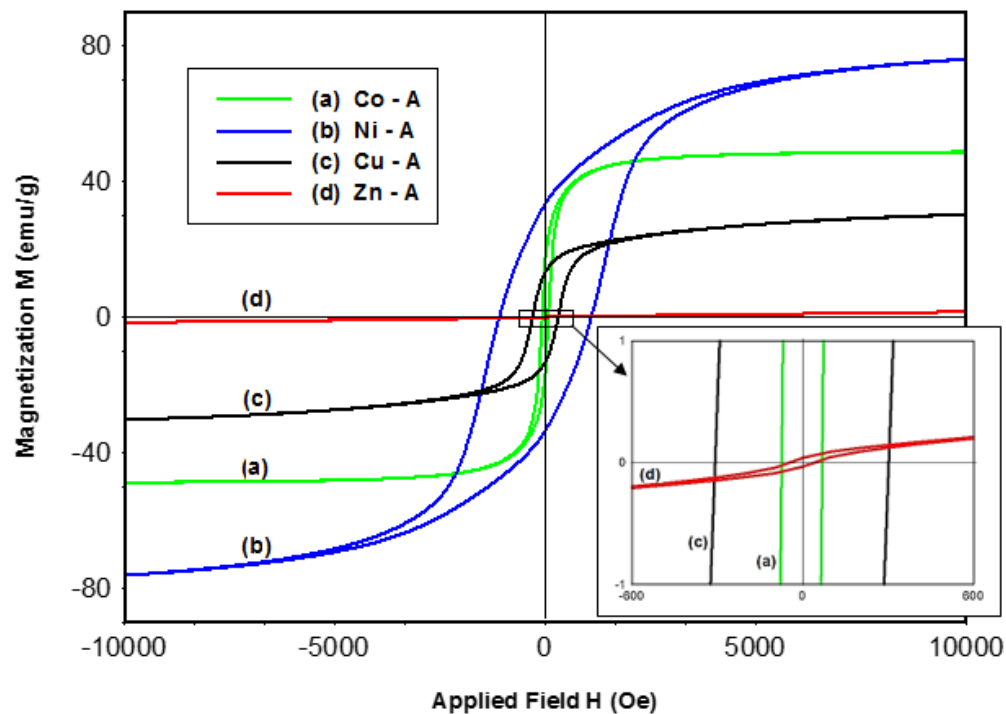


Fig.4.12 M - H curves measured at room temperature for annealed $M\text{Fe}_2\text{O}_4$ samples. The inset shows low field parts

Table 4.3 Mass of MFe_2O_4 , coercivity, remanent magnetization, saturation magnetization and remanence ratio M_r/M_s

As-prepared					
	Mass (mg)	H_c (Oe)	M_r (emu/g)	M_s (emu/g)	Remanence ratio
CoFe_2O_4	9.800	120.8	4.191	13.23	0.3169
NiFe_2O_4	10.10	976.2	19.73	43.15	0.4571
CuFe_2O_4	10.00	183.6	1.399	5.647	0.2478
ZnFe_2O_4	11.10	81.99	1.091	5.629	0.1938
After annealing					
CoFe_2O_4	9.800	71.40	17.27	48.72	0.3544
NiFe_2O_4	8.600	1095	33.55	76.11	0.4408
CuFe_2O_4	10.70	305.0	13.35	30.20	0.4421
ZnFe_2O_4	8.200	43.65	33.86×10^{-3}	1.569	0.0229

