CHAPTER 1

INTRODUCTION TO NANOMATERIALS AND NANOFERRITES

1.1 Nanotechnology and nanomaterials

The concept of nanotechnology is attributed to the Nobel laureate Richard Feynman, 1959. According to him, 'There's plenty of room at the bottom'. Feynman's definition was expanded by Eric Drexler 1986 in a most stimulating and lateral thinking way. According to him, nanotechnology is the principle of atom manipulation atom by atom, by controlling the structure of the material at the molecular level. It enables to build molecular systems with atom-by-atom precision, yielding a variety of nanodevices. Binning et al. 1982 expanded Drexler's theories in a practical way. They were first to 'see' atoms and making nanotechnology possible. The term 'nano' originates from the Greek word for dwarf, but in scientific jargon, nano means 10^{-9}. Technology means building of useful things using scientific principles. Thus nanotechnology means building useful machines at the nanoscale.

Nanomaterials are those, which have structured components with atleast one dimension less than 100 nm. Nanostructured materials are classified as zero dimensional, one dimensional, two dimensional and three dimensional nanostructures (Tiwari et al. 2012). Materials that have one dimension in the nanoscale are layers such as thin films or surface coating. Some of the features of computer integrated chips come in this category. Materials that are nanoscale in two dimensions include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles like precipitates, colloids, quantum dots and nanocrystalline materials. Conventional materials contain several billions atoms and

have grain sizes ranging from microns to several millimetres. Nanometre sized grains possess only about hundreds of atoms each.

Nanomaterials and systems can be designed rationally to exhibit novel and significantly improved properties, phenomenon and processes because of their reduced size. When structural features are intermediate in between isolated atoms and bulk material (10^{-9} to 10^{-7} m), the materials often display physical behaviours substantially different from those exhibited by atoms or bulk materials. As particle decreases in size, a greater proportion of atoms are distributed at the surface than those present inside so that there is a significant increase in the volume fraction of grain boundaries. For example, particle of size 30 nm has 5% of its atoms on its surface, those of 10 nm has 20% of its atoms and 5 nm has 50% of its atoms. Hence nanoparticles possess a much greater surface area per unit mass when compared with larger particles. As growth and catalytic chemical reaction occurs at surface a given mass of material in nanoparticulate form will be very much reactive than the same mass of the material made up of large sized particles (Supriya Singh et al. 2013).

1.1.1 Properties of nanomaterials

The properties of nanocrystalline materials are greatly influenced by their grain size and the atomic and electronic structure of their internal boundaries. They possess increased strength and hardness, enhanced diffusivity, improved ductility and toughness, reduced density, higher electrical resistivity, enhanced magnetic behaviour etc (Yang et al. 2006; Vedernikova, 2015). The improved behaviour of nanomaterials is due to the large surface to volume ratio and quantum confinement (Raghavender et al. 2009; Kumar et al. 2014).

Thermal properties

The heat capacity of a solid is directly related to its atomic structure and thermodynamic properties. Measurements of the heat capacity as a function of temperature in nanocrystalline materials reveal the fundamental difference between the nanocrystalline and amorphous state. The heat capacity of a solid is related to its vibrational and configurational entropies and is significantly affected by the nearest configurations. A large number of grain boundaries inside the nanocrystalline materials certainly contribute to the enhancement in the heat capacity. Moreover, the effects of the sample porosities, grain boundary junctions and the lattice distortion in the nanocrystallites should be seriously considered in interpretations of the heat capacity for nanocrystalline materials (Wellong Song et al. 2018).

The linear thermal expansion coefficients are much higher for the nanocrystalline materials than those of the crystalline and amorphous states. Normally the grain boundary has an enhanced thermal expansion coefficient relative to the crystal lattice due to its excess volume and the amount of enhancement is found to be different from different investigations (Nikolaev et al. 2000).

Electrical properties

The crystallites whose size is smaller than the electron mean free path, have dominating grain boundary scattering and hence the electrical resistivity and the temperature coefficient increases. The electrical resistivity is also strongly influenced by lattice imperfections in solids, such as vacancies and dislocations (Dapeng Chen et al. 2009).

Mechanical properties

Many experimental measurements reveal that in conventional polycrystalline materials, the hardness increases with decreasing size. When the grain size is reduced there are more grain boundaries that form effective dislocation barriers, making the material hard (Siti Nikmatin et al. 2017).

