CHAPTER 1

INTRODUCTION

1.1 Origin of Nanotechnology

The thought that proved a mile stone to the world of nanotechnology were first conferred by legendary physicist Richard Feynman in 1959 in his converse There's Plenty of Room at the Bottom, in which gave the idea of possibility of production through direct manipulation of atoms. The word "nanotechnology" was first exercised by Norio Taniguchi , while it was not that extensively known.

Drexler was the one whose efforts lead to provide the platform to the nanotechnology as a field and due to the popularity gained for the most part of nanotechnology has engaged in the investigation of several routes to make mechanical devices from small number of atoms [1]. Two major inventions sparked the expansion of nanotechnology in present age. First was of the scanning tunneling microscope (STM) that provided prophecy of individual atoms and bonding. STM was productively used to manipulate individual atoms. Second was the discovery of Fullerenes.

1.2 Brief Idea of Nanotechnology and Nanomaterials

The term Nanotechnology can be defined as the science cum engineering of functional structures at the molecular level. It covers both existing work as well as ideas that are more progressive. Practically, nanotechnology is defined as the science and engineering involved in the aim, preparation, characterization, and function of devices with smallest functional unit on the nanometeric scale is one dimension or it is billionth part of a meter division. Initially, a common depiction of nanotechnology [2-3] referred to the specific technological objective of precisely controlling atoms and molecules for production at macro scale level, which is now termed as molecular nanotechnology. These definitions reflect the statement that quantum mechanical results are significant at quantum size scale so a modification in the definition was opted from a specific technological objective to a general research division including all eras of researches and technologies that cope with the unique characteristics of matter that arise below the macro size threshold. Thus the main and important trait of nanotechnology/ nanoscale technology that is exceptional factor of the broad field of research in the area of nanotechnology is size. Fig. 1.1 represents the comparisons of size of nanomaterials. Size dependent nanotechnology is of course an extremely vast area of research undertaking the diverse fields of science including microfabrication [4], medicine science, surface science, organic chemistry, microelectronics, materials chemistry, molecular biology, biotechnology, semiconductor physics, information technology, energy storage [5-6], molecular engineering, etc [7]. Nanotechnology/nanoscience has its branch spread in all dimensions of science, it is not limited to only one type. Nanotechnology/nanoscience has its branches widespread from extensions of typical device physics to entirely innovative approaches based upon self assembly of molecules [8] and also from building up novel materials with nanoscale dimensions to atomic level direct control of matter .

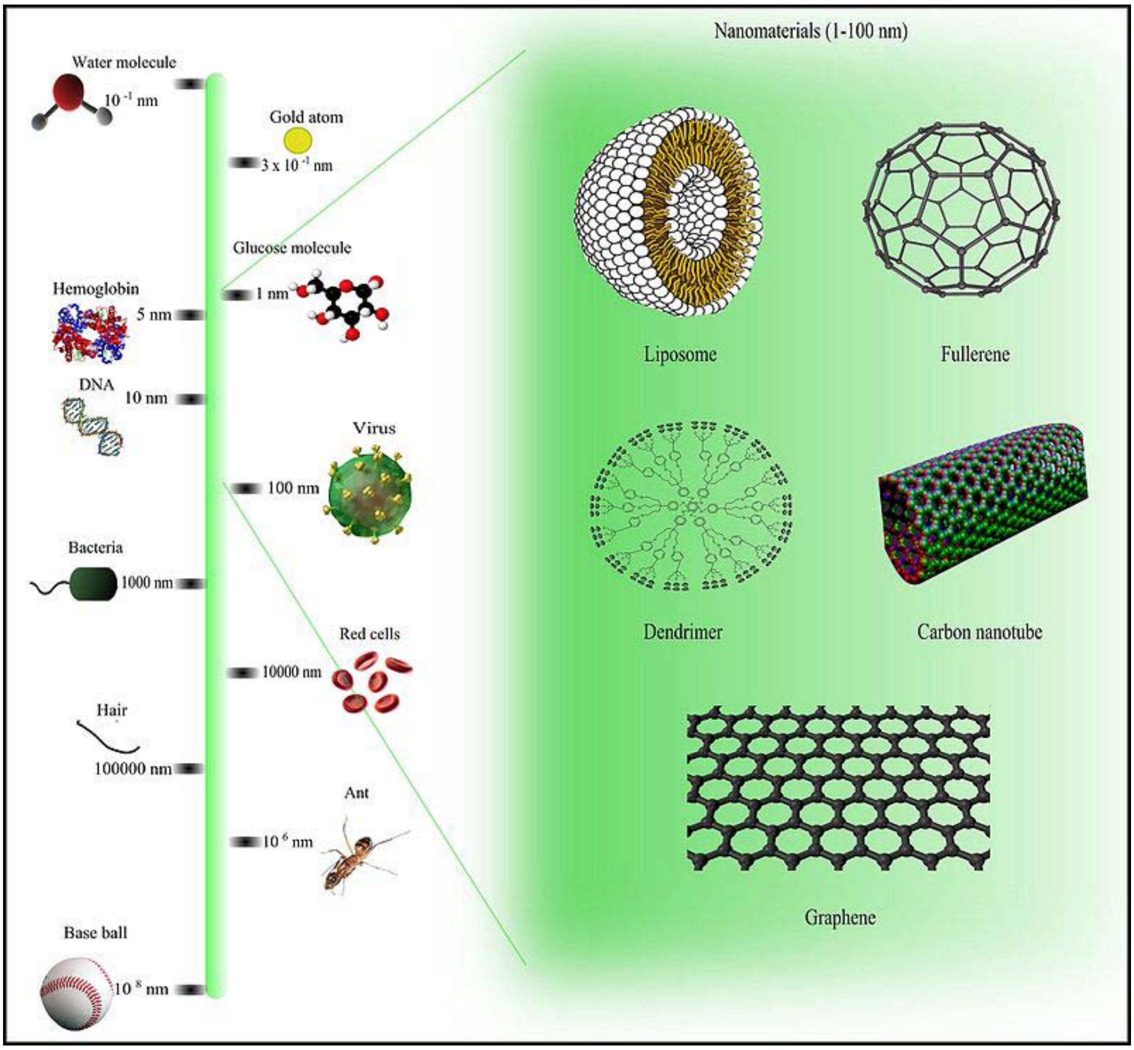

Fig. 1.1: Comparison of nanomaterials size

A significant number of materials emerging from nano building block like glass, ceramics, fibers and polymers are assembling their route to the marketplace and are at hand in all profiles and shapes in routine life.

