CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

Nanotechnology is a fast growing field of research in various dimensions as well as in different disciplines and exploration into the field of this ultra strong, yet extremely light nanoparticle preparation and processing has the potential to reshape the world around us.

Nanotechnology and nanostructured materials have the potential to significantly impact on energy efficiency, storage and production. Such applications can be used to monitor and remediate environmental problems, curb emissions from a wide range of sources and develop new, green processing technologies that minimize the generation of undesirable by-product effluents. As well as being an excellent experimental means of studying fundamental magnetic phenomena, these low dimensionality magnets may in the future form the basis of technologies (information storage, permanent magnets, colour printers, etc.). Nanomagnetism includes the artificial structuring of magnetic materials on a sub micron level and natural occurring magnetic entities such as molecules and clusters. A dramatic increase in research activities on nanostructured magnetic materials and their based industrial applications has been created a great demand to do research work in this area. An extensive survey on
various synthesis and characterization techniques of ferrite nanoparticles has been carried out in this chapter.

2.2 SURVEY OF LITERATURE

Cobalt ferrites (inverse spinel structures) were prepared by Mendelovici et al (1998) by progressive heat treatments (270-600-1000°C) in air of synthetic Fe:Co alkoxides of glycerol having different Fe:Co ratios. X-ray diffraction (XRD) examination indicated that the crystallization of the cobalt ferrites was initiated at 270°C and thereafter, it strongly increases between 600°C and 1000°C. Moreover, at 1000°C, XRD and chemical analyses showed a shift of the resulting cobalt ferrite d-spacings to lower values when the ferrite contains more cobalt, suggesting that cobalt partially replaces iron in the spinel structure. At 1000°C, the XRD lines of some co-products like hematite and Co$_3$O$_4$ previously formed at 600°C, either strongly decreased or disappeared. The surface areas of cobalt ferrites range from 131 to 165 m$^2$/g. Such high values were unusual for spinel oxides obtained by calcination at 1000°C.

Co-ferrite nanoparticles were prepared by Bensebaa et al (2004) in a microwave system using the polyol method. XRD spectra showed that a single-phase ferrite was obtained. The magnetic behaviour of the precipitate was consistent with an assembly of single domain particles with a distribution of blocking temperatures. The saturation magnetization measured at 10 K was found to be larger than both the bulk values for CoFe$_2$O$_4$ and for powders obtained using conventional heating methods. A possible reason for this finding might be the presence of some partly or unreacted Co and Fe.
Nanocrystalline Co$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ has been synthesised by Dey & Ghose (2003) using the co-precipitation method. XRD showed that the spinel ferrite was formed after sintering the sample at 393 K. Nanoparticles with average particle size of 5 to 65 nm were obtained by sintering the samples between 393 - 1173 K. Fourier Transform - Infrared Spectroscopy (FT-IR) showed that spinel ferrites prepared by precipitation method retain some hydroxyl groups, which were not removed completely by sintering at temperatures $\leq$ 873 K. Saturation magnetization of the samples increased with increasing average particle size upto 11 nm and for samples with particle size $>$ 11 nm, the saturation magnetization decreased with increasing particle size.

Ayyappan et al (2009) have investigated a facile method to control the size and magnetic properties of CoFe$_2$O$_4$ nanoparticles by varying the solvent dielectric constant. The structural, thermal and magnetic properties of CoFe$_2$O$_4$ nanoparticles were reported and XRD analysis confirmed the cubic spinel phase of CoFe$_2$O$_4$ nanoparticles. The average particle size increased from 10 - 16 nm as the dielectric constant of the solvent was increased from 47 to 80. The room temperature magnetization measurement confirmed that the saturation magnetization increased with particle size. The linear dependence of the dielectric constant of the medium on particle size was in good agreement with nucleation theory. The experimental findings of the present work unambiguously confirmed that the change in supersaturation has a significant influence on the nucleation rate and the particle size.

Monodispersed nanocrystalline Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ particles have been synthesized by forced hydrolysis method by Duong et al (2007). The obtained materials were single phase and monodispersed nanocrystalline with an average grain size of about 3 nm. These materials
were superparamagnetic at room temperature and ferrimagnetic at temperatures lower than the blocking temperature. When the zinc substitution increased from \( x = 0 \) to 0.4 at 4.2 K, the saturation magnetization increased from 72.1 to 99.7 emu/g. The high saturation magnetization of these samples suggested that this method was suitable for preparing high-quality nanocrystalline magnetic ferrites for practical applications.