Optical properties

The most important property of a semiconductor nanostructure material is its optical behaviour which also differs with the grain size. Optical properties include absorption, spectral response, photoluminescence and Raman scattering and they respond to grain size. All these properties are various manifestation of the size quantization effect which occurs due to the increasing quantum confinement of the electrons and holes when the size of the crystallites is reduced and the consequent change in the electronic structures. The nanoparticles can be used to produce light of different colours by band gap tuning employing grain size effects. The best value of the band gap is obtained from optical absorption measurement which also explains the size quantization effect (Lance Kelly et al. 2003).

Magnetic properties

The diverse applications of magnets require the magnetization curves to have different properties. Nanostructuring of bulk magnetic materials can be used to design the magnetization of the material, leading to soft (with zero coercive field to minimize energy loss) or hard magnets (large coercive fields) with improved properties. The magnetic behaviour of a material normally depends on the structure of the material and on its temperature. When the magnet size is reduced, the number of atoms on the surface

becomes an important fraction of the total number of atoms. Thus surface effects become important and quantum effects start to prevail. When these domains size reaches the nanoscale, the materials show new properties like the Giant Magneto Resistance effect, a fundamental nano-effect which is being used in modern data storage devices (Bashar Issa et al. 2013).

1.1.2 Preparation of nanomaterials

The two ways to achieve nanosize are: coming to the smaller sizes from the larger and it is called as 'top-down processes'. The other way of fabricating the nanostructure is synthesizing them directly from atom, associating them or forming clusters out of them. This is called 'bottom-up processes' (Sabatier, 1986). Top-down approach involves the division of bulk solid into smaller and smaller portions to get nanometre size. Top-down approach involves solid state route such us ball milling, whereas wet chemical routes such as sol-gel, co-precipitation, hydrothermal, microemulsion, gas-phase methods, microwave synthesis method etc come in the category of bottom-up approach.

1.1.2.1 Bottom-up approach

Bottom-up approach includes condensation of atoms or molecular entities in solution or a gas phase to form the material in nanometre range. The bottom-up approach is extensively popular for the synthesis of nanoparticles since it gives a homogeneous size distribution than the top-down approach (Yuliang Wang et al. 2004). The following are a few methods for synthesizing nanomaterials by bottom-up approach.

Plasma arcing

Plasma arcing has been important in forming carbon nanotubes. A typical plasma device consists of two electrodes where an arc passes from one electrode to the other. The

first electrode (anode) vaporizes when electrons are taken from it by the potential difference. Carbon electrodes are used to make carbon nanotubes and atomic carbon cations are produced. These positively charged ions pass to the other electrode and pick up electrons and get deposited to form nanotubes (Emil Omurzak et al. 2007).

Chemical vapour deposition

This method involves deposition of nanoparticulate materials from the gas phase. Material is heated to form a gas and then deposited as a solid on a surface under vacuum. The deposition may be direct or by chemical reaction to form a new product which differs from the material volatilized. This method readily forms nanopowder of carbides and oxides of metals if vapours of carbon or oxygen are present with the metal (Dai et al. 1996).

Sol-gel Process

The sol-gel process involves the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursor for synthesizing these colloids consists of metal ions. Sol-gel formation occurs in four stages:

i) Hydrolysis

ii) Condensation and polymerization of monomers to form particles

iii) Growth of particles

iv) Agglomeration of particles followed by the formation of networks that extends throughout the liquid medium which results in thickening to form a gel (Nurul Nadia Mohd Zorkiplia et al. 2016).

Electrodeposition

Electrodeposition has been used over a long period to make electroplated materials. By controlling the number of electrons transferred, the weight of material transferred can be determined in accordance with the Faraday's law of electrolysis. Nanotechnology aims at placing only a single layer or more of coverage on a surface by electrodeposition in a very controlled manner (JunlingLu et al. 2016).

From natural nanoparticles

There has been reasonable interest in producing pores in materials that moderately sized small molecules of the order of 10 nm or so can fit into and react on the surface. Nanostructured zeolites, phyllosilicates have been synthesized from natural nanoparticles by a small change in chemistry by some interesting new developments (Ana Marija Grancaric et al. 2009). Pillared clays are being used to form composite clay nanostructures.

Spray conversion processing, combustion flame spraying, self assembly (physical and chemical) are the other methods of synthesis of nanomaterials in bottom-up approach.

1.1.2.2 Top-down approach

In top-down approach generally a bulk material is taken and machined to modify into a desired shape and product. Some of the synthesis methods in top-down approach are discussed in brief below:

Ball milling

In this method, macrocrystalline particles are allowed to rotate inside a drum and drop with gravity force on to a solid enclosed in the drum. On milling, the structure breaks down into nanocrystalline particles. The main advantage of this method is that it can be

readily implemented commercially. By ball milling nanotubes and metal oxides can be prepared (Agnieszka Kołodziejczak-Radzimska et al. 2014).

