CHAPTER - I

INTRODUCTION TO NANOCRYSTALLINE FERRITES

"All materials consist of electrons and nuclei. However, nature has the ability to magnify small variations into vast differences."

Sir Alan Cottrell

"I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get as enormously greater range of possible properties that substances can have."

Sir Richard Feynman

CHAPTER – I

INTRODUCTION TO NANOCRYSTALLINE FERRITES

INTRODUCTION

Today the science and technology of materials is in such an advanced stage as to allow the application of physico-chemical principles for the design of desired new-materials in ceramic, single crystal and/or amorphous forms. This advancement of science and technology of solids is mainly due to the awareness that structure and properties are related at the molecule level. Semiconductors, ferrites, magnetic garnets, solid state lasers, piezoelectrics, ferroelectric, ultraviolet and infrared sensitive crystals, magnetic bubbles etc. are a part of the several solid state devices that are in use today.

Technology in twenty first century requires the miniaturization of devices into nanometer sizes when their ultimate performance is dramatically enhanced. Nanophase and nanostructured materials, the new branches of material research are attracting a great deal of attention because of their potential applications in areas such as electronics [2], optics [3], catalysis [4], ceramics [5], magnetic storage [6,7] and nanocomposites. The unique properties and the improved performances of nano-materials are determined by their size, surface structures and interparticle interactions. The role played by particle size is comparable in some cases to chemical composition, adding another flexible parameter for designing and controlling their behaviour.

1.1 HISTORICAL

The word nanotechnology was coined by Norio Taniguchi at University of Tokyo. During 1950's Von Hippel A.R. of Massachussetts Institute of Technology (MIT) coined the term "molecular devices". However, it was in 1959 Richard Feynman in his talk "There's plenty of Room at the Bottom" was the first to present the concept of nanotechnology to the world. He suggested that the manipulation of individual atom could revolutionize science. He suggested that using nano-scale engineering miniature motor could be built, it would be possible to read and write information on a tiny scale. He even appealed physicists to improve the electron microscope. The scanning tunneling microscope was a development in this line.

Feynman's lecture was considered too far fetched, so no serious work was done until Eric Drexler, Chairman of the Foresight Institute, unaware of Feynman's ideas, came to similar conclusions in his work, "Engines of Creation" and took the whole concept much further. Drexler uses the term nanotech in his book which is a specialized sub set of Nanotechnology or MNTC (Molecular Technology) as it is now called.

Drexler's future plan was the one where everything would be built from the bottom up by tiny machines ("nanomachines" or "assemblers") that would place each atom with absolute precision. Since then lot of developments have taken place in this field.

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The milestones in Nanotechnology are as listed below [8] :

Year	Development
1857	Michael Faraday synthesized gold colloids of nanosize
1915	W. Ostwald a famous chemist wrote a book "world of Neglected Dimension" in German
1931	E. Ruska and M. Knoli developed first electron microscope
1951	E. Muller developed field Ion Microscope which enabled imaging of atoms from the tip of metallic samples
1959	R. Feynman delivered his now very famous talk "There is plenty of Room at the Bottom" pointing out to the scientist that reduced dimensionality of material could bring fascinating results.
1968	A.Y. Cho and J. Arthur developed molecular beam epitaxy technique for layer by layer growth of materials
1970	L. Esaki demonstrated quantum size effects (QSE) in semiconductors
1980	A.I. Akimov showed QSE in Cds, Cd Se in glass triggering the research on nanoparticles
1981	G. Binning and H. Rohrer developed scanning tunneling microscope (STM) by which atomic resolution could be achieved.
1985	R.F. Curl, H.W. Kroto and R.F. Smalley synthesized sixty atoms carbon molecule later named as Fullerence

1989	D.M. Elger wrote letter 'IBM' using Xenon atoms
1991	S. Iijima discovered carbon nanotubes
1999	C.A. Miskin developed Dip pen Lithography
2000	D.M. Elgler devised quantum mirage using Fe atom on Cu substitution.