1.2.1 Brief Introduction to Nanomaterials

Nanomaterials are keystones of nanotechnology. Nanoscience and nanotechnology of nanostructured materials is a wide and extensive area of study and development that has been growing so rapidly and explosively all around world. Nanomaterials include fields that tend to study or fabricate materials with extraordinary properties occurring from nanoscale dimensions [9]. It has the capability for revolutionizing the system in which materials are fabricated. Research on nanomaterials consider materials science based technique to nanotechnology resulting progress in the methodology of materials and preparation which lead to development of microfabrication research. Materials having nanoscale structure often have exclusive electronic, optical, magnetic and mechanical properties [10]. Nanomaterials are gradually developing into commercialization and emerging as commodities [11-12]. Nano-objects/nanomaterials are generally divided as out of the three dimensions how many of them falls in the nanoscale region. Nanostructured materials are generally classified by phases of matter they include. Nanomaterials can be categorized in 0 dimensional, 1 dimensional, 2 dimensional and 3 dimensonal nanomaterials as shown in figure 1.2

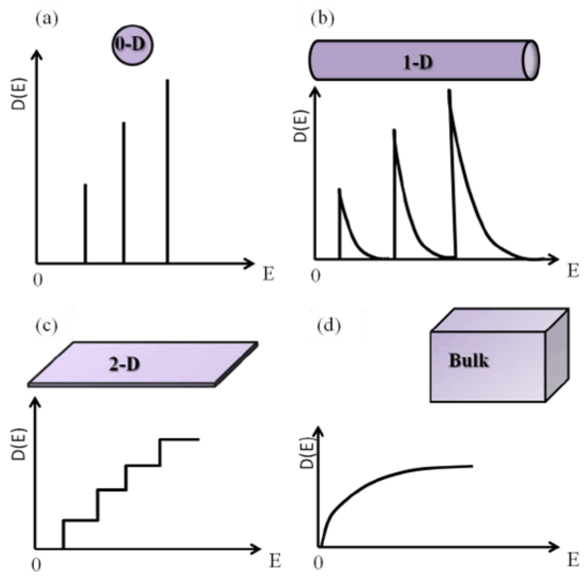

Fig. 1.2: Schematic representation of (a) 0-dimension (0-D), (b) 1- dimension (1- D), (c) 2- dimension (2-D) and (d) 3-dimension (3-D)

A nanoparticle is classified a nano-object when all of its three external dimensions fits in the nanoscale, with its longest and the shortest axes are almost of equal measurement and do not vary significantly. For example nanofiber has one in and two out dimensions in the nanoscale region, either nanotubes (hollow nanofiber) or nanorods (solid nanofiber). Similarly nanofilm has two in and one out measurement in the nanoscale region. For nanofiber/ nanorods/ nanotubes and monofilms, the remaining dimensions necessarily not be in the nanoscale but should be considerably larger [13]. Figure 1.3 represents the examples of size based nanomaterials.

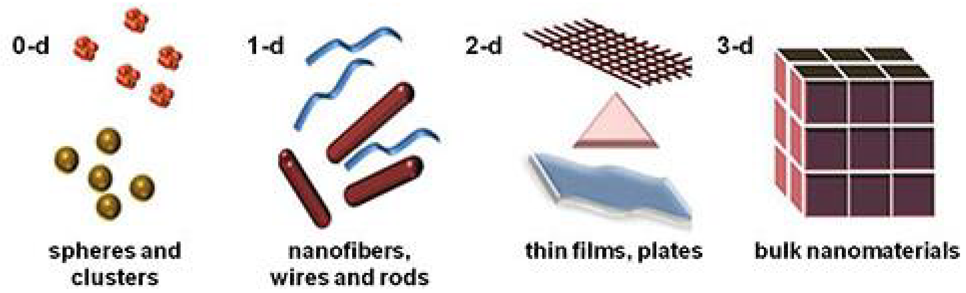

Fig. 1.3: Examples of size based nanomaterials

As nanocomposites are nanomaterials enclosing minimally one chemically or physically dissimilar region, or group of regions, having minimally one dimension in the nanoscale. A nanofoam has a matrix made up of some liquid or solid, enclosing a gaseous phase, where any of the phase can have dimensions on the nanoscale. Simlarly nanopores of the nanoporous material have its cavities lying in the range of nanodimensions. Also nanocrystallite has a important fraction of the crystal grains grown in in the nanoscale range [14]. The dimensions of nanomaterials play a significant role in analysing the properties of nanomaterials. The unique fact about nanomaterials is their surface to volume ratio. At nanoscale level surface-to-volume ratio is observed to be increase while in bulk matter it follows reverse criteria. This suggests that diminutive nanomaterials possess higher surface area in comparison to bulk.

1.3 Properties of Nanomaterials

The properties of nanomaterials possess exceptionally close dependence on the dimensions, size, shape and morphology. Nanomaterials acquire the structural features that are boundary line between atoms and the bulk matters. Whereas micro-structured materials possesses about comparable features that to corresponding bulk matter but when it comes to nanometric scale, the properties of nanomaterials drastically changes and almost entirely different properties from the those signified by bulk matter and atoms. For instance the properties possessed by the bulk material such as electronis structutre, mechanical strength, electrical conductivity, toxicity and solubility are completely different when analysed at nano level [15].This is chiefly as a result of the nanometric size showing feature like hefty portion of surface atom, spatial confinement, comparatively high surface energy and diminished imperfections.

1.3.1 Optical Properties

Optical properties of nanomaterials consist of laser, optical detector, device sensor, solar cell, displaying and imaging, photocatalysis, biomedicine and photoelectrochemistry. The optical properties of nanomaterials are based on features like grain size, shape, surface to volume characteristics, doping, substitution and dealing with the surroundings or other nanostructured materials. Figure.4 represents the difference in the optical properties of metal as well as semiconductor nanoparticles. In figure 1.4, a slight change in the size of CdSe semiconductor nanoparticles amends the optical properties of the CdSe nanoparticles. For the For the samples of nanospheres of gold when the size of metal nanoparticles is extended then only a slight change in optical properties of nanomaterials is seen. Here it is noticed that colour of gold nanoparticles goes from deep red to black.

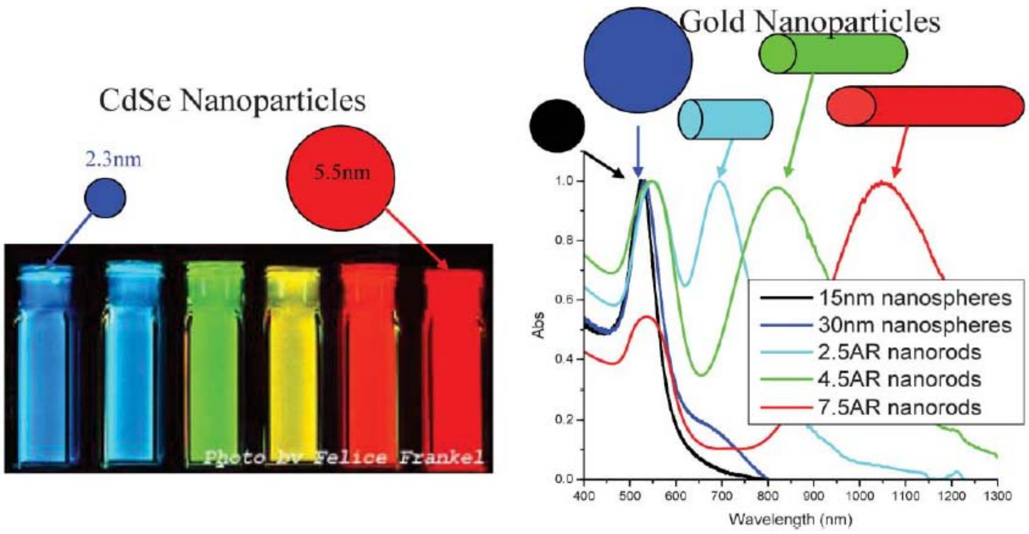

Fig. 1.4: Emission of CdSe quantum dots of various sizes and absorption spectra of gold nanoparticles

It is due to the fact that in semiconductors, with decreasing particle size the band gap increases. The outcome of increasing band gap is shifting of absorption of light to the region of inclined to high energy and vice versa. As a consequence the band positions of valence and the conduction bands also varies from stabilized to destabilized and in reverse manner too. Thus leading to the increasing in oxidation and reduction capability of the semiconductor.