Hankare et al (2007) have studied the effect of sintering temperature on the properties of Cu-Co ferrites prepared by oxalate precipitation method. The samples of the compound \( \text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4 \) were heated at different temperatures in the range of 773 K - 1173 K and were characterized by XRD and Scanning Electron Microscopy (SEM) techniques. The results of XRD showed the formation of single-phase cubic spinel structure. The lattice parameters showed a minimum value for a sample heated at 1073 K. It has been observed that grain size increased with the increase in temperature and was maximum (3.2 \( \mu \)m) for the powder sintered at 1173 K.

El-Sayed (2009) has studied the effect of induced magnetic anisotropy on the hysteresis parameters of Co-ferrite prepared from nanosized particles. Co-ferrite nanoparticles of size 18 nm could be obtained by chemical co-precipitation method at low temperature. The application of an external magnetic field on the sample during pressing causes great effect on the magnetic properties of Co-ferrite. During this work an enhancement of the squareness of Co-ferrite was obtained. Also, the increase of the magnetic anisotropy due to the application of the magnetic field during the pressing caused an increase in the coercivity of the Co-ferrite.
Zheng Jiao et al (2008) have synthesized cobalt ferrite nanoparticles by an improved chemical precipitation called spraying co-precipitation. The results showed that the CoFe$_2$O$_4$ nanoparticles prepared by spraying co-precipitation have smaller size and are more uniform than those prepared by regular co-precipitation. The mechanism of spraying co-precipitation was also investigated.

Khedr et al (2006) have investigated magnetic nanocomposites. In this study, various preparation techniques were used to produce cobalt ferrite nanoparticles namely, (i) ball milling of a homogeneous mixture of cobalt(II) acetate and iron(III) acetate (basic) treated by a novel self flash combustion, (ii) precipitation of cobalt(II) chloride (CoCl$_2$·6H$_2$O) and iron(III) chloride (FeCl$_3$), and (iii) ceramic method by firing of cobalt oxide (CoO) and iron oxide (Fe$_2$O$_3$). These techniques helped to obtain particle sizes ranging from a few micrometers to about 20 nm. Thermal analysis (Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)), X-ray diffraction, SEM, Transmission Electron Microscopy (TEM), magnetic and surface area measurements have been used for characterization of the prepared samples. Results showed that saturation magnetic flux density ($B_s$) and remanent magnetic flux density ($B_r$) varied with crystallite size. The measured surface area ($S_{BET}$) for the prepared Co-ferrite particles ranged from 5.327 - 47 m$^2$/g. The effects of different nanosizes on the total pore volume, adsorption energy, average pore diameter and micro pore volume have been studied. Nanocrystalline CoFe$_2$O$_4$ showed a catalytic activity towards CO$_2$ decomposition with the formation of carbon nanotubes.

Cedeño-Mattei & Perales-Pérez (2009) have synthesized high-coercivity cobalt ferrite nanocrystals. They showed that a suitable control of CoFe$_2$O$_4$ nanocrystals size can accomplished through a precise control
of the over saturation conditions during the ferrite formation in aqueous phase. Optimum over saturation was attained by monitoring the flow-rate of the addition of reactants, which should have also promoted heterogeneous nucleation and hence crystal growth. The average crystallite size in ferrite powders synthesized under flow-rate-controlled conditions was around 24 nm, which was almost twice the size obtained when there was no control on the flow-rate. The favourable effect on crystal growth was reflected in the enhancement of the coercivity values for ferrite nanocrystals produced at different flow-rates. The coercivity values were increased from 237 Oe, with no control of flow-rate, up to 1337 Oe, when the flow-rate of the addition of reactants was kept constant at 10 mL/min. The reaction time was as short as 5 min. The coercivity was enhanced even further when a suitable combination of flow-rate of reactants additions and concentration of NaOH was selected. Under optimum synthesis conditions, the coercivity at room temperature was as high as 5840 Oe. The obtained results suggest the viability in optimizing magnetic properties of cobalt ferrite nanocrystals by restricting crystal growth within the single-domain region.