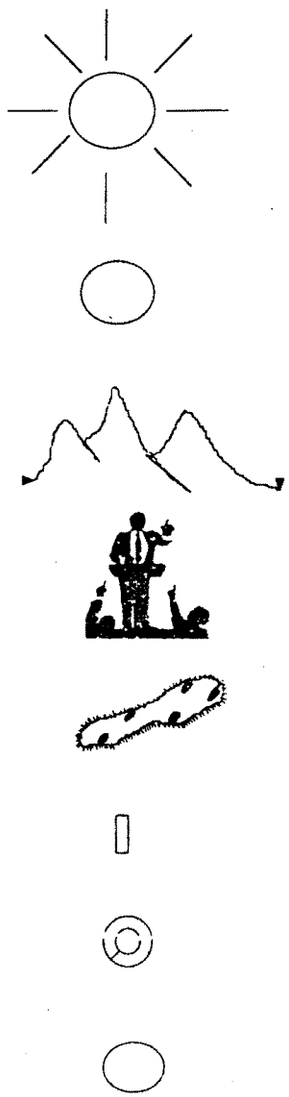
Nanomaterials are classified into nanostructured materials and Nanophase/nanoparticle materials. The former refers to condensed bulk materials that are made of grains with grain sizes in the nanometer size range, while the later are usually the dispersive nanoparticles. The nanometer size covers a wide range which can be as long as 100-200nm. How big are nanoparticles compared to some commonly known objects in as shown in the Fig. 1 [9].

1.2 CLASSIFICATION OF NANOCRYSTALLINE MATERIAL

Nanocrystalline materials can be classified based on the modulation dimensionality (μ)and magnetic nature.

1.2.1 (1) On the basis of modulation dimensionality (μ) nanocrystalline materials are single phase or multiphase polycrystals, the crystal size of which is of the order of a few (typically 1 to 100) nanometers in at least one dimension.

Fig 1.1 **How big are nanoparticles compared to some commonly known objects**



Diameter of Sun	1,393,000 km
Diameter of Earth	12,800 km
Height of mount Everest	8848 m
Average height of a man	1.65 m
Paramoecium length	100 μm
Typhoid bacterium	3 μm
Polio Virus	2 - 3 nm
CdS nanoparticle	1 - 6 nm

(a) Three – dimensional (μ=3)

When nanocrystalline materials are equiaxed in nature they will be turned as nanostructure crystallites or three-dimensional.

(b) Two-dimensional (μ=2)

When they are filamentary in nature, they are turned as two dimensional.

(c) One-dimensional (μ=1)

When they consist of a lamellar structure they are turned as layered nanostructure or one-dimensional.

(d) Zero-dimensional (μ=0)

They are atoms clusters or cluster assemblies. Fig. 2 illustrates the four types.

Nanostructured materials are also classified based on the correlation between their morphology and magnetic properties. The following classification is designed and proposed by Rieke and co-workers to emphasize the physical mechanism responsible for the magnetic behaviour. The four categories are

1. Type A: The ultra fine particle system with large interparticle spacing to have the non-interacting particles. Ferro fluids belong to this category since the magnetic particles are surrounded by surfactant which prevents the interparticle interactions in the fluid.

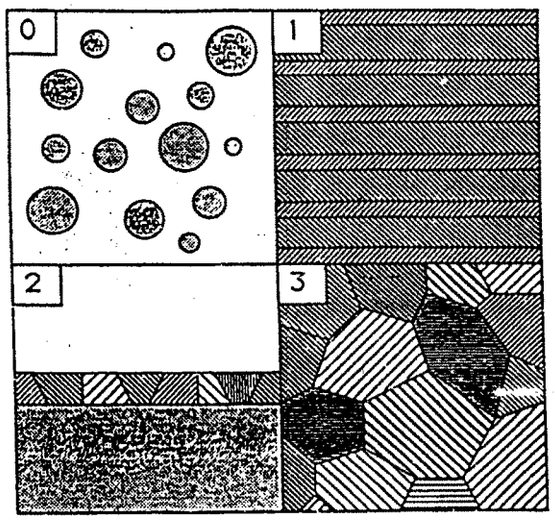


Figure 1.2 Schematic of the four types of nanocrystalline materials (Siegel 1994).

Type B: Materials include fine particles with a core shell morphology is nanoparticles in iron.

Type C: Nanocomposites composed of small magnet particles embedded in chemically dissimilar matrix e.g. Ni-Zn ferrite in glass matrix.

Type D: Materials consist of small crystallites dispersed in non-crystalline matrix of identical or a second phase material e.g. nanometer sized Fe_2O_3 powder obtained by the oxidation of amorphous Fe powder. Type D materials are bulk materials with nanoscale structure in which a substantial volume is of interfaces and grain boundaries.