1.3.2 Electronic Properties

The variations resulting in the electronic properties is reduction of system length that caused due to increasing quantum mechanical effects of the system resulting from the wave-like property of the electrons. Again, as the size of the nanomaterials matches with de Broglie wavelength, the discrete character of the energy states comes into play and a discrete energy spectra is examined when the system remain confined to three dimensional region. At nanoscale level some conducting materials transform their behavior and act as insulators due to the overlapping of energy bands. This led to the migration of electrons from one region to another region of close lying nanostructures. At that stage with the application of voltage , the discrete energy stages tend to align themselves in a particular manner resulting in the resonant tunneling or flowing of tunneling current which adds up to increase the tunneling current flow. All these processes can be used to manufacture various types of components for many applications.

1.3.3 Electrical Properties

Flow of electric current through the conductor is because of free movement of electrons through the atomic lattice. The flow of electric current is measured by the amount of charge throughout the conductor.

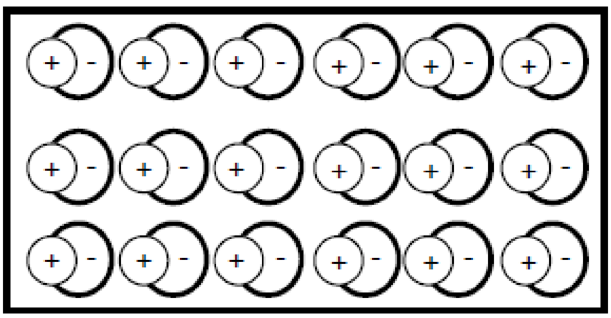

Fig. 1.5: Shifting of electron cloud against lattice

This charge is not quantized but discrete as ih may have fractional value too. This results in the movement of the electrons against the lattice. This shift changes continuously and therefore the flowing charge is considered as continuous quantity shown in figure 1.5.

But if any ordinary conductor is disturbed by tunnel junction, then the movement of electric charge will happen by both the pathways that are continuous as well as discrete. Because only discrete electrons are allowed to pass through the junctions, then charge will build up on the surface of the electrode beside the isolating layer, unless a high adequate bias has developed across the junction in figure 1.6. Thus transfer of one electron will take place.

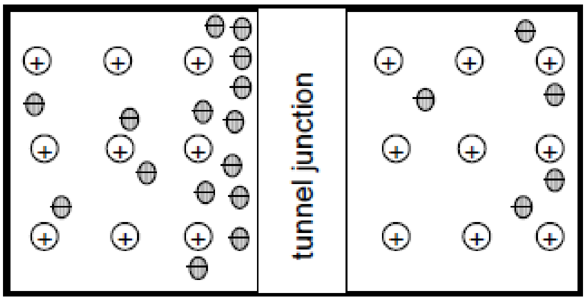

Fig. 1.6: Accumulation of electrons at tunnel junction

1.3.4 Mechanical Properties

Dielectric strength is the strength of applied voltage that a object can hold before suffering breakdown. Dielectric strength is dependent on the thickness of the manufacturing material and is usually expressed as voltage gradient defined as voltage per unit length. The voltage gradient at position of breakdown is much higher at the very thin piece of material's section (<100µm thick) than that for thick regions. The impact of dielectric strength for a sample is also influenced by physical conditions employed to the specimen such as temperature and humidity, any cavities or presence of foreign substances in the specimen, and also the testing conditions, making it complicated to compare data obtained from other sources. Dielectric materials are widely used in the electronic applications the same as capacitors in electronic appliances.

1.3.5 Magnetic Properties

Some materials possess magnetic behavior only at nanoscale that is their nonmaterial form. Magnetic properties are more noticeable at nanolevel. For example Platinum and gold at their bulk level behaves non- magnetically but these materials attain their nano level they show magnetic character. At nano range, the interactions of surface atoms with other element are also improved and surface atoms at nano level are different to those of bulk atoms. This occurrence suggests new ways of capping the nanoparticles with other species to offer improve physical properties. Figure 1.7 gives a diagrammatic representation of magnetic properties of nano materials.Also, in the nano range there is possibility that a ferromagnetic nano material have originate from a non- ferromagnetic material at its bulk. For example Pt, Pd and Au are non-magnetic when present at their bulk but as they attain the nano level they turn out to be magnetic. Gold material shows unexpected behaviour of magnetism at nano range because of its diamagnetic nature at bulk level. The reason for palladium and platinum to posses ferromagnetic behaviour is the siize effect resulting into structural changes which is the most key application of nano science. While ferromagnetic behaviour of gold particles arose from capping behaviour. Due to capping of gold particles with some other material the charge appears on the surface which is responsible for its ferromagnetic character. Gold particles at surface shows ferromagnetic character at nano range while gold particles present at its core in nano region shows paramagnetic behaviour within a diameter of 2 nm. Unexpectedly, Gold nano particles when observed at room temperature achieve permanent magnetic behaviour these are capped by thiol particles. At their bulk level, gold particles have very low density of states and show diamagnetic characteristics. This study suggests that to attain ferromagnetic character at nano range, the d-band structures need to be modified by the chemical bonding among the particles.

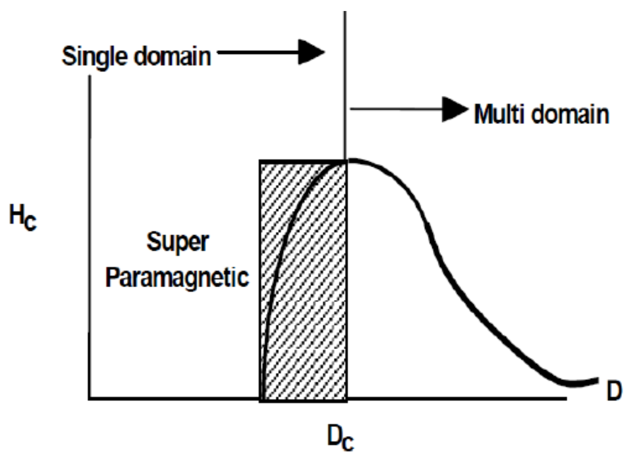

Fig. 1.7: Magnetic properties of nano structured materials

1.4 Synthesis Approaches to Nanoscale Structures

For the advancement of technology there is need of new materials that could meet the requirements/demands of modern era. As this is time of nanotechnology so more efforts are emphasized to the production and development of nanomaterials with enhanced properties, better functionality, economical cost, environment friendly and reliable by the material scientists and researchers. For the achievement of above said properties, a number of physical and chemical methods have been employed to acquire the better performance of nanomaterials than the previous one aiming to attain better structural properties realized by the control over the particle size and distribution [16].