Magnetic particles of nanocrystalline cobalt ferrite have been synthesized successfully by Mehrnaz Gharagozlou (2009) by polymeric pre-cursor method and the influence of the calcination temperature on the particle sizes and magnetic properties of the synthesized samples have also been investigated. The particles have been calcined at different temperatures varying from 400 to 800°C. The results indicated that the ferrite samples obtained by this method have the nanocrystalline pure single-phase spinel structure and good magnetic properties. TEM images showed almost spherical nanoparticles which uniform both in morphology and particle size distribution with sizes are varying in the range of 13 to
145 nm with the calcination temperature. The gradual increase in the crystallite size with the calcination temperature indicated the formation of bigger particles on the calcination. Magnetic properties of the products were found to be greatly affected by the average crystalline size of the nanoparticles. The saturation magnetization and remanent magnetization values of the samples increased as a function of the calcination temperature. Their results showed this method facilitates the magnetic tunability of the Co-ferrite nanoparticles by using proper temperature for the thermal treatment and greatly expanding the range of applications.

Structural parameters along with magnetic and electrical behaviour of nanosize Co-Ni spinel ferrites synthesized by co-precipitation method were reported by Gul et al (2007). The crystallite size was found to be within the range of 14 - 21 nm. Temperature-dependent DC electrical resistivity showed the semiconductor nature of the samples. Activation energy calculated from the DC electrical resistivity with respect to temperature for all the samples ranges from 0.561 to 0.764 eV. Drift mobility increased with increasing temperature. The dielectric constant and loss factors decreased with increasing frequency for all the samples. Hence, the much lower dielectric constants as well as loss factors obtained for the ferrites warrant their application at high frequencies.

Highly crystalline cobalt ferrite nanoparticles have been prepared by Virden et al (2007) in order to investigate the cubic anisotropy of these materials. The particles were prepared by co-precipitation and the decomposition of an organo-metallic complex. The crystallinity of the particles was investigated by high-resolution TEM. Magnetic measurements of remanence and coercivity as a function of temperature were carried out using Vibrating Sample Magnetometer (VSM). An anisotropy field of 1.6 T was extracted from the measurement of
coercivity as a function of temperature for highly crystalline samples. The large magnetocrystalline anisotropy leads to these particles finding potential applications as magnetic inks and the hysteresis heating to biomedical uses.

Nanocrystalline Ni$_{0.4}$Co$_{0.6}$Fe$_2$O$_4$ ferrite sample was prepared successfully by Mathe & Kamble (2008) using chemical co-precipitation technique. The spinel cubic structure having lattice parameter $a = 8.362$ Å was confirmed from XRD data analysis. Nanocrystalline nature of the sample was confirmed from microscopic analysis. The anomalous electrical and dielectric behaviour observed in the temperature range 723 K - 833 K was explained on the basis of migration of Fe$^{3+}$ ions from ‘A’ site to ‘B’ site. The behaviour around 833 K was attributed to transition from ordered state (ferrimagnetic) to disordered state (paramagnetic).

The spinel-type structures of ferrites were prepared by a solid state method and their ability to produce H$_2$ by a thermo-chemical cycle was investigated by Sang Bum Han et al (2007). During the thermo-chemical cycle, the ferrites were reduced by thermal energy and water was decomposed to produce hydrogen with the reduced ferrites. The XRD measurements showed that the prepared ferrites had the spinel structure of a single phase. The structures of Ni ferrite and (Ni, Mn) ferrite were not changed after the redox reaction, while the structures of Cu ferrite and (Cu, Mn) ferrite were changed to Fe$_3$O$_4$, CuFeO$_2$ and MnFe$_2$O$_4$ following the redox reaction. In the H$_2$O decomposition reaction, Ni ferrite produced H$_2$ volumes of 0.442 cm$^3$/g per cycle, and the volumes of H$_2$ for Cu ferrite, (Ni, Mn) ferrite and (Cu, Mn) ferrite were 0.002, 0.013 and 0.017 cm$^3$/g per cycle respectively. Ni ferrite produced the largest amount of H$_2$, as compared with the other ferrites, indicating that Ni ferrite had the optimal redox properties to produce hydrogen by the thermo-chemical cycle.
Magnetic nanoparticles of Co-ferrite were prepared by Sagrario M. Montemayor et al (2005) by the polymerized complex method. Heating in vacuum of a precursor solution containing Citric Acid (CA), Ethylene Glycol (EG), cobalt and iron salts with a molar ratio of Co/Fe/CA/EG = 1/2/9/22.5 at 130°C produced a brownish transparent polymeric gel, which has been characterized by IR and Nuclear Magnetic Resonance (NMR) spectroscopy. The exposed results by FT-IR and $^{13}$C-NMR spectroscopic techniques support the supposition made about the formation of metal-CA complexes and successive esterification reactions between CA (free and complexed) and EG. Controlled thermal treatments between 400 and 700°C of the resin allowed obtaining nanoparticles of pure CoFe$_2$O$_4$. The powders obtained were found to have ferrimagnetic behaviour and the saturation magnetization values were increased from 55.6 to 79.8 emu/g for particles with average size between 20 nm and 40 nm respectively.