The magnetic behaviour of these categories may be explained broadly. In type A the magnetic properties are due to the small number of non interacting magnetic particles with practically no contribution from their mutual interactions.

In type B the shell may prevent particle interaction but the core shell interactions are possible mainly because in many cases shells are formed due to oxidation of core particles and are magnetic.

In type C the magnetic interactions are decided by the volume fraction of the magnetic particles present in the matrix.

In type D the magnetic behaviour is a result of the contributions from both the interparticle interaction and size effects.

1.3 QUANTUM CONFINEMENT

A specific parameter introduced by nanomaterials is the surface/ interface to volume ratio. A high percentage of surface atoms introduces many size dependent phenomena. A finite size of particle confines the special distribution of electrons, leading to the quantized energy levels due to size effect. This quantum confinement has applications in semiconductor, optoelectronics and non linear optics. Nanocrystals provide an ideal system for understanding quantum effects in nanostructured system which could lead to major discoveries in solid state properties.

The spherical like shape of nanocrystals produced surface stress (+ve or –ve) resulting in lattice relaxation (expansion or contraction) and change in lattice constant. [10]. It is known that electron energy band structure and band gap is sensitive to lattice constant. The lattice relaxation introduced by nanocrystal size could affect its electronic properties [11].

1.4 PROPERTIES OF NANOCRYSTALLINE MATERIALS

The nanocrystalline materials exhibit a variety of properties increased strength/hardness, enhanced diffusitivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher thermal expansion

coefficient, lower thermal conductivity and superior soft properties in comparison to conventional coarse-grained materials.

1.4.1 Diffusion and sinterability

Since nanocrystalline materials contain a very large fraction of atom at the grain boundaries, the numerous interfaces provide a high density of short circuit diffusion paths. Consequently; they are expected to exhibit an enhanced diffusivity in comparison to single crystal or conventional coarse-grained polycrystalline materials with the same chemical composition (Horrath et al 1987, Birringer et al 1988) [12-14]. This enhanced diffusivity can have a significant effect on mechanical properties such as creep and superplasticity, ability to efficiently dope the nanocrystalline material with impurities at relatively low temperatures and synthesis of alloy phases in immiscible metals and at temperatures much lower than those usually required in other system.

The increased diffusivity (and consequently the reactivity) leads to increased solid solubility and limits formation of intermetallic phases (at temperature much lower than those required for coarse grained materials and sometimes new phases) and increases sinterability of nanocrystalline powders.

A dramatic example in the achievement of 17 at % (40wt%) solubility of Hg in nanocrystalline Cu, against an equilibrium value of <1at% [15]. The enhanced solid solubility limits in these systems have

been explained on the basis of elastic strain at the interfaces demonstrated to be the reason both theoretically and experimentally for various alloys earlier.

The high diffusivity and reactivity of nanocrystalline materials results in alloying by diffusion along the grain boundaries resulting in the formation of stable and metastable phases at relatively low temperatures. Another important consequence of increased diffusivity is that sintering of nanocrystalline powders can occur at temperature lower than those required for sintering coarse grained polycrystalline powders. In addition to sintering at lower temperatures. They even retain the ultra fine grain size after sintering to full density.

1.4.2 Mechanical Properties

It is known that mechanical properties of a solids depend strongly on the density of dislocations, interface-to-volume ratio and grain size. An enhancement in damping capability of nanostructured solid may be associated with grain boundary sliding [16] or with energy dissipation mechanism localized at the interface [17]. A decrease in the grain size significantly affects the yield strength and hardness [18]. The grain boundary structure, boundary angle, boundary sliding and movement of dislocations are important factors that determine the mechanical properties of the nanostructured materials. The elastic constant of nanocrystalline materials have been found to be reduced by 30% or less.

These results were interpreted as due to the large free volume of interfacial component spacing in the boundary regions [19]. The reduction in Young's modulus values interpreted by others [20] to be due to level of porosity and state of cracks in the samples.