Lithography

This technique is another best method used for the synthesis of nanomaterials by top-down approach. Corbierre et al. 2005 have synthesized gold nanoparticles by electron beam lithography.

1.1.3 Applications of nanomaterials

Nanotechnology will provide the potential to create affordable products with drastically improved performance. This happens by basic understanding of the way to control and manipulate matter at the nanometre scale and by incorporating the nanostructures and nanoprocesses into technological innovations. Nanoscience and engineering could drastically affect the molecular understanding of nanoscale process that take place in the environment; the generation and remediation of environmental problems; the control of emissions; the development of new 'green' technologies to minimize the production of undesirable by products and remediation of existing waste (Chang et al. 2011). Nanotechnology also affords the removal of the smallest. Listed below are some important applications of nanomaterials:

(i) Ferrites are better magnetic materials than pure metals because of their high resistivity, lower cost, easier manufacture and improved magnetization properties. Ferrites are extensively used in radar, audio-video and digital recording, bubble devices, memory cores of computers, satellite communication and microwave devices (Ruirui Qiao et al. 2009; Salunkhe et al. 2016).

(ii) Nanophase ceramics are of particular interest due to their high ductility at elevated temperatures when compared to the coarse-grained ceramics (Vaben et al. 1999).

(iii) Nanostructured semiconductors are known to show varied non-linear optical properties. Semiconductor quantized particles show quantum confinement effects which may lead to special properties, like the luminescence observed in silicon powders and silicon germanium quantum dots and are used as infrared optoelectronic devices. Nanostructured semiconductors are used in solar cells for window layers (Carmen Cavallo et al. 2017).

(iv) Nanosized metallic powders have been used for the production of gas tight materials. Cold welding properties along with ductility make them suitable for metal-metal bonding particularly in the electronic industry (Lerner et al. 2009).

(v) Single nanosized magnetic particles are known as monodomains. One expects that in magnetic nanophase materials, grains correspond to domains and the boundaries correspond to disordered walls. When a particle's size is very small the particles have special atomic structures with discrete electronic states, which give rise to superior properties in addition to the superparamagnetism behaviour (Khandan Fadafan et al. 2018).

(vi) The magnetic nanocomposites have been used extensively for mechanical force transfer (ferrofluids), high density information storage (Garcia-Cerda et al. 2004) and magnetic refrigeration (Farhad Shir et al. 2003).

(vii) Nanostructured metal clusters and colloids have been used in catalytic applications (Ji Xiang et al. 2015).

(viii) They serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been proved to provide substantial advantages concerning activity,

selectivity and lifetime in chemical transformations and electro catalysis (fuel cells). Enantioselective catalysis was also achieved with chiral modifiers on the surface of metal nanoparticles (Xiuru Xue et al. 2018).

(ix) Nanostructured metal-oxide thin films are receiving a great attention for the realization of gas sensors (NO_2, CO, CO_2, CH_4 and aromatic hydrocarbons) with improved sensitivity and selectivity. Nanostructured metal-oxides (MnO_2) can be applied as rechargeable batteries for cars and consumer goods (Glezer, 2011).

1.2 Nanoferrites

Basically ferrites are ceramic materials, dark grey or black in appearance. The word ferrite comes from the Latin word 'ferrum' meaning iron. Ferrites are an important group of magnetic materials and it is also called as ferri magnetic materials. They are complex compounds of various metals and oxygen, exhibiting the phenomenon of ferromagnetism. The general chemical formula of a ferrite molecule is $MOFe_2O_3$, where M is a divalent metal. The commonly used divalent metals are iron, copper, manganese, nickel, cobalt, zinc, magnesium etc. Ferrites are classified as:

i) Spinels: The general formula is MFe_2O_4 (M=Cd, Co, Mn, Cu, Mg, Zn). They are cubic in structure.

ii) Garnets: The general formula is $M_3Fe_2O_{12}$ (M=Y, Sm, Eu, Gd, Tm, Lu) and possess cubic structure.

iii) Magnetoplumbites: The chemical formula is $MFe_{12}O_{19}$ (M=Ba, Sr) with hexagonal structure.