Annealing increases M_s for all the samples, except ZnFe_2O_4 , with Ni-A has the highest value of 76 emu/g. Although magnetization increased with the increase of the crystallite size at room temperature, it decreased for ZnFe_2O_4 upon annealing (Fig. 4.13). This is not a surprise where such behavior, for zinc ferrite particularly, has been reported elsewhere among the other nanoferrites with spinel structure (Yelenich *et al.*, 2014; Singh *et al.*, 2012; Blanco-Gutierrez *et al.*, 2011; Lemine *et al.*, 2011). It is known that ZnFe_2O_4 is normal spinel that can be transformed to inverse spinel upon annealing; thus the drop in magnetization upon annealing takes place (from 5.6 to 1.6 emu/g). The reason for this can be that the cations site occupancy, where a re-distribution of Zn^{+2} (paramagnetic with $\mu_B \approx 0$) and Fe^{+3} ($\mu_B = 5.92$) has taken place. Upon annealing, Zn^{+2} ions move from tetrahedral to octahedral sites, whereas Fe^{+3} occupy both octahedral and tetrahedral sites equally. The net magnetic moments of Fe^{+3} are antiparallel and cancel out each other to a large degree; therefore, the net magnetic moments and spin alignments of Zn^{+2} dominate the magnetization of zinc ferrite. Fig. 4.14 shows that M_s varies linearly with μ_B (M). The value of M_s , after annealing, increases significantly for CoFe_2O_4 , NiFe_2O_4 and CuFe_2O_4 . This can be associated with cations site occupancy re-distribution. The cations of CoFe_2O_4 and NiFe_2O_4 behave similarly as of ZnFe_2O_4 , however, Co^{+2} ($\mu_B = 3.88$) and Ni^{+2} ($\mu_B = 2.83$) exhibit ferromagnetic behavior. Therefore, an increase in saturation magnetization is observed. Cu-A showed a significant increase in M_s after it has transformed into tetragonal phase due to annealing. Thus, there is a strong correlation between the magnetic properties and the cation distribution in SFs. Additionally, as the NPs grow due to annealing, the remnant magnetization of the samples increases except in Zn-A (Fig. 4.15). This supports the ferrimagnetic behavior of the samples while for Zn-AP a paramagnetic component dominates such that the effect of CS is negligible. Table 4.3 shows the coercivity to be in

the range of 82 to 976 Oe for M-AP and 44 to 1095 Oe for M-A. This is an indication that the samples exhibit ferrimagnetic (and not superparamagnetic) properties at room temperature. This is also supported by $M-H$ curves (Fig.'s 4.11 and 4.12) where hysteresis loops are observed. Thus, the M-AP and M-A samples did not display superparamagnetic behavior as the size of the synthesized nanoparticle did not fall in the critical size range. Ni-A displayed the highest H_c and this may be caused by the strong spin interactions in highly crystalline NiFe_2O_4 during spin alignment (Li *et al.*, 2017). The coercivity vs. CS is shown in Fig. 4.16. NiFe_2O_4 and CuFe_2O_4 witnessed an increase in coercivity after annealing. Therefore large external fields applied in the opposite direction are required for demagnetization. ZnFe_2O_4 exhibited a decrease in coercivity after annealing (Fig. 4.16), so paramagnetic behavior is dominant (Zn is non-magnetic). Coercivity of CoFe_2O_4 was dropped as well. Generally speaking, several factors may affect coercivity: intrinsic behavior of each spinel phase due to the magnetic nature of the elements; the phase composition before and after annealing; the particle size distribution (broad size distribution is observed); particles morphology, surface effects, secondary phases at surface, structural (such as vacancies) and microstructural (lattice strain) defects, cation distribution, and strain, etc. (Yadav *et al.*, 2017).