Basically, the two main approaches for the synthesis of nanomaterials are top-down and bottom-up approaches shown diagrammatically in figure 1.8 [17].

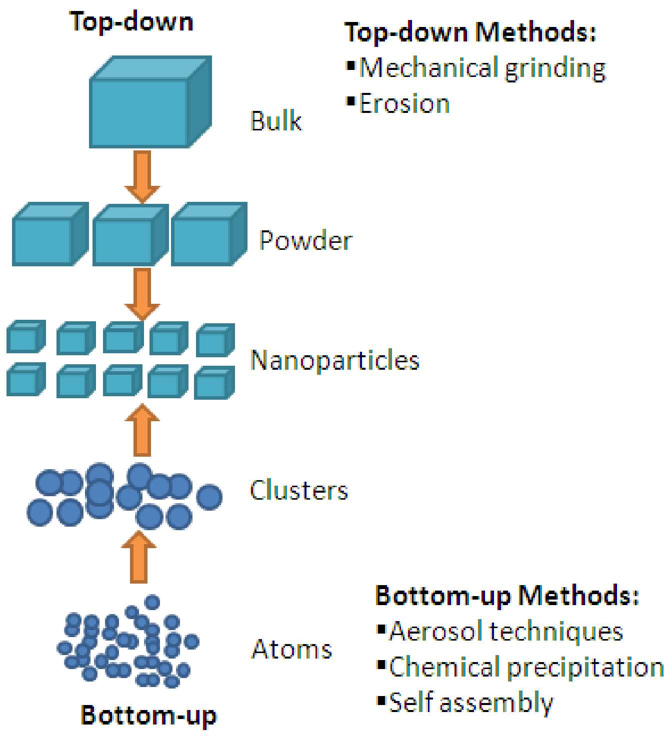

Fig. 1.8: Bottom-up and Top-down approach

Top-down approach is mainly used in the solid state processing of the materials. This route is based with size reduction of the bulk material to make it smaller, making up large particles the smaller one is done by using physical processes including crushing, ball milling or grinding. Generally this method is not appropriate for preparation of materials with uniform shape. The challenge to deal with this method is the imperfect structure at surface. Physical properties of nanostructured materials are highly affected by these imperfections. The main disadvantage of the top-down approach is that it can cause a major damage to the crystallographic patterns.

Bottom up approach as its name indicates refers to the making of materials from lower unit to higher one. Here a material is developed from the bottom that is the assembly of atom-atom, molecule-molecule or cluster-cluster. This route works on the removing imperfection caused by top-up approach that is non uniformity and emphasize on preparation of nanomaterials that have uniform shape, size and uniform distribution of particles over the surface. In this method rate of chemical reaction is controlled to restrain further particle growth.

The choice of preparation and synthesis of nanoparticles is very challenging factor that has to be deal with particle size, purity, cost effectiveness, environment friendly and many other factors. There are many methods of preparation and synthesizing nano particles such as hydrothermal, combustion technique, chemical coprecipitation, ball milling, gas-phase methods, microwave synthesis and sol-gel processing [18-25]. This research focuses on chemical coprecipitation technique, sol gel technique and characterization techniques to study various properties of ferrite nanoparticles.

1.5 Introduction to Ferrites

The analysis of nano crystallites is a dynamic and interesting area of research in almost all the branches of science and technology like materials engineering, physics, chemistry, medical sciences and also in multidisciplinary streams. In this day and age, the spotlight of the material science is the invention of new and novel materials with enhanced structural and surface properties and improved synthesis techniques to deal with the increased technological demands and requirements.

Nanocrystallite materials are in the limelight due to their remarkable properties and applications. Ferrites are non conducting ferrimagnetic ceramic chemical compounds with the representation MFe_2O_4, where M represents divalent metallic element like Mg, Fe, Co, Ni, Cu etc. These are the divalent and trivalent oxides of iron[26]. On account of their coercitivity referring to magnetic properties, ferrites are classified as soft and hard ferrites. Soft ferrites comprise small value of coercitivity comparable to that hard ferrites possess high value of coercitivity. A common soft ferrite having low coercitivity value is MnZn made up of manganese and zinc oxides is a temporary ferrite. While hard ferrites are permanent magnets that shows high value of remanent magnetization after magnetization. Hard ferrites have also high value of magnetic permeability and also conduct flux in their saturated state thus having more capability to accumulate stronger magnetic field than iron [27].

Ferrites are also semiconducting in nature which have numerous applications by their technical point. Commonly ferrites are used in many devices such as core of transformer, activators, sensing devices, memory chips microwave, transducers, permanent magnets, high density magnetic recording media and computer technology etc [28-30]. Nanocrystalline ferrites also have applications in new emerging fields [31-33]. Ferrites also reveal dielectric properties. As a consequence of dielectric properties ferrites do not conduct even with the passage of electromagnetic waves. So ferrites acquire advantage on the verge of dielectric properties over other magnetic transition elements. Porosity is another unexpected feature shown by ferrites which make ferrites ahead of metals as metals do not have porosity. Porosity opens up ferrites to be used in many new applications where metals are insignificant. These considerations accounts for the preference of ferrites over others and leading the ferrite technology toward the better tomorrow [34].

1.6 Physics of Ferrites

The advancement in physics and chemistry of materials has lead to much development in science and technology. It has focussed on different aspects on materials, their configuration, composition as well as their electrical and magnetic behaviour, structure of elements, presence of voids and interstitial sites for doping and substitution of different chemicals to achieve new and enhanced novel features to be use in various applications. This leads to a revolutionary change in science and technology. An appropriate realization of the nature, behaviour to a certain environment, structure and properties of materials outline the basis for preparation and development of new tailor made materials by framing the desirable and useful properties that to be used in many technical devices. Ferrites as stated above are ferromagnetic ceramic compounds dark grey or black in look containing metal oxides. A ferrite core is constructed by pressing the powder form made from the raw constituents. Required shape is achieved by pressing the powder and then sintering is done to convert it into a ceramic compound. In the commercial ferrites, they can be divided into three important classes, with each one having a specific crystal structure. On the commercial basis they can be divided in to three categories named as spinel ferrite, hexagonal ferrites and garnet, each having a different and specific crystal structutre.