1.2.1 Properties of nanoferrites

The electrical and magnetic properties of a ferrite material are governed by the distribution of iron and divalent metal ions among the tetrahedral and the octahedral sites

of the lattice (Swain, 1993; Ravikumar et al. 2012). Ferrites are essentially ceramics and they are brittle, difficult to machine and have low tensile strength. Generally, bulk ferrites have high permeabililty, high resistivity ($>10^5$ ohm-cm), low dielectric loss, low eddy current loss but large hysteresis loss.

The properties of ferrites are more sensitive to processing conditions, composition and microstructure. When the size of the particle is reduced to nanosize they have enhanced and varied properties (Rashad et al. 2012; Kamellia Nejati et al. 2012; Prakash Chand et al. 2017). Listed below are the enhanced properties of nanostructured ferrites:

- High magnetic permeability

- Low magnetic loss

- High thermodynamic stability

- Low electrical conductivity

- Enhanced catalytic activity

- Increased mechanical strength

- Increased sensitivity and selectivity

- Resistance to corrosion and so on.

Thus the distinguished properties of ferrites at nanoscale make it possible for many practical applications particularly in biomedicine and fabrication of optoelectronic devices.

1.2.2 Structure of spinel ferrites

The simplest among the ferrites are the spinel ferrites. Spinel ferrites crystallize in the form of a cubic structure. Each and every corner of a ferrite unit cell consists of a ferrite molecule. Thus in a ferrite unit cell, there are eight ferrite molecules. In a ferrous ferrite unit cell, there are eight ferrous (Fe^{2+}) ions, 16 ferric (Fe^{3+}) ions and 32 oxygen ions.

If only the oxygen ions in a ferrite crystal are considered, it is found that they constitute a closed packed face centred cubic (FCC) structure. In a ferrite unit cell, there are 16 octahedral sites (surrounded by six O^{2-} ions) and eight tetrahedral sites (surrounded by four O^{2-} ions). Metal ions occupy these sites (Figure 1.1, Bashar Issa et al. 2013). Thus, in ferrites, the number of octahedral sites is twice the number of tetrahedral sites.
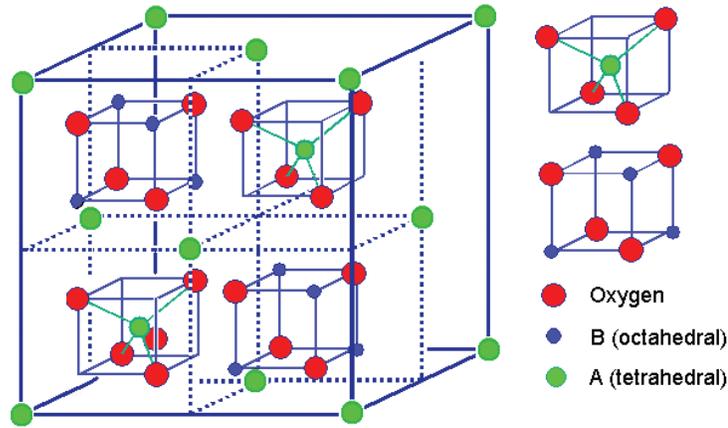
Figure 1.1 Structural image of spinel ferrites

The general formula of a spinel ferrite is $[M_{\delta}^{2+}Fe_{1-\delta}^{3+}]^A [M_{1-\delta}^{2+} Fe_{1+\delta}^{3+}]^B$ where A and B corresponds to the tetrahedral and octahedral sites respectively (Kale et al. 2013). Thus we have two types of structure in ferrites namely, regular spinel (δ=1) and inverse spinel (δ=0). In the regular spinel, each trivalent metal ion occupies an octahedral site (B) and each divalent ion occupies a tetrahedral site (A). A few examples are Zn^{2+}, Ni^{2+} and Mg^{2+}. In the inverse spinel, half of the ferric ions occupy the octahedral site, whereas the remaining half occupies the tetrahedral site. Fe^{2+} is a best example. A variety of cations (divalent, trivalent or combination of them) can accommodate tetrahedral and octahedral site enabling wide variation in the properties of ferrites. M can be replaced by other divalent metal ions and we can have number of spinel ferrites (Rapolu Sridhar et al. 2012;

Ahamed Kandu Sahib et al. 2014; Bhavana Godbole et al. 2013; Baljinder Kaur et al. 2016). Fe^{3+} ions can be replaced by other trivalent ions like Al^{3+}, Cr^{3+}, Ga^{3+} etc. Fe^{3+} ions can also be replaced by combination of divalent and trivalent ions.