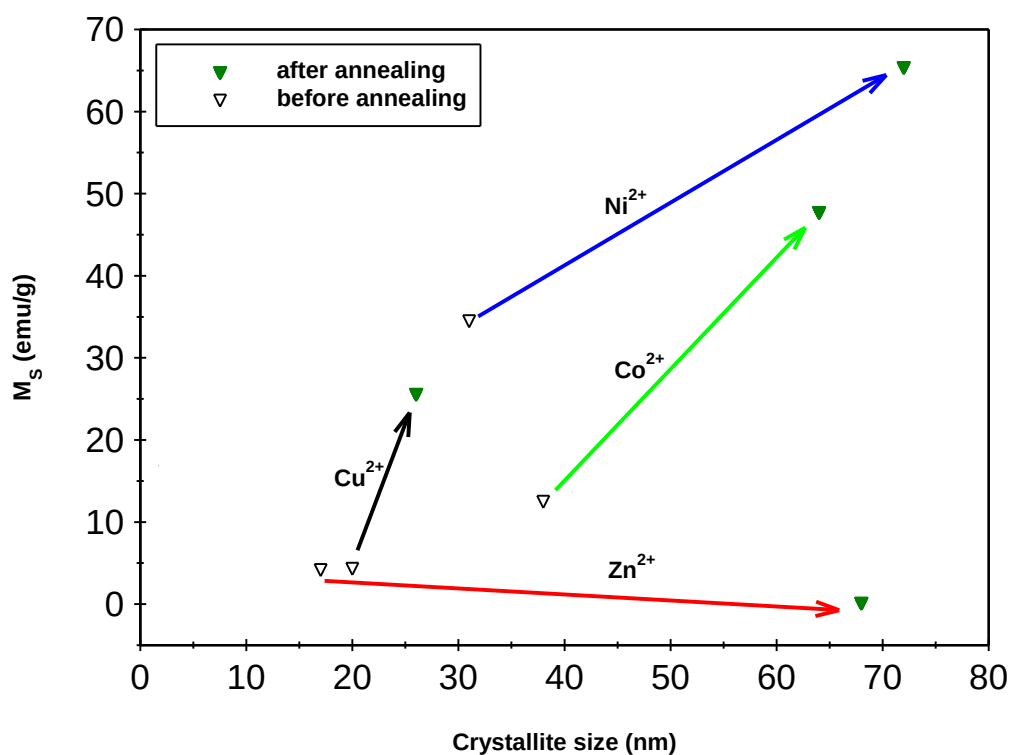


Fig. 4.13 Room temperature saturation magnetization (emu/g) vs. crystallite size (nm), before and after annealing

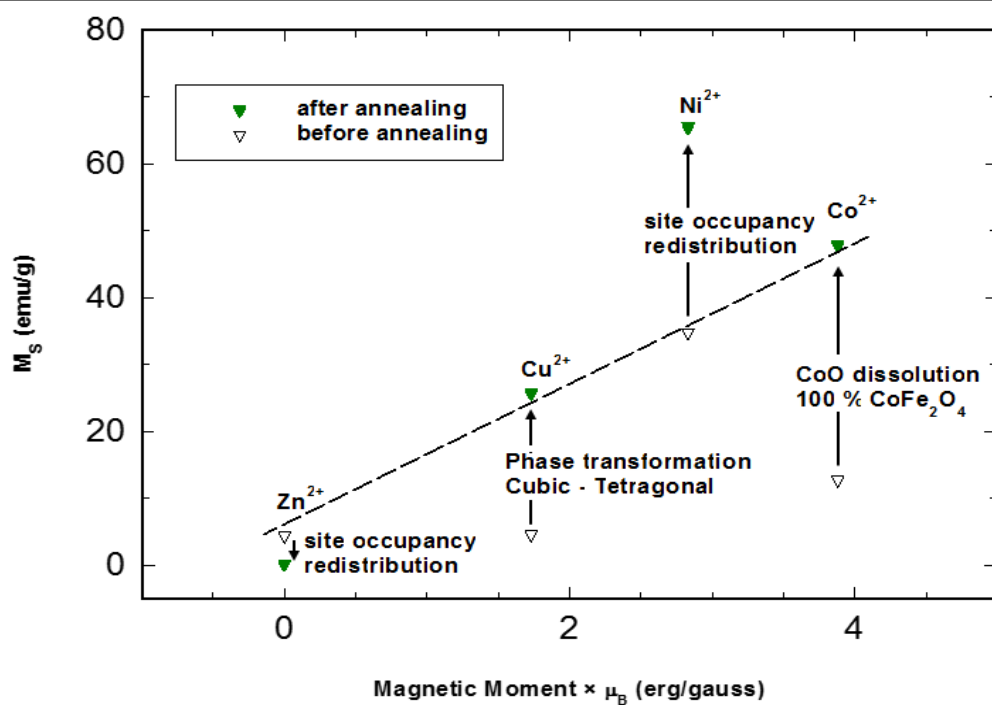


Fig. 4.14 Room temperature saturation magnetization (emu/g) vs. magnetic moment $\times \mu_B$, before and after annealing.