1.7 Classification of Ferrites

Ferrite can be classified into four different categories

(i) Spinel Ferrite

(ii) Hexagonal Ferrite

(iii) Cubic Garnet

(iv) Ortho Ferrite

1.7.1 Spinel Ferrite

Spinel or cubic ferrites are the most extensively used group of ferrites. Spinel ferrite possesses high electrical resistivity and small eddy current losses make them useful for microwave applications. The structure of spinel ferrite represented by mineral spinel $MgAl_2O_4$ was primarily observed by Bragg and Nishikawa in 1915 [35, 36]. The general representation of a spinel ferrite is MFe_2O_4, here M represents divalent metal ion for instance Zn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Mg^{2+}, Cu^{2+} or a combined form of these ions . The unit cell of spinel ferrite is face centred cubic (FCC) shown in figure 1.9 and its formula can be written as $M_8Fe_{16}O_{32}$. In FCC structure tetrahedron at centre is created by four oxygen ions. Out of which three oxygen ions combine with each other resides in a plane while the fourth one places itself on the top of the plane at central position formed by three ions. The void created by three oxygen ions provides space for cations. Octahedron is created by six oxygen ions and interstitial is present at its centre. Here four anions made contact with each other while remaining two places themselves above and below the plane created by four anions symmetrically. The radius of interstitials to fit in spinel ferrites for tetrahedron site is 0.30 Å and that for octahedron sites is 0.55 Å [37]. Two types of interstitial positions occur and these are filled by the metallic cations. There are on total 96 interstitial sites out of which 64 are tetrahedral (A) sites and 32 octahedral (B) sites. In case all the tetrahedral sites are vacant and entire the octahedral sites are occupied then the crystal will possess rock salt structure and if there is a case in which all the tetrahedral sites are filled then structure looks like zinc-blend structure. Cations present in each type of intrinsic spinel ferrites are double the number of occupied octahedral and tetrahedral sites. Mixing of zinc blend structure and rock salt structure in a uniform manner can be considered as composing spinel ferrites [38].

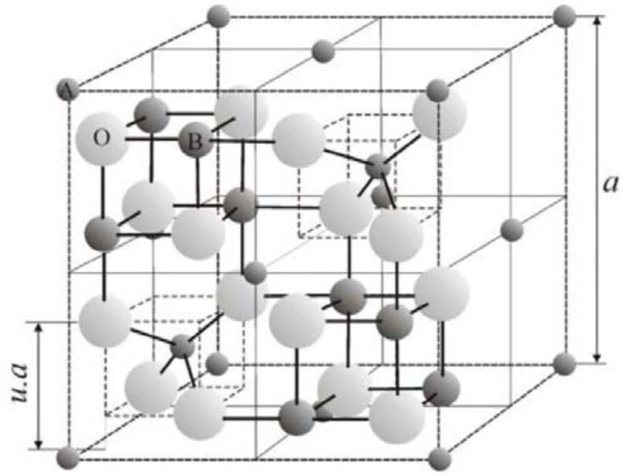

Fig. 1.9: Face centred cubic spinel crystal structure

On the basis of cation distribution on crystallographic sites, the spinel compounds can be grouped into three categories [39].

(i) Normal spinel ferrite

(ii) Inverse spinel ferrite

(iii) Mixed spinel ferrite

(i) Normal Spinel Ferrite

A spinel ferrite is normal if it is having only one type of cations on the octahedral site. In normal spinel ferrites, tetrahedral positions (A) are taken by divalent cations and octahedral positions (B) are occupied by trivalent cations. The formulated representation of normal spinel ferrites is (M^{2+}) A $[Me^{3+}]$ BO_4. Where M stands for divalent ions and Me signify trivalent ions. A common example of normal spinel ferrite is bulk $ZnFe_2O_4$.

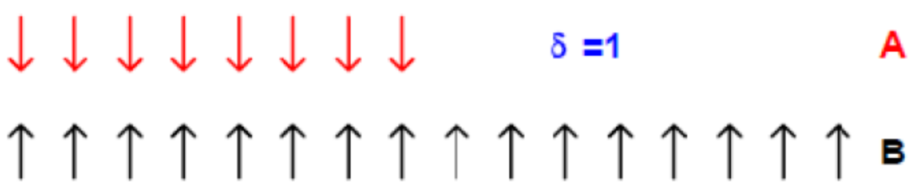

Fig. 1.10: Normal spinel ferrite

Here 'δ' represents degree of inversion that determines the type of ferrite.

(ii) Inverse Spinel Ferrite

In inverse spinels, complete tetrahedral (A) and half of octahedral (B) sites are occupied by half of the trivalent cations, the left behind half of trivalent cations distributes over remaining octahedral sites asymmetrically. The inverse spinel ferrites are symbolized by the formula $(Me^{3+})_{tetra}\,[M^{2+}Me^{3+}]_{octa}O_4$. A common example of inverse spinel ferrite is Fe_3O_4 [40].

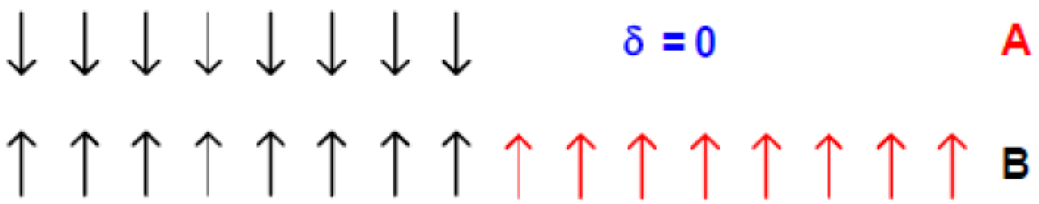

Fig. 1.11: Inverse spinel ferrite

(iii) Mixed Spinel Ferrite

Spinel ferrites that possess their cationic distribution in-between normal and inverse are acknowledged as mixed spinel ferrites for example $(M^{2+}_{\delta}\,Me^{2+}_{1-\delta})_{tetra}\,[M^{2+}_{1-\delta}\,Me^{3+}_{1+\delta}]_{octa}O_4$. Common example for mixed or random spinel ferrites are $MgFe_2O_4$ and $MnFe_2O_4$.

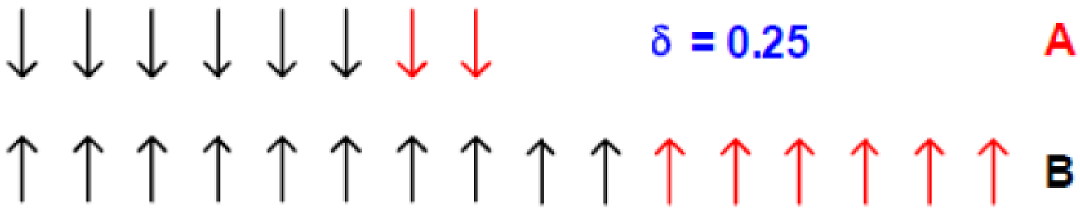

Fig. 1.12: Mixed spinel ferrite

1.7.2 Hexagonal Spinel Ferrite

Hexagonal or rhombohedral ferromagnetic oxides are represented as $MFe_{12}O_{19}$, where M is divalent ion having large ionic radii like Ba^{2+}, Pb^{2+} or Sr^{2+}. Some trivalent ions also participate in hexagonal ferrites like La^{3+}, Cr^{3+}, Al^{3+}, Fe^{3+}. In hexagonal ferrrites with formula $MFe_{12}O_{19}$, oxygen ions comprise closed packed hexagonal crystallography. These are permanent magnets and uses very high frequency to operate. In hexagonal ferrites, for charge to compensate, for every formula unit one divalent iron ion is there. If crystal structure of barium is observed than it is seen that unit cell is composed of two formulae unit. Its structure resemble to spinel structure instead of fact it contains a series of hexagonal sheets of oxygen ions lying in a direction perpendicular to (111) plane.