1.2.3 Synthesis of nanoferrites

At present a number of methods have been employed to synthesize nanoferrites. Many of them are chemical methods of which co-precipitation method, sol-gel method, hydrothermal method, microemulsion method, combustion method are a few commonly used methods. Each method has its own advantages and disadvantages. The synthesis process needs the control of various physical and chemical parameters such as precursors, pH, temperature, pressure, concentration, doping etc (Gnanaprakash et al. 2007; Roberto Valenzuela et al. 2009; Faiyas et al. 2010).

Co-precipitation method

At present many researchers use co-precipitation method for the synthesis of nanoferrites in bulk. This is one of the simplest low temperature methods in which the precursors are taken in appropriate ratio in an aqueous medium at a desired pH and temperature. This is then heated to get the ferrite nanomaterials. High purity products can be obtained in this method (Polina Yaseneva et al. 2011; Petcharoen et al. 2012).

Sol-gel method

This is another easiest method used for the synthesis of nanoferrites. Here the precursors are dissolved in organic solvent that reacts to form a gel. The gel is further heated to high temperature to obtain the nanoferrites (Gopathi Ravi Kumar et al. 2012).

Hydrothermal method

The hydrothermal technique is becoming one of the most significant tools for processing materials, owing its advantages in synthesizing nanostructured ferrites. It helps in processing monodispersed and highly homogeneous nanoparticles. The reactions are

carried out in a pressurized vessel (autoclave) in the presence of aqueous solvents/mineralisers. In this method control of crystallite size, phase, morphology, surface chemistry are made possible by regulating the solution composition, pressure, reaction temperature, additives, aging time and so on (Byrappa et al. 2007; Srinivasa Thimmaiah et al. 2001).

Combustion technique

This is an excellent method that yields well crystalline nanoferrites with large surface area. This involves a rapid heating of a solution. During combustion, at high temperatures the material becomes crystalline. For combustion technique citric acid, urea, glycine are some commonly used fuels (Khot et al. 2013).

Microemulsion method

The preparation method forms one of the most important challenges that would determine the particle size, shape, size distribution, surface chemistry and properties. Microemulsion method is an efficient technique which yields monodispersed colloids consisting of uniform nanoparticles (Sanjeev Kumar et al. 2012).

Sonochemical method

Passing ultrasonic waves through a material induces chemical changes. Sonochemical method is a powerful tool that utilizes ultrasound and generates cavitations in a liquid in which it passes. Cavitations are the generation, growth, and implosive collapse of the bubbles, resulting in intense collapse conditions, locally but at millions of locations. These intense conditions generated are responsible for uniqueness of materials obtained in the process (Sivakumar et al. 2004).

1.2.4 Applications of nanoferrites

The ferrites are an important group of magnetic materials that have wide range of applications extending from low to high permeability devices. The superparamagnetic

behaviour of materials finds its application in biomedicine (Wang et al. 2009; Waqas et al. 2009). Their high permittivity, low electrical conductivity, medium magnetization, narrow ferromagnetic resonance, line width, low magnetic and dielectric losses relative to their bulk counterparts provide them with unequivalent potential applications (Araujo-Neto et al. 2014; Goswami et al. 2017; Raul Valenzuela, 2012). An increasing demand of magnetic materials arises for high frequency applications such as telecommunications and radar systems as microwave technology requires frequencies even up to 100 GHz (Yang et al. 2006; Cho et al.1999). Listed below are some of the most important applications of nanoferrites:

Biomedicine

Nanoferrites possess high magnetic moment, reduced coercivity, AC magnetically induced heating capacity and good biocompatibility. Hence they play a most significant part of magnetic fluid in hyperthermia treatment, the process of cancer treatment. The affinity ligands attached to the surface helps and enable nanoparticles to target specific tissues or cells. Minhong Jeun et al. 2014 have synthesized magnesium manganese nanoferrites ($Mg_{0.285}Mn_{0.715}Fe_2O_4$) that have larger AC heating capacity and magnetic saturation to be used for treating hyperthermia. Also nanoferrites are used in cellular and molecular level to produce advances in the herd of life sciences and health care such as detection of biological entities, clinical diagnosis, magnetic bio separation, Magnetic Resonance Imaging (MRI), protein immobilization, tissue repair, detoxification etc (Mahmoudi et al. 2011; Hongwei Gu et al. 2006; Chomoucka et al. 2010; Saptarshi et al. 2013).

Environment

The rare earth elements doped nanoferrites have high AC conductivity which is capable of uptaking dye contained in coloured waste water. They are excellently

biocompatible and have great concern with environmental impacts compared to the metallic nanoparticles. Ferrites on precipitation scavenge pollutant materials such as mercury from waste streams. Ai et al. 2010 have synthesized $Zn_{0.5}Co_{0.5}Al_{0.5}Fe_{.04}Fe_{1.46}O_4$ with Sm, Pr, Ce, La as rare earths in which La substitution uptakes about 90% of the dye from the waste water.