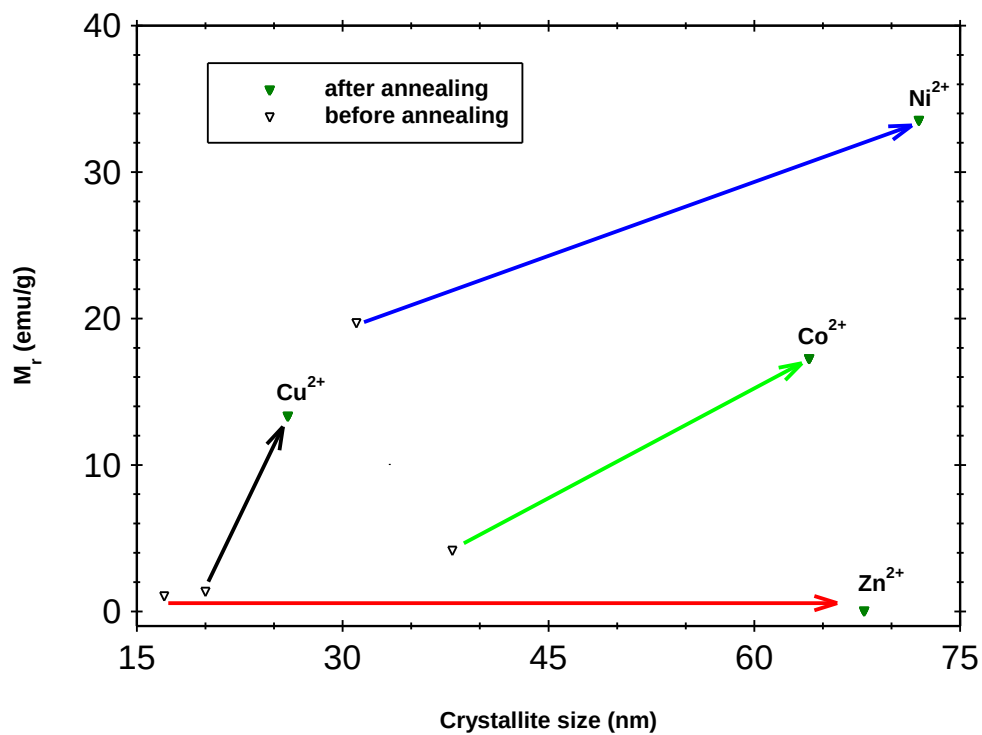


Fig. 4.15 Remanent magnetization (emu/g) vs. crystallite size (nm), before and after annealing.

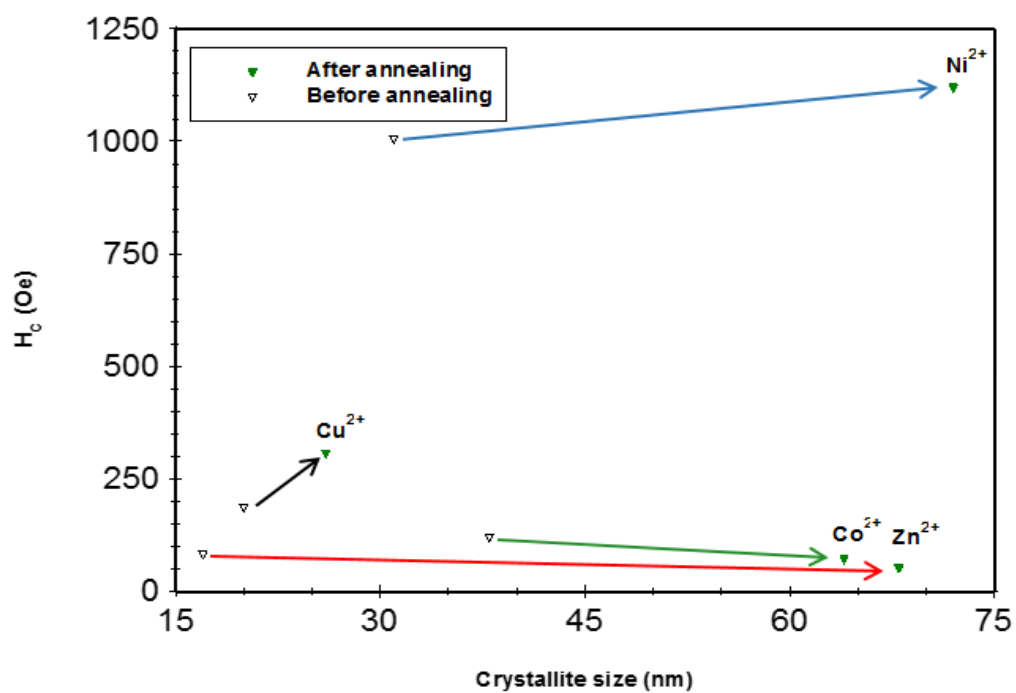


Fig. 4.16 Coercivity (Oe) vs. crystallite size (nm) for the samples, before and after annealing.