1.7.3 Cubic Garnet

Yoder and Keith were the first who constructed silicon free garnet. They produced $Y_3Al_5O_{12}$ with substitution of Y^{3+} Al^{3+} on place of Mn^{2+} Si^{4+} in $Mn_3Al_2Si_3O_{12}$ [41]. The general chemical representation of cubic garnet is $Me_3Fe_5O_{12}$.Here Me stands for trivalent ion that may be rare earth or yttrium. The garnet is composed of eight molecules of single cubic unit $Me_3Fe_5O_{12}$ on total having160 atom as a whole. The metal ions are dispersed on three kinds of sites. The Me ions dwell in the dodecahedral sites (C) and are enclosed by 8 oxygen ions also Fe^{3+} ions spread over tetrahedral (A) and octahedral (B) sites in the ratio of 3:2. Keeping in mind the distribution of ions on the different sites and ratio of distribution the garnet is formulated as $Me_3^cFe_2^aFe_3^bO_{12}$.instead of $Me_3Fe_5O_{12}$.

1.7.4 Ortho Ferrite

Typical formula for the ortho ferrites is $MeFeO_3$. Me represents here a large trivalent metal ion which could be rare earth ion or yttrium. They form crystals on a distorted pervoskite structure. The unit cell for these ferrites is orthorhombic. Ortho ferrites are weak ferromagnetic ferrites undergoes canting effect of alignment when two anti ferromagnetic materials are coupled. This canting produces a small ferromagnetism in a direction perpendicular to spin of anti ferromagnetism. The example of ortho ferrite is $HOFeO_3$ and $ErFeO_3$.

1.8 Cobalt Ferrites

Cobalt ferrite nanomaterials [42, 43] being an intermediate magnet is not limited to its multifunctional magnetic properties but it has many interesting catalytic and medical applications based upon its morphology and microstructure. Cobalt ferrite being a stable compound physically and chemically has the capability to be used in the manufacturing of high density digital recorders, magnetic tapes, permanent magnets, magnetic fluids and catalysts. This ferrite has inverse spinel structure and displays large value of coercivity. Orientation dependent cobalt ferrite behaves anisotropically. The direction of magnetization coincides with that of strong magnetic flux occurred and supported by the exchange interaction. The direction of magnetic flux interacts with crystallographic axes and thus bring into being magneto-crystalline anisotropy. In recent times these metal-oxide nanocomposites are a matter of great interest and attraction because of extra ordinary properties framed by them. These nanocomposites offers remarkable optical, dielectric, physicochemical, electrical, electronic, magnetic and chemical characteristics that are much different and advanced from bulk matter. These nanocomposites must possess wholesome phase, particular domain, high coercivity and magnetization[44]. Cobalt ferrite changes its characteristic corresponding to its size and dimensional attainment. It has different properties when at bulk level and properties changes drastically when reaches to nano level because at nano level surface to volume ratio is high while at bulk it has low values. Variation of magnetic properties with reference to particle size is described by many scientists [42-46]. As a consequence of these fascinating and appealing features, nanocrystalline ferrites are of the upmost interest to researchers. To achieve these appealing and interesting properties, it is essential to obtain the nanocomposites that can achieve these features. Hence required fabrication processes [42-45, 46, 47-49] have to be developed and processed. To avoid problems emerging from high reactivity and agglomeration of nanoparticles and also to develop novel materials with unusual properties, nanocomposites could be dispersed in some matrix like silica matrix. Dispersing nano.material to silica matrix attains a control over size, improves the dispersion rate and also reduces agglomeration of the synthesized samples [50-58].

1.9 Applications of Ferrites

Generally, Ferrites are considered superior magnetic materials over pure materials. It is due to the attracting features offered by them for example ferrites are easy to fabricate, economical to manufacturer, high resistivity, improved reactivity and enhanced magnetic properties. Ferrites are wide applications in digital tapes, audio video recording, memory sensors, radar communication system, cores of computers and transformers, mechanical devices, isolators, ultrasonic generators, television picture tubes, antenna core microwaves and satellite devices [59-61].

In modern times, use of ferrites is not limited to a single domain but it has its roots spread over all technical and scientific fields like it is employed in telephone exchange, components of computer, main constituent of magnetic devices. Ferrite being a magnetic material is majorly divided into two types that is soft ferrite and the hard ferrite as discussed earlier. Soft ferrite is division of magnetic materials used in many devices that realize magnetic effects as television picture tube and its core, medical and industrial area, communication devices etc.

Hard ferrites are utilized as permanent magnets mostly in loud speakers and micro motors. As hard ferrites offer better performance and low losses, so these can be primarily work for high frequency range devices. For the good performance in application, suitable and reliable functioning , the technological features responsible are magnetic parameters that are

saturation magnetization (M_S), coercivity (H_C), remnant magnetization(M_R), permeability (μ) and magnetic losses. Some improvements in ferrites are required to get best of these applications as only ferrites are not enough capable to get the best of combinations of these features for some particular application. The one and other ways to advance the ferrites is varying the composition of precursors used, doping or substitution, employing different suitable preparation and synthesis technique so that a control over parameters in a direction can be realized.

Some other functions of ferrites are stated below

High Density Optical Recorder

Blue wavelength of thin films obtained as a product from defected spinel ferrites could be taken up to work as once written and read many times media in optical recorders. These non-stoichiometric spinel ferries being metastable in nature can be altered to extremely hard stable phases at modest temperatures using laser. This transformed section has unlike optical indices as that from initial thin film, favoring the readout process [62].

Magnetic Sensors

Ferrites due to its high permeable nature can be used for space missions as magnetic sensors. These are also applied in temperature control devices. The ferrites having definite Curie temperature can be developed to construct these devices.

Magnetic Shielding

Ferrite materials can be used as to provide magnetic shielding performance like ways highly permeable metals. For example radar absorbing paint made up of ferrite is primarily developed to inform an aircraft, submarine about unknown obstacles which are invisible to radar system.

Ferrite Electrodes

Ferrites that having suitable conductivity and possess good resistant to corrosion have been extensively used as electrode in coating applications to avoid degrading of material for example chromium plating.

Ferrites in Entertainment

Entertainment modes like television, radios and computers broadly made use ferrite of components. These are used in deflection processes, in built transformers etc.

Ferrites are also used in inductors for selective frequency circuits, in storage devices, matching devices, monitors of electronic devices, in chokes, in transducers, in vending machines, as catalysts, in cancer treatment, ultrasonic cleaners, as scattering agent in smog screens, in medical drugs, in hard drives, radar paints, dyes and many more.