Catalysis

Nanoferrites have potential use as catalyst or catalyst support to enhance the rate of a reaction. These ferrites are usually synthesized by chemical co-precipitation technique. Nanocatalysis can help in designing catalysts with excellent activity, greater selectivity and high stability. These characteristics can easily be achieved by tailoring the size, morphology, shape, composition, electronic structure and chemical and thermal stability of the particular nanomaterial. Nanocatalysts furnish several advantages over conventional catalyst systems (Sharma et al. 2016).

Communication device

Nanoferrites are attractive materials for microwave to radiofrequency application. The sending, receiving and manipulation of electromagnetic signals are quite large (Sucheta Sharma et al. 2015).

Sensors and magnetic shielding

Nanoferrites have been used to design magnetic sensors which are used for temperature control with sharp and definite Curie temperature (Pankhurst et al. 2003; Richa Srivastava et al. 2012). A radar absorbing paint containing ferrite has been developed to identify an aircraft submarine invisible to radar (Pardavi-Horvath 2000).

Power circuits and others

Ferrites are widely used in radio and television sets. They are used for power circuits such as computers, all kinds of peripherals and also from small to large sized instruments (Goldman, 2006). Further they are used as pigments, inks, paints, electrode material in the process of ozonation etc (Abe, 2000; Soohoo, 1960).

Thus the excellent properties of nanoferrites provide a very promising present and future in various fields.

1.3 Literature studies

Nanoferrites with a cubic inverse spinel crystalline structure are found to be more suitable for the biomedical applications such as magnetic resonance imaging, drug delivery, cancer treatment etc. The lattice of cubic inverse spinel ferrites possess more octahedral sites than the tetrahedral sites and hence exhibit a higher value of magnetization. The size, shape and composition of the magnetic nanoparticles largely depend on the type of salts used (e.g., sulphates, chlorides or nitrates), type of base, pH value, mixing rate, ionic strength of the media, reaction temperature, reactants addition sequence (Tresilwised et al. 2005; Wu et al. 2007). Too many studies have been reported for pure and mixed nanoferrites. They were characterized by various structural, morphological, optical, magnetic, electrical, biological analyses to understand their behaviour and also to enhance their performance for improved applications. Listed below are some literature studies made on nanoferrites for the development of the research:

Shen et al. 2014 synthesized monodispersed magnetite nanoparticles by chemical co-precipitation technique whose shape (nanospheres, needles, cubes) and size was controlled by the surfactant and UV-Visible light respectively. Also they were

characterized by TEM, XRD, FTIR and VSM. Chen et al. 2012 synthesized Fe_3O_4 nanoparticles by co-precipitation method. The particles were investigated using XRD, TEM, SEM, EDS and VSM. Therapeutic effects were evaluated by 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H-tetrazolium bromide and flow cytometry assays which reveals that Fe_3O_4 nanomagneto fluid thermotherapy inhibited MCF-7 cell proliferation and found to be applicable in hyperthermia.

Ayala-Valenzuela et al. 2005 synthesized spherical $Co_xFe_{3-x}O_4$ with x=0, 0.2 and 0.4 by co-precipitation method and magnetic fluids by peptization process using kerosene and oleic acid as liquid carrier and surfactant respectively. The material has been characterized by powder XRD, BET, TEM, VSM and short circuited transmission line technique. The magnetic properties could be tailored by changing the cobalt content. Polina Yaseneva et al. 2011 synthesized $Zn_xCo_{1-x}Fe_2O_4$ (x=0 to 0.5) by co-precipitation method calcined at 500 °C and 800 °C. Zn substitution largely decreases the Curie temperature from ∼440 °C for the undoped sample to ∼180 °C with x= 0.5. For x=0.3 the Curie temperature shifts from ∼275 °C to ∼296 °C after calcination at 500 °C and 800 °C respectively.

Mg–Co–Ti substituted strontium hexaferrite ($SrFe_{12-2x}(Mg,Co)_{x/2}Ti_xO_{19}$ with x = 0 to 2.5) were synthesized by Gordani et al. 2014 employing the co-precipitation method. The samples were studied by XRD, FTIR, SEM, VSM and vector network analysis. It was found that the particle size decreases with an increase in Mg−Co−Ti substitution with crystallite size in the range of 40-45 nm. Vector network analysis measurements showed that the doped samples had much more effective reflection loss values than those of undoped ferrites.