1.4.3 Ductilization of ceramics and intrametallics

The finite grain size and high rates of diffusivity observed in nanocrystalline materials suggest that considerable ductility can occur in these materials even at room temperature. This follows from the expression for strain state dr/dt during diffusional creep

$$\frac{dr}{dt} = \frac{\sigma\Omega}{d^2kT}\left(B_1Dr + \frac{B_2\Delta D_b}{d}\right) \qquad \ldots 1.1$$

where σ - applied stress B_1 B_2 - constants

Ω - atomic volume Dr – volume diffusion constant

d – grain size D_b – grain boundary diffusion coefficient

k – Boltzman constant Δ - grain boundary width

T – Temperature

At low temperatures, where boundary diffusion dominates dr/dt can be written as [21]

$$\frac{dr}{dt} = \frac{B_2\,\sigma\Omega\Delta Db}{d^3kT} \qquad \ldots \quad 1.2$$

Thus the diffusional creep rate of a polycrystalline sample is increased by reducing the grain size and/or by increasing the grain boundary diffusivity. The grain size of nanocrystalline material is reduced by three orders of magnitude compared to conventional polycrystalline materials (from about 10 μm to nm) and the boundary diffusivity is higher by three order of magnitude. Accordingly, nanocrystalline ceramic intermetallic compounds are generally expected to exhibit a 12 order of magnitude increase in diffusional creep [22].

1.4.4 Specific heat

The specific heat of a material is closely related to its vibrational and configurational entropy, which is significantly affected by the nearest neighbour configurations. The increase in the specific heat of nanocrystalline material has been attributed to small crystal size (and consequent large interfacial component). If this is so, grain growth should reduce the specific heat of nanocrystalline material. This was in fact observed [23].

1.4.5 Thermal expansion

Measured thermal expansion coefficients of nanocrystalline Cu, Pd, Fe-B-Si and Ni-P alloys were almost twice the value for single crystals [24-26]. By varying the interfacial volume (by changing the grain size) one can tailor the coefficient of thermal expansion to any predetermined value.

1.4.6 Optical properties

Only a limited amount of information is available on optical properties of nanocrystalline materials. In spite of this, the results are interesting and show that the optical transparency can be changed by controlling the processing parameters.

1.4.7 Magnetic properties

The ferromagnetic properties of materials are influenced by changes in the interatomic distances. Thus the saturation magnetization (Ms) and ferromagnetic transition temperature of nanocrystalline materials are considerably reduced with respect to the bulk materials. The Ms of 6nm – iron is 130 emu/g [27] while that of normal polycrystalline α-Fe is 220 emu/g and that in iron-base metallic glasses 215 emu/g. Similarly a reduction in the Curie temperature (Tc) of Ni by about 40°C was reported if the crystal size was reduced to about 70 nm [28]. These reductions were attributed to the deviation of interatomic spacings in the interfacial regions as compared to crystalline component supported by Mossbauer spectroscopy measurement. The magnetic property of nanosize particles differ from those of bulk mainly in two points. The large surface to volume ratio results in the different local environment for surface atoms in their magnetic coupling/interaction with neighbouring atoms leading to the mixed volume and surface magnetic characteristics.

Unlike bulk ferromagnetic materials which usually form multiple magnetic domains several small ferromagnetic particles could consist of only single magnetic domain. In the case of single particle being a single domain, the super paramagnetism occurs in which the magnetizations of particles are randomly distributed and they are aligned only under an applied magnetic field and the alignment disappears once the external field is withdrawn.

The magnetic microstructure of nanocrystalline Fe was found to differ from that in polycrystalline or amorphous Fe and iron alloys. In fact every crystal of a nanocrystalline Fe specimen appeared to be a single ferromagnetic domain.

Another useful magnetic property that nanocomposites offer is called the magnetocaloric effect. When a material containing extremely small magnetic particulates in a non-magnetic or weakly magnetic matrix is placed in a magnetic field, the magnetic spins of the particulates tends to align with the field. This increase in magnetic order lowers the magnetic entropy of spin system. If this process is performed adiabatically (i.e. no heat is exchanged with surroundings), the reduction in spin entropy is offset by an increase in lattice entropy and the specimen's temperature will rise. This temperature rise is reversible (the specimen cools dawn on removal of magnetic field) and is known as the magnetocaloric effect.

1.4.8 Catalytic properties

Since majority of methods to produce bulk nanocrystalline materials involve consideration of fine particles (except for e.g. in crystallization of rapid solidified amorphous alloy ribbons), the total surface area available can be accordingly tailored by controlling the porosity in the samples. One can obtain full theoretical density to achieve the best mechanical properties or one can produce a highly porous material to obtain a very large surface area, or one can even have an intermediate value of porosity.