1.10 Nanocomposites

Nanpcomposites are multi phase solid materials having each phase in a definite and one of the phases has one, two or three dimensions in nano range that is less than 100 nm.
A nanocomposite is a multiphase material including properties of the component phases with improved and better properties of resulting product. To achieve advanced properties and to optimize the properties, a possible way is to merge different types of elements to form a single material called nanocomposite. Choice of elements depends upon the type of requirement and applications to acknowledge. If anyone of the phases of the constituents has nano scale dimension, then product is called nanocomposite. [55,63]. Nanocomposite formed by metallic oxide or other metallic precursors dispersed in some vitreous matrices like silica matrix have significant applications as a result of the development of advanced materials with desired properties. Magnetic nanocomposites have grown interest for researchers and scientists due to striking and astonishing features shown by these materials. Nanocomposites systems such as Ni/SiO_2, Fe_3O_4 $/SiO_2$, $CoFe_2O_4$ $/SiO_2$, $ZnFe_2O_4$ $/SiO_2$, $NiFe_2O_4$ $/SiO_2$, $CoFe_{2-x}RE_xO_4$ $/SiO_2$ have been exclusively investigated in the previous years as these nanocomposites reveal dissimilar behaviour from bulk [63-68]. Matrix enclosed nanocomposites comprises better structural and chemical stability. Nanocomposites possess important feature is texture or consistency of the matrix, surface area, size and distribution of pore distribution, which has a great control over the properties [69-72].

1.11 Doping of Rare Earth Ions in Ferrites

The rare earth ions on the basis of their radius can be grouped into two classes.

(i) First class is rare earth ions having radius lying close to Fe ions.

(ii) Second class consists of rare earth ions having radius values greater than Fe ions [73].

In the outer most shell of rare earth ions, there are unpaired 4f electrons. The 4f electrons of the rare earth are surrounded by nearby $5S^2$ $5P^6$ and are shielded from the outside potential. Fe has unpaired 3d electrons. When rare earth ions are doped into ferrites coupling between 3d of Fe and 4f of rare earth occurs, that is responsible for magneto- crystalline anisotropy. This magneto-crystalline anisotropy in rare earth doped ferrites tends to improve the magnetic and electric characteristics of product ferrites [74-77]. The rare earth ions generally occupy octahedral (B) sites. In the present study, we have doped gadolinium and neodymium rare earth ions into cobalt ferrite: silica matrix. These rare earth (radius of Gd^{3+} =0.0938 nm, Nd^{3+}= 0.0995nm) have their ionic radii much larger than that of Fe^{3+} (0.064nm).

1.12 Literature Survey

Nanocomposites materials are a centre of attraction to the researchers and scientists in recent years, now a day nanotechnology is like a back bone to many of technical devices. There are many physical and chemical methods for the preparation and synthesis of nanocomposites. Nanocomposites materials offer a vast range of applications in many fields.

M. Houshiar et al. (2014) [78] carried out comparative study based on size, morphology and magnetic properties of cobalt ferrite nanoparticles synthesized by different techniques. From VSM characterization a direct relation between particle size and magnetization is seen. Saturation magnetization and coercivity values have great dependence on synthesis methods as these are small in coprecipitation method by highest in combustion method.

Cobalt ferrite nano powder was synthesized by A.B. Shinde [79] using sol-gel auto combustion technique. Fuel used was citric acid. Synthesis was carried out at low temperature. Structural, micro structure and morphological studies were carried out via XRD, SEM, EDS characterization techniques respectively. The nature of phase of cobalt ferrite samples was observed by X-ray diffraction. EDS spectrum confirms the presence of iron, cobalt and oxygen in proper ratio. Behavior of D.C. resistivity with temperature is observed and found to follow Arrhenius plot.

HUANG Xianghui & CHEN Zhenhua [80] reported the preparation and characterization of $CoFe_2O_4/SiO_2$ nanocomposites using metal nitrates and tetra ethyl ortho silicate as precursors of $CoFe_2O_4$ and SiO_2 respectively. The composites were characterized and analysed by DSC (differential scanning calorimetry), FTIR (fourier infrared spectroscopy), TEM (transmission electron microscopy), XRD (X-ray diffraction) , Raman spectroscopy and VSM (vibrating sample magnetometer) to study various parameters. It was observed that Xerogel synthesized at low temperatures were amorphous in nature. On further heating prepared object at 400 an incomplete structure of $CoFe_2O_4$ clusters resulted. On raising temperature to 600 ^oC, clusters of $CoFe_2O_4$ were created, at high temperature nearly 800 ^oC cobalt ferrite nanocomposites were dispersed in silica matrix. A migration in the magnetic properties paramagnetism to superparamagnetism is seen with raising temperature.On more increasing the temperature, outcome is transformation of magnetic properties from superparamagnetism to ferromagnetism.

S.A. Khorrami and Q.S. Manuchehri [81] prepared and synthesized cobalt ferrite by wet chemical route. Magnetic properties were analysed by VSM technique. XRD, SEM, TEM characterization techniques were employed to study structural and micro structural parameters. S. A. Khorrami concluded that hydrothermal method noticeably promotes the development of the $CoFe_2O_4$ ferrite in comparison to co-precipitation method. Also hydrothermal method is better in forming smaller and fine nanoparticles. Super paramagnetic behaviour was shown by nano particles.

Many researchers [82-87] synthesized cobalt ferrite embedded in silica matrix by sol-gel synthesis method. Formation of single phase cobalt ferrite was confirmed. Uniform morphology is seen without any aggregation of nanoparticles. Due to coating of silica, there is reduction in magnetization values as compared to non coated cobalt ferrite. Silica matrix has larger surface area, pore size and total pore volume than that of the nanocomposite; disadvantage is that it is less stable to temperature fluctuation. Saturation magnetization of composites is linearly related to crystallite size. The results obtain from research carried out by scientists showed that the precipitated ferrite particles into the pore walls mostly are of cobalt in the xerogel diffuses with the rise in temperature. The magnetic nanoparticles present in the porous matrices retain their structure due to inert nature of matrix thus avoiding the much variations in the parameters of prepared materials like porosity, specific surface area and structure of the matrix. This description influences the features of the nanocomposites, such as activity of catalyst, reactivity and saturation magnetization. Owing to the new and promising structural, magnetic and textural features of these nanocomposites, they are proven as potential candidate for numerous technical applications in field of medicine, electronic, industrial and catalytic applications.

Erum Pervaiz and I.H.Gul [88] reported the synthesis of nano sized $CoGd_xFe_{2-x}O_4$ by sol-gel method with concentration of Gd i.e. x varying from 0.0 to 0.1.Synthesized samples are without any impurity. An increase in lattice constant and size of nanocomposite is observed with increasing dopant concentration. Lattice strain increases with increasing doping concentration resulting lattice distortion. Due to replacement Fe^{3+} by Gd^{3+} ion there exist a lattice disorder and increase in AC conductivity is noticed with raising Gd^{3+} composition.