Fabbiyola et al. 2016 synthesized $Zn_{1-x}Fe_xO$ $(0 \leq x \leq 0.2)$ by co-precipitation method with Tween-80 as surfactant. The XRD and Rietveld analysis confirms wurtzite structure of all doped samples. Also SEM, EDAX, photoluminescence, DRS and magnetization-field studies were also carried out. Hamid Ghayour et al. 2017 synthesized zinc doped nickel ferrite nanoparticles ($Ni_{1-x}Zn_xFe_2O_4$) by mechanical milling followed by scattering. The mobility of zinc ions within the lattice structure has been investigated. The variation and importance of magnetization under DC magnetic field has been studied. Zaki et al. 2013 synthesized $Mg_{0.5}Zn_{0.5-x}Cu_xFe_2O_4$ by co-precipitation technique. The sample was characterized for structural, electrical and magnetic studies. The Mossbauer spectra show superparamagnetic relaxation.

Microwave heated (100 ^{o}C) manganese zinc ferrite nanoparticles were synthesized using co-precipitation method by Zhenyu et al. 2007. The XRD reveals pure ferrite nanocrystalline phase. The TEM studies shows agglomerated state with particle size about 10 nm and increases on longer microwave heating. Sharma et al. 2006 prepared $Mg_{0.95}Mn_{0.05}Fe_2O_4$ nanoparticles by high energy ball milling and the samples were characterized by PXRD, SQUID and VSM studies. The sample shows a blocking temperature at 246 K. Mohseni et al. 2012 have synthesized $Mn_xMg_{0.5-x}Zn_{0.5}Fe_2O_4$ nanoparticles by autocombustion technique. The samples were characterized by PXRD, HRSEM, FTIR, VSM and the average crystallite size obtained is 35-67 nm.

Amighian et al. 2006 synthesized manganese ferrite ($MnFe_2O_4$) powder by co-precipitation method. Here the dried powder was heat treated for 2 hours at different temperatures in argon atmosphere and cooled rapidly to room temperature, using water quenching. XRD patterns show that the annealed (1050 °C) sample is single phase with mean crystallite size 80 nm. Magnetic measurements of cold pressed pellets gives small

value of saturation magnetization (1330 G) compared to bulk sample (5000 G). Ahmed et al. 2016 synthesized a series of copper doped manganese ferrites ($Mn_{1-x}Cu_xFe_2O_4$, $0.0 \leq x \leq 0.7$) by auto-combustion method. The materials were examined by various characterization techniques such as XRD, EDX, SEM and dielectric studies (frequency range 100 KHz to 5 MHz). The dielectric constant increases upto x = 0.3 and then decreases. Valesca Donizeti de Oliveira et al. 2016 prepared mixed $Mn_xCu_{1-x}Fe_2O_4$ with x=0.40, 0.42, 0.44, 0.46, 0.48 and 0.50 by uniaxial pressing at 1000 ^{o}C for 45 hours, finally heated to 1200 ^{o}C for 5 hours at room atmosphere. The synthesized materials were investigated to study their structural, electrical and magnetic properties.

Awati et al. 2012 studied the structural and magnetic properties of $Ni_{0.8-x}Cu_xZn_{0.2}Fe_2O_4$ (x=0.0 to 0.6) nanoparticles prepared via auto-combustion method. The particle size calculated from XRD pattern ranges from 25 to 40 nm. They were further characterized by SEM, TEM, VSM and dielectric studies for as prepared samples and sintered at 700 ^{o}C with improved performance as copper content increases. Khot et al. 2011 studied the magnetic properties of $Mg_{1-x}Zn_xFe_2O_4$ (where x = 0.3, 0.4, 0.5, 0.6) ferrites synthesized by oxalate co-precipitation method at different temperature. The magnetic nanopowders were characterized by XRD, far IR absorption, SEM and the average size determined from SEM is 0.350 μm. The magnetization ranges from 2 emu/g to 8.28 emu/g for samples synthesized below 100°C. The magnetic studies show that the Curie temperature lies in the range of 27 ^{o}C to 75 ^{o}C. Uzma Ghazanfar et al. 2005 prepared nickel zinc ferrites ($Ni_xZn_{1-x}Fe_2O_4$, with x=0.66, 0.77, 0.88 and 0.99) by ceramic solid-state reaction method with a few wt% of Si to improve the resistivity. From electrical resistivity measurements the activation energy is found to increase with increasing resistivity (Ni content). Mobility decreases with increasing resistivity and increases with

temperature (30 to 180 ^{o}C). Nikam et al. 2014 fabricated cobalt zinc ferrite ($Co_{0.5}Zn_{0.5}Fe_2O_4$) nanoparticles of size 19 nm. XRD, TEM, VSM and AC magnetic heating characteristics have been investigated. The Specific Absorption Rate was measured as 167.5-335.2 oersteds at 265 KHz.