4.4 Self-heating Characteristics

Experiments were conducted for measuring the heating ability of M-AP and M-A samples, dispersed in deionized water and under the application of AC magnetic field. The independent variables in the investigation are the particle concentration, the annealing temperature and the metal type (Co, Ni, Cu or Zn); the dependent variable is the SAR value; and the controlled variables are the synthesis method, the amplitude and frequency of the applied magnetic field. The rise in temperature versus time for each sample, at two different particles concentration of 5 and 15 mg/mL, is shown in Fig. 4.17. The graphs were used to determine the initial slope and calculate the heat generated by SFMNPs in terms of SAR (equation 1). The self-heating measurements are listed in Table 4.4 where M-AP-5 and M-AP-15 represent the as-prepared samples for particle concentration of 5 and 15 mg/mL respectively. Similarly M-A-5 and M-A-15 represent the annealed ones. SAR values are generally comparable to those in the literature (Kombaiah *et al.*, 2018; Raja *et al.*, 2017; Hedayatnasab *et al.*, 2017), except few like Abdel-Hamid *et al.* who reported high value of SAR (298.5 W/g) for cobalt ferrite (Abdel-Hamid *et al.*, 2017). The differences between the recorded values in literature may be attributed to several factors such as the synthetic route, the annealing temperature, the applied field amplitude, the frequency amplitude, the particle concentration, etc. In order for the NPs to be used for hyperthermia, their SAR value should be as high as possible, their used amount should be minimized and the product of the applied frequency and magnetic field should be less than $5 \times 10^9 \text{ Am}^{-1} \text{ s}^{-1}$ (Khot *et al.*, 2013).