C. Murugesan and G. Chandrasekaran [89] worked on sol-gel auto combustion method to prepare Gd^{3+} substituted cobalt ferrite. Main aim of this work was to analyse the effect of Gd^{3+} substitution on parameters cobalt ferrite such as structural parameter, electrical properties and magnetic behaviour. Here, lowering the size of nanocomposites is observed with raising the amount of Gd^{3+}. As a consequence of substitution the particle size reduces due to the fact that Gd^{3+} ions accumulate at boundaries and hinder the growth of nano crystallites and also results a change in the parameters. The Powder X-ray diffraction pattern confirms the formation of spinel $CoGd_xFe_{2-x}O_4$ nanocomposite showing the presence of GdFeO3 phases. Tetrahedral and octahedral sites are revealed by FTIR and Raman spectroscopy analysis. The magnetic parameters that increased with Gd ion concentration are coercivity and magneto-crytalline anisotropy and the factor decreased is saturation magnetization. It is observed that dielectric constant and ac conductivity resemble Maxwell-Wagner’s model.

W. Wang et al. [90] also reported the synthesis and characterization of gadolinium doped cobalt ferrite. He carried out hydro thermal technique to study the effect of gadolinium doping on Congo Red (CR) absorption capability. TEM reveals the narrow grain distribution and small size of processed nano particles.

The structural and magnetic parameters of Gd doped $CoFe_2O_4$ ferrites were studied by Y. He et al. [91] also. Structural factors like crystallite size, lattice parameter, phase of nanocrystallite are analysed and variations recorded with concentration of Gd. Mossbauer spectra confirmed the ferromagnetic activity of $CoGd_xFe_{2-x}O_4$ nano particles. Scanning electron microscopy explains the grain distribution and morphology. Agglomeration of some particles is the outcome of inter particle magnetic interactions.

Many other researchers like I. Ahmad and M.T. Farid [92] worked on Gd Substituted cobalt ferrite. A series of cobalt ferrite samples with small substitution of Gd, concentration of Gd is varied from 0.00 to 0.25 in small steps of concentration 0.05, were prepared by conventional ceramic technique. XRD confirm the cubic spinel structure of nanocomposites with small traces of $GdFeO_3$ phase. Lattice parameters keep on varying with Gd concentration and presented non linear behaviour. A different behaviour of magnetic properties was observed on varying Gd concentration. Magnetic parameter that is saturation magnetization and remnant magnetization increased with Gd ion concentration increased while coercivity revealed a reverse behaviour with Gd.

Many researchers have used wet chemical methods of preparation of cobalt ferrite in silica matrix [82-87]. Also doping / substitution of rare earth to ferrites is an attractive topic of research. As doping / substitution of rare earth brings an interesting variations in structural and magnetic properties of nanocomposites [89-92]. Also employing a shield of amorphous silica matrix is proved to be a great tool as it prevents agglomeration and stabilize the nano particles from any rough effects. Temperature also plays a great role to the structure, magnetic and morphology of the nanocomposites. As development of ferrite nano particles occur at higher temperature of 600 ^{o}C while at lower temperature crystallites are not fully developed and amorphous behaviour of silica dominates.

1.13 Scope and Outline of the Research Work

The research work carried out and proposed in this thesis incorporates with the preparation, synthesis and characterization of cobalt ferrite in silica matrix ($CoFe_2O_4$: SiO_2). In addition to this, the research work presented also deals with doping of rare earth elements into cobalt ferrite embedded in silica matrix represented as $CoFe_{2-x}Gd_xO_4$:SiO_2 and $CoFe_{2-x}Nd_xO_4$:SiO_2 nanocomposites. Wet chemical route was employed to carrying out preparation and synthesis procedure. Coprecipitation and sol-gel methods are incorporated in wet chemical route. The other methods to synthesize nano materials are hydrothermal method [93], electrochemical method [94], Chemical vapour deposition method [95] etc. Ferrites in silica matrix are a matter of great interest to scientists to deal with due to its unusual and advanced applications. Ferrites show advanced properties and considered as superior magnetic materials than pure metals. Ferrites are given special attention because of the unique magnetic properties possessed by them. Variation in temperature as well as doping concentration has a great impact on structural and magnetic properties of ferrites. The structural parameters that increase with increasing annealing temperature are crystallite size, lattice constant, and grain size while magnetic parameters that vary are saturation magnetization and coercivity. Saturation magnetization and magneton number increases while coercivity decreases with increase in annealing temperature. A decrease in activation energy is also realised with increasing annealing temperature. The increase in doping concentration of rare earth also lowers the particle size.

The main objective of the research work carried out is to synthesize and study structural and magnetic properties of some nanocomposites. The synthesis and description of nano composites along with the analysis of characterization results are presented chapter wise.

The first chapter throws light on the general facts about nanotechnology including its origin, general introduction to nanotechnology and nanomaterials, classification, applications and properties of nanotechnology & nanomaterials. General behaviour of ferrites and their taxonomy is also discussed. The methods of synthesis are also summarized with related diagrams. Ferrites having atypical magnetic properties are also described. A brief review on literature survey is also presented.

Second chapter deals with the methods of preparation, synthesis and characterization techniques carried out during research work. The preparation and synthesis of nanocomposites is carried out via wet chemical route that include coprecipitation method and sol-gel method. Also characterizations techniques are discussed broadly. Various characterization techniques are employed to study different parameters. Characterization techniques discussed are X-ray diffraction (XRD), Fourier transform infrared (FTIR), Thermogravametric analysis (TGA), Scanning electron microscope (SEM), Tunneling electron microscope (TEM) and Vibrating sample magnetometer (VSM).

In the third chapter, preparation of $CoFe_2O_4$: SiO_2 nanocomposites by coprecipitation method is discussed. The as prepared sample followed further heat treatment at different temperatures. Effect of heat treatment on nanocomposites is analysed by TGA characterization technique. XRD, FTIR, SEM, TEM characterization techniques are employed to study structural parameter, micro structure, morphology, grain size distribution, bonding between constituents. Magnetic parameters were studied by VSM technique gives idea of magnetic parameters. Effect of heat treatment on the as prepared and synthesized sample is also analysed.

The fourth chapter include the synthesis of $CoFe_{2-x}$ Gd_xO_4:SiO_2 nanocomposites by sol-gel method. The doping concentration ranges from 0.00 to 0.01. Effect of gadolinium concentration and annealing temperature is examined. XRD, FTIR, TEM, TGA, VSM techniques were employed to study various parameters. The processed and analysed results were compared with the work carried out earlier by other researchers.

The fifth chapter deals with the synthesis and characterization of $CoFe_{2-x}$ Nd_xO_4:SiO_2 nanocomposites. Synthesis process was carried out by sol-gel preparation technique. Neodymium doping concentration was $0< x< 0.1$. Structural study was done by relevant characterization approaches.

The sixth chapter contains the conclusion part. Conclusion was drawn on the basis of research work carried out. Perspective of future work is also proposed.

1.13.1 Objectives of the Study

The following are the main objectives of the study as per the topic of the thesis:

(i) To synthesize binary oxides and their nanocomposites by wet chemical route.

(ii) A systematic investigation of physical properties such as grain size, structural, thermal, optical and magnetic etc of synthesized and thermally treated samples.

(iii) To study the influence of different solvents, precursors, pH, annealing temperature and time on some physical properties of product as mentioned above.

The work presented in this thesis is highly informative to contributor. Contributor deeply believes that work presents important basic information to preparation and analysis of cobalt ferrite nanocomposites. It is also expected that the work carried out in the thesis could open new possibilities for diverse applications of ferrites.

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