XRD, TEM, VSM analyses were carried out for cobalt aluminium ferrite ($CoAl_yFe_{2-y}O_4$) nanopowders synthesized by microwave assisted sol-gel autocombustion method by Waghmare et al. 2017. The grain size increases and the magnetization decreases with increase in non magnetic Al^{3+} concentration. Shadab Dabagh et al. 2016 synthesized $Co_{1-x}Cu_xFe_{2-x}Al_xO_4$ ($0.0{\leq}x{\leq}0.8$) nanopowders by the co-precipitation method. The effect of Cu–Al substitution has been investigated from XRD, FTIR, FESEM and VSM studies. They form a secondary phase, α-Fe_2O_3 and the crystallite size of the powder calcined at 800 ^{o}C lies in the range of 19-26 nm.

Shirtcliffe et al. 2007 prepared aluminium substituted barium and strontium ferrite with chemical formula $BaAl_xFe_{(12-x)}O_{19}$ and $SrAl_xFe_{(12-x)}O_{19}$ respectively by sol-gel route followed by auto-combustion reaction. All the samples consist of particles smaller than 1 μm. Characteristic structural and morphological changes were observed as they move from iron to aluminium ferrites. Vijaya Kumar et al. 2015 fabricated $Ni_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0) nanoparticles by sol-gel auto combustion method. They were characterized using XRD, SEM, EDX, FTIR and VSM. The crystallite size is found in the range of 17-52 nm. The composition x=2.0 exhibits superparamagnetism with nearly zero coercivity and retentivity.

1.4 Scope of the present work

In many of the synthesis discussed in the literature high stirring speeds, controlled atmospheres, reaction medium and drying temperatures were required. Of the preparation

methods co-precipitation method is one of a facile and convenient way to synthesize magnetic nanoferrites from aqueous salt solution (Ahmed et al. 2015; Bhuvaneswari et al. 2016). It is not only a simple method but also have low environmental impact, as it is carried out in aqueous solutions without using any organic solvents under the conditions of relatively low reaction temperatures (Faraji et al. 2010). In the present study a very easy method for which the use of controlled atmospheres and high stirring speed is not necessary has been employed. In the present work only mild magnetic stirring is used, the reactions are carried out in an alkaline atmosphere created by the sodium hydroxide solution and the nanoparticles obtained are air dried. Considering the biological and technological importance of mixed nanoferrites the author has synthesized and studied in detail some useful mixed manganese ferrite nanoparticles. The main objectives of the present work are:

- To synthesize mixed magnesium manganese nanoferrites ($Mg_{0.5}Mn_{0.5}Fe_2O_4$), zinc manganese nanoferrites ($Zn_{0.5}Mn_{0.5}Fe_2O_4$), nanocrystalline copper manganese ferrites ($Cu_XMn_{1-X}Fe_2O_4$; X=0, 0.25, 0.5, 0.75 and 1) and Al^{3+} substituted copper manganese ferrite ($Cu_{0.5}Mn_{0.5}Al_{0.5}Fe_{1.5}O_4$) nanoparticles by chemical co-precipitation technique.

- To analyse the structure of all the synthesized samples through powder X-ray diffraction studies and hence to calculate the crystallite size and various structural parameters from the XRD pattern.

- To examine the morphology, shape and also to determine the crystallite size from the images taken using high resolution transmission electron microscope. To view the crystallinity of the samples from the diffraction ring pattern obtained using selected area electron diffraction taken along with HRTEM.

- To view the morphology and to identify the shape from the images obtained from scanning electron microscope. Also to identify the elemental composition and to confirm the purity of the synthesized samples by energy dispersive X-ray spectroscopic analysis.

- To carry out UV-Vis spectral analysis and to determine the band gap energy, refractive index and optical dielectric constant from the absorption spectra obtained.

- To investigate the superparamagnetic behaviour and hence to determine the magnetic parameters from the hysteresis curve obtained at room temperature using vibrating sample magnetometer.

- To carry out the dielectric analysis and to examine the frequency response of dielectric constant and dielectric loss at some selected temperatures. Also to study the frequency response of AC conductivity at the selected temperatures.