A large percentage of surface atoms greatly increase surface activities. The unique surface structure electronic states and largely exposed surface area are required for stimulating and promoting chemical reactions.

1.4.9 Corrosion behaviour

The corrosion behaviour of nanocrystalline materials has received very little attention until recently [29]. Thorpe studied the corrosion behaviour of nanocrystalline $Fe_{32}Ni_{36}Cr_{14}P_{12}B_{16}$ alloy obtained by crystallization of melt-spun amorphous ribbon, while Rofagha et al [30,31] studied nanocrystalline Ni-P produced by the electrode deposition technique.

The average dissolution rate of nanocrystalline Ni was found to be higher than that for coarse grained material. However while coarse

grained Ni suffers excessive intergranular corrosion in acidic media nanocrystalline Ni exhibited more uniform corrosion morphology.

1.4.10 Thermodynamic properties

The large surface to volume ratio of nanocrystals greatly change the role played by surface atoms in determining their thermodynamic properties. The reduced co-ordination number of surface atoms greatly increases the surface energy so that atom diffusion occurs at relatively lower temperature. The melting temperature of Au particles drops to as low as 300°C for particles with diameter smaller than 5 nm much lower than the bulk melting temperature 1063°C for Au [32]. The density of surface atoms changes significantly for different crystallographic planes, possibly leading to different thermodynamic properties.

1.5 APPLICATIONS OF NANOCRYSTALLINE MATERIALS

1. One of the most important applications of nanostructured materials is in super plasticity the capability of a polycrystalline material to undergo extensive tensile deformation without necking or fracture. Due to this materials 100 times stronger and lighter than comparable materials of today can be produced. As a result ultra light vehicles offering les internal friction and air resistance will be in use space transportation cost will be reduced drastically.

2. In ultra compact information storage [33,34] for e.g. the size of the domain determines the limit of storage density. Magnetic

nanocrystals have other important applications such as in color imaging [35] bioprocessing [36] magnetic refrigeration [37] and ferro fluids [38].

3. Metallic heterostructured multilayers comprised of alternating ferromagnetic and nonmagnetic layers such as Fe-Cr and Co-Cu have been found to exhibit giant magnetoresistance (GMR). GMR has important applications in data storage and sensors.

4. Semiconductor nanocrystals are zero dimensional quantum dots in which spatial distribution of the excited electron hole pairs are confined within a small volume resulting in the enhanced non linear optical properties [39-42]. The quantum confinement of carriers converts the density of states to a set of discrete quantum levels. This is fundamental for semiconductor lasers.

5. Mesoporous materials can be synthesized by a wide range of techniques. The low density of the materials results in very low dielectric constant, a candidate for low loss electronic devices. The large surface area of the porous materials is ideal for catalysis. The synthesis of mesoporous materials can be useful for environmental cleaning [43] avoiding pollution and energy storage [44].

6. Nanocrystalline alloys are a new class of soft magnetic materials supplementing the existing spectrum with high permeability's. The reliability of the production processes by rapidly quenching techniques low cost raw materials and the consequences of zero magnetostriction make VITROPERM the most prominent representative of these new alloys.

VITROPERM has a wide field of applications like magnetic cores in transformers for pulse current sensitive earth leakage circuit breakers, current transformers with small errors in phase angle and amplitude common mode radio frequency chokes for EMC and KW power transformers.

1.6 REVIEW OF THE LITERATURE

The $Ni_{0.2}Zn_{0.5}Fe_2O_4$ crystals with dimensions varying from 13 to 35 nm have been synthesized within a silica glass matrix by sol-gel method. The coercivity values for different heat treated samples were found to be in the range of 20-90 Oe which are significantly larger than that for samples having grain sizes of order of a few microns [46]. Magnetic and electrical properties of nanocrystalline ferrites depends on cations distribution (such as Fe^{2+} and Fe^{3+} cations) in the spinel structure [47].

Magnesium-doped nanocrystalline ferrites with grain sizes between 50 and 11 nm were prepared by ball milling. The hyper fine magnetic fields derived from Mossbauer spectra are remarkably suppressed when the grain sizes are reduced below 20 nm [48]. Ball milled Ni-Zn ferrite nanoparticles were prepared and properties were studied [49].