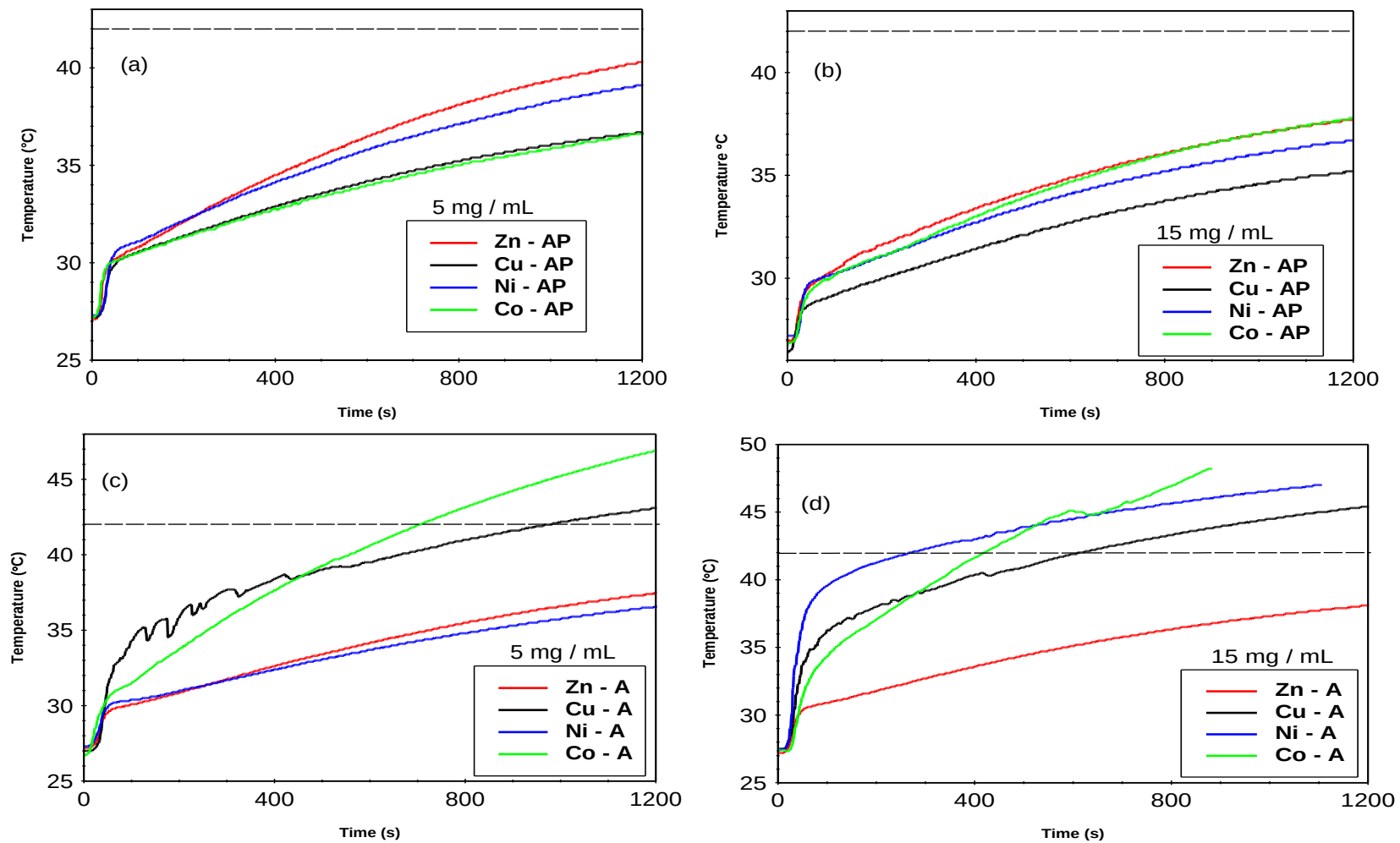


Fig. 4.17 Temperature vs. time curves for M-AP and M-A (5 and 15 mg/mL). The dotted line indicates hyperthermia threshold temperature.

Table 4.4 SAR values, initial slope and maximum temperature for the first 20 min. *Annealed CoFe₂O₄ of 15 mg/mL (Co-A-15) reached 48.2 °C after 14 min; **annealed NiFe₂O₄ of 15 mg/mL (Ni-A-15) reached 47 °C after 18 min.

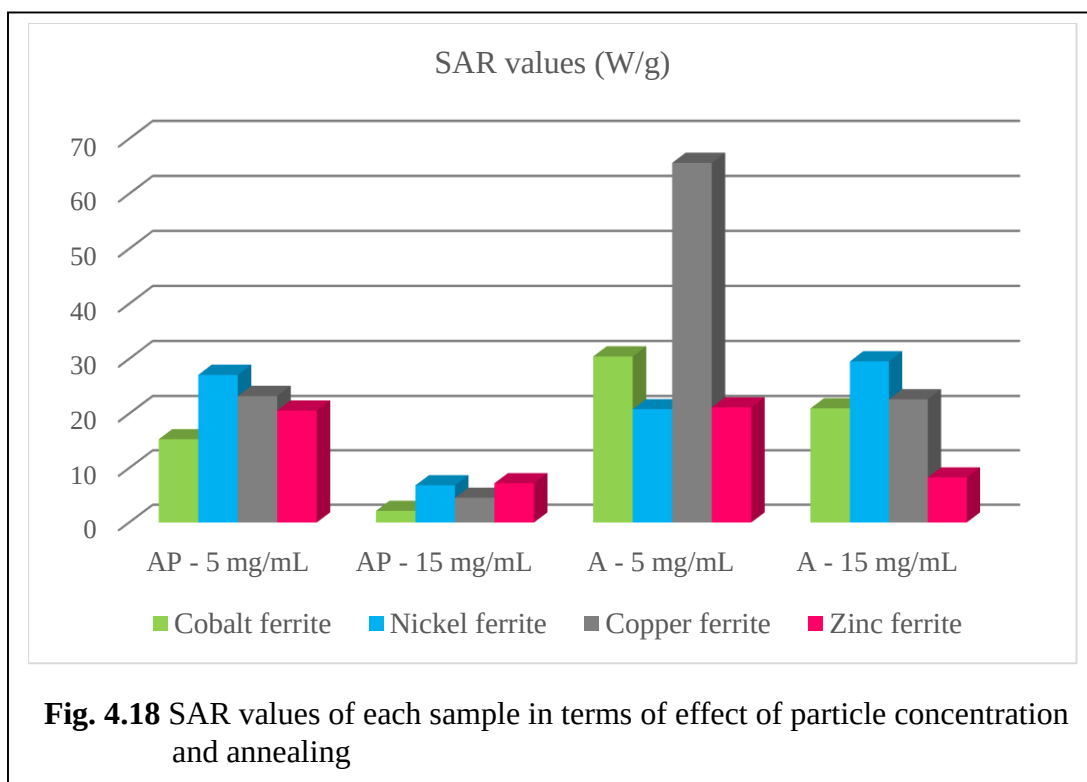
As-prepared samples	Initial linear slope (°C / s)	SAR (W / g)	Maximum Temperature for the first 20 min (°C)	Annealed samples	Initial linear slope (°C / s)	SAR (W / g)	Maximum Temperature for the first 20 min (°C)
Co-AP-5	0.0183	15.299	36.6	Co-A-5	0.0364	30.430	46.9
Ni-AP-5	0.0324	27.086	39.1	Ni-A-5	0.0249	20.816	36.5
Cu-AP-5	0.0278	23.241	36.7	Cu-A-5	0.0785	65.626	43.1
Zn-AP-5	0.0246	20.566	40.3	Zn-A-5	0.0253	21.151	37.5
Co-AP-15	0.00765	2.132	37.8	Co-A-15	0.0753	20.984	48.2*
Ni-AP-15	0.0245	6.827	36.7	Ni-A-15	0.106	29.539	47**
Cu-AP-15	0.0163	4.542	35.2	Cu-A-15	0.0812	22.628	45.4
Zn-AP-15	0.0259	7.217	37.7	Zn-A-15	0.0297	8.276	38.1

By analyzing Fig. 4.17, one can observe a sudden change in slope at about 50 s splitting each graph into two stages: an initial stage with a high slope and a following stage that is less steep. At first, the NPs are aligned under the applied magnetic field (first stage) and once this is completed, the normal heating loss dominates the process (second stage) (Reyes-Rodríguez *et al.*, 2017). The rapid temperature rise in the initial stage is mainly due to the magnetic hysteresis loss and Neel rotation of each ferrimagnetic NP activated by the applied AC magnetic field. Taking into consideration that the heating process of the powder samples are taking place in water then the Brownian loss is negligible. Additionally, Eddy current losses are minor because the samples have very low electric conductivity (Lee *et al.*, 2007). Due to the broad particle size distribution, both superparamagnetic and ferrimagnetic NPs may co-exist in the present samples. This is an advantage for heating ability purposes because the interparticle gap may be filled up with smaller particles increasing the particle interaction energy and the coupling exchange energy, thus improving the magnetic moment as well as magnetic susceptibility (Khot *et al.*, 2013).

For easy comparison, Fig. 4.18 shows the 16 calculated SAR values which are taken from Table 4.4. It clearly indicates that SAR is affected by both particles concentration and annealing. It is found that SAR increased due to annealing and surprisingly for low particles concentration. This can happen because of the agglomeration of particles which has a higher probability to take place in high particle concentration medium; hence, the interparticle dipolar interaction increases dramatically, and the power dispersal to the medium is less. Phong *et al.* showed that increasing the sample concentration is not an obvious reason to obtain high SAR values (Phong *et al.*, 2017). However, the two SAR values of NiFe₂O₄ showed contrary behavior where one of them increased after increasing the

particles concentration of Ni-A (20.816 W/g for 5 mg/mL increased to 29.539 W/g for 15 mg/mL), and the other one decreased after annealing of the 5 mg/ mL particles concentration (27.086 W/g for Ni-AP decreased to 20.816 W/g for Ni-A). This could be due to low agglomeration rate and broad particles size distribution.

The rise of temperature associated with the heat delivered by the SFMNPs to reach the hyperthermia threshold temperature (42 °C) is a necessity condition to destroy cancer cells. The threshold was reached by Co-A and Cu-A for both particle concentrations and by the 15 mg/mL of Ni-A only. But the highest SAR value was for Cu-A (65.6 W/g) with the least CS (26 nm). The formation of larger particles in the other annealed samples has led to low SAR values and this could be attributed to coalescence of smaller grains to form agglomerated “network” at high temperatures. Hence, and under all the conditions provided herein, we might conclude that low concentration of Cu-A serves as a potential candidate for hyperthermia.



CHAPTER 5

Conclusions

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Magnetic nanoparticles demonstrate great potential in nanotechnology because of their ability to be remotely excited by an applied magnetic field. This property advances MNPs as viable therapeutic candidates in biomedical field as heat generators to kill malignant cells while sparing surrounding healthy tissues. Recently, the experimental work has been focused on spinel ferrites magnetic nanoparticles to address their optimization in terms of morphology and size, magnetic properties, in addition to specific absorption rate.