Nanocrystalline structure of mechano-synthesized Zn ferrite with a large amount of strain and defects introduced during the mechanical treatment is characterized by x-ray powder diffraction, TEM and

Mossbauer spectroscopy. It was observed that zinc ferrite leads to its crystallization at temperatures which are lower by 300k than those at which the crystalline zinc ferrite is formed by conventional thermal method, commonly involving solid state reaction [50].

The nanocrystalline anisotropy constant for nanocrystalline Ni-Zn ferrite is found to be an order of magnitude higher than that for the bulk material [51]. Nanocrystalline ferrite powders are very reactive and can be sintered in inert atmosphere at very low temperatures to nearly theoretical density without sintering additives. In compact, prepared from superstoichio metallic powders the formation of inter granular porosity was observed when the sintering temperature exceed 1000^0C [52].

The hydrothermal powder preparation route is suited for achieving a very homogenous nanocrystalline ferrite powder. The microstructure is free of pores compared to conventionally produced powders. Excellent magnetic properties can be achieved by sintering under considerably lower temperature [53].

A nanocrystalline spinel ferrite phase $MnFe_2O_4$ was formed after annealing at 600-700°C was found to exhibit good soft magnetic properties [54]. In the past few years mechano chemistry has proved to be an exciting technique for modification of existing materials and synthesis of new materials [55].

Nanocrystalline alloys are a new class of soft magnetic materials supplementing the existing spectrum with high permeability. The reliability of the production process by rapidly quenching techniques, low cost raw materials and the consequences of zero magnetostriction make VITROPERM the most prominent representative of these new alloys [45], [56].

Mechanical alloying process in four $MeFe_2O_4$ [Me: Zn, Cu, Ni, Mg] systems by high energy ball milling from simple oxide powder mixtures in both open and closed tungsten carbide containers have been investigated [57]. Acid recovery plant powder, a solid by product of stainless steel industry with high iron chromium and nickel content was used to synthesize a nanocrystalline Zn-Cr-Ni ferrite [58]. High ferrite magnets were prepared by mechanical alloying [59]. Young's modulus of nanocrystalline ferrites with spinel structures was determined by atomic force acoustic microscopy as a function of oxidation temperature was cooled and zero field magnetization measurements show super paramagnetic behaviour of the nanocrystalline ferrite samples [61]. A chemical method utilizing sol-gel reactions was investigated to uniformly incorporate small amounts of additives of Si and Cu into nanocrystalline $MnZnFe_2O_3$. Fast firing did not seem to affect densification of the chemically modified MnZn ferrite nanopowder but was found to contribute to suppression of grain growth in nanocrystalline ferrite crystals [62].

It is observed that in a nanocrystalline ribbon the power losses can be determined even at higher induction amplitudes by the frequency dependence of complex reversible permeability [63].

At high frequencies (>100KHz) the specific loss in power ferrites is remarkably lower than in the nanocrystalline material if induction values usually used in power supplies are applied [64].

1.7 ORIENTATION OF THE PROBLEM

The technological importance of ferrites can be judged from the wide range of applications from microwave devices to storage discs of computers and telecommunications.

Conventional ceramic method of ferrite preparation suffers some drawbacks viz.

1. Requires high temperatures.
2. At high temperatures evaporation of certain elements occurs resulting in chemical inhomogeniety.
3. Large grain size of ferrite is obtained.
4. Oxygen evolution and reabsorption increase the porosity of ferrite obtained making it impossible to densify.

In view of these chemical methods can be advantageously used in the preparation of ferrite.

The substitution of diamagnetic ions by ferromagnetic ions in ferrites is known to upgrade their magnetic properties and modify their microstructured as well as electrical properties.

Amongst Ni-Zn ferrites $Ni_{0.7}Zn_{0.3}Fe_2O_3$ shows minimum conductivity and a negative Seebeck coefficient [88]. The effect of substitution of Ni by Mg ions on the electrical and magnetic properties in the nanocrystalline ferrite series $Ni_{0.7-x}Mg_xZn_{0.3}Fe_2O_4$ where x varies from x = 0.1 - 0.5 in steps of 0.1 prepared by chemical method has been studied.

It is therefore proposed to undertake the studies on nanocrystalline ferrite prepared by chemical method. The studies include -

1. Preparation of the sample
2. X-ray diffraction studies to characterize the samples.
3. Study of SEM structure to correlate the grain size to electrical and magnetic properties.
4. Study the electrical properties dc resistivity and dielectric properties.
5. Study the magnetic properties magnetization and magnetic moment.

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