In this research work, MFe_2O_4 ($M = Co, Ni, Cu$ and Zn) magnetic nanoparticles were prepared by the modified sol-gel method. The structural studies indicated that the nanocrystalline powders had spinel-type structures. With the help of Rietveld analysis, the lattice parameters and the microstructural parameters in terms of crystallite size and microstrain were determined. The magnetic study revealed the ferrimagnetic behavior at room temperature of the studied spinel systems. Nickel ferrite NPs exhibited the highest magnetic parameters, whereas zinc ferrite NPs showed the lowest. The effect of annealing was studied where an increase in the crystallites size and a decrease in lattice parameter were observed for all samples. However, the magnetic parameters of the SFMNPs responded differently to annealing, while an enhanced morphology was observed. The investigation of heat generation by SFMNPs indicated that the specific absorption rate was dependent on the concentration of MNPs in the

ferrofluid, where heating originated from hysteresis losses. The highest value of SAR was around 66 W/g for the annealed CuFe_2O_4 . This was attained for the lower concentration (5 mg/mL) and within the threshold temperature of hyperthermia where the temperature reached 42 °C after 18 min. Thus the present results provided grounds for further studies such as the heating ability of coated spinel ferrites, the effect of changing the strength of the applied magnetic field and frequency, and studying the annealing at different temperatures, and so on.

In spite of their significant potential in many fields, SFMNPs are not ready yet to be used in clinical applications due to the absence of validated measurements of SAR values with accurate determination of uncertainty and traceability to national standards in the laboratory conditions. Thus a thorough analysis of the magnetically induced heating is required, taking into consideration the synthetic conditions and the appropriate applied fields in order to obtain the optimal operating conditions. Furthermore, there should be a significant advance in the mathematical modelling of the interaction dynamics of the field induced MNP heating mechanism. Achieving all of the above advancements is crucial because the development of these materials is promising as a lifeline in cancer therapy which is a widespread disease affecting almost every person.

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ملخص الأطروحة

يتركز البحث على أربعة جسيمات ممغنطة نانوية مؤلفة من مركب السبينيل الحديدي. الجسيمات هم كالتالي: الكوبالت الحديدي، النيكل الحديدي، النحاس الحديدي و الزنك الحديدي. أعتمدت طريقة تركيب الجسيمات على طريقة معدلة من محلول الجل ومن ثم عملية التلدين على حرارة 1000 درجة مئوية لمدة خمس ساعات. بعدها تم دراسة خصائصهم البلورية، البنية المجهرية و المغناطيسية. إن إستخدام الأشعة السينية أكد وجود أشكال سبينيل مكعبة مطابقة لمجموعة $Fd\bar{3}m$ لكل الجسيمات النانوية وحالة بلورية واحدة لإثنين من الجسيمات النانوية التي لم تتعرض للتلدين وهي النيكل الحديدي والنحاس الحديدي. غير أن جسيمات الكوبالت الحديدي و الزنك الحديدي النانوية الغير المعرضة للتلدين أظهرت وجود قمم إضافية من أوكسيد الكوبالت و أوكسيد الزنك إضافة الى ثاني أوكسيد الحديد على التوالي. أضف الى ذلك، تراوح حجم البلورة بين 16 و 40 نانومتر. أظهر تحليل ريتفلد حالة بلورية واحدة و زيادة في حجم البورة لجميع العينات التي تعرضت للتلدين، حيث أن حجم البلورة تراوح بين 25 و 73 نانومتر. تحددت خصائص المتغيرات المغناطيسية بإستخدام جهاز الإهتزاز المغنطيسي. تأكد وجود التصرف المغنطيسي للعينات على درجة حرارة الغرفة. إن التشبع المغنطيسي للجسيمات تتناقص على الشكل التالي: النيكل الحديدي < الكوبالت الحديدي < النحاس الحديدي < الزنك الحديدي، بناءً على نفس طريقة التركيب و نفس حرارة التلدين. إن معدل الإمتصاص المحدد الذي يصدر عن مجموعة من الجسيمات المركبة المعرضة الى حقل كهرومغناطيسي متناوب تم إحتسابه بإستخدام القياسات التجريبية. سجلت القيمة القصوى لمعدل الإمتصاص المحدد في هذا البحث للنحاس الحديدي المتلدين (65.6 وات لكل غرام واحد) حيث بلغت حجم بلورته 26 نانومتر وهي الأقل حجماً بالنسبة للجسيمات الأخرى. و يعتقد أن خسارة التخلف المغنطيسي هي السبب لتبديد الحرارة بواسطة جسيمات السبينيل الحديدية النانوية المذكورة في هذا البحث. و هكذا يعتبر النحاس الحديدي المتلدين مرشح محتمل للتطبيقات الطبية من بين الجسيمات الأخرين.

جامعة البحرين

قسم الفيزياء

كلية العلوم



خصائص و قدرة توليد الحرارة لجسيمات السببيل الحديدية MFe_2O_4 النانوية

أطروحة مقدمة كجزء من متطلبات الحصول على درجة الماجستير في الفيزياء التطبيقية

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