Nanoparticles of chromium substituted cobalt zinc ferrite have been synthesized by Ram Kripal Sharma et al (2005) by a chemical co-precipitation method. XRD studies of the nanoparticles of Cr$_x$Co$_{0.5-x}$Zn$_{0.5}$Fe$_2$O$_4$ ($x = 0.1$ to $0.5$) heat-treated at 300°C showed that the particle sizes were in the range of 2 to 7 nm. Room temperature Fe-57 Mössbauer spectra of all the samples showed only two doublets, confirming the presence of superparamagnetic relaxation in the nanoparticles. An exponential decrease in the superparamagnetic blocking temperature, with increasing chromium concentration, was observed for these samples.

Cobalt-Zinc nanoparticles Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ (with $x$ varying from 0 to 0.7) to be used for ferrofluid preparation were prepared by Vaidyanathan & Sendhilnathan (2008) by chemical co-precipitation method. The fine particles were suitably dispersed in transformer oil using oleic acid as the surfactant. The saturation magnetization ($M_s$) and the size of the particles...
were measured at room temperature. The magnetization ($M_s$) was found to decrease with the increase in zinc substitution. The magnetic particle size ($D_m$) of the fluid was found to vary from 11.19 to 4.25 nm decreasing with the increase in zinc substitution.

The magnetization studies on nanocrystalline nickel ferrite as powder particles and as diluted dispersion (10 wt.%) in polymer matrix (polymer nanocomposites) were presented by Nathani & Misra (2004). The two polymer-based nanocomposites were prepared via ball-milling and in situ polymerization, respectively. The magnetization measurements provided strong evidence of surface effects to magnetization, which explained the non-saturation of magnetization at high fields. The differences in the magnetization behaviour of nickel ferrite as powder particles and in the ball-milled nanocomposite and the nanocomposite prepared via in situ polymerization were attributed to the different extents of inter particle interactions between the particles and the preparation route. The magnetization versus applied field behaviour of the three ferrite systems showed a similar jump in the initial part of the magnetization curve in all the cases which implies the existence of a core-shell like morphology of the particles over a large temperature range and its dominance over the inter particle interaction effects between the particles.

Nanocrystalline NiFe$_2$O$_4$ ferrite powder was prepared by Seyyed Ebrahimi & Azadmanjiri (2007) by a sol-gel auto-combustion method from metal nitrates and citric acid. The combustion process was an oxidation-reduction reaction in which the NO$_3^-$ ion was oxidant and the carboxyl group was reductant. The thermal analysis of nitrate-citrate gels and the phase evolution of as-burnt powder with different ratios of Fe/Ni and calcined powder were investigated by DTA/TG and XRD techniques respectively. SEM and Hysteresis graph were reported by them.
Their results revealed that the nitrate-citrate gel exhibited self-propagating combustion behaviour. They were obtained NiFe$_2$O$_4$ ferrite powder with the crystallite size as 20 - 40 nm with suitable soft magnetic properties.

Arelaro et al (2008) have investigated the influence of different M$^{2+}$ cations on the effective magnetic anisotropy of systems composed of MeFe$_2$O$_4$ (Me = Fe, Co and Mn) nanoparticles. They prepared samples by the high-temperature (538 K) solution phase reaction of Fe (acac)$_3$, Co (acac)$_2$ and Mn (acac)$_2$ with 1,2 octanodiol in the presence of oleic acid and oleylamine. The final particles were coated by an organic layer of oleic acid that prevents agglomeration. TEM images of their samples showed that particles presents near spherical form and a narrow grain size distribution, with mean diameters in the range of 4.5 - 7.6 nm.

Alarifi et al (2009) have synthesized NiFe$_2$O$_4$ nanoparticles by a simple and cost-effective method using Ni and Fe nitrates and glycine. The significant effect of the ratio between glycine and nitrates on the physical parameters like crystalline phase, crystallite size, particle size, lattice constant and magnetic properties of the nanoparticles have been investigated. Their X-ray diffraction, FT-IR and Selected Area Electron Diffraction (SAED) results indicated that the synthesized nickel ferrite particles have the nanometer size and inverse spinel structure. Room temperature magnetization results showed a ferromagnetic behaviour of the NiFe$_2$O$_4$ nanoparticles, with saturation specific magnetization values in the range of 2.387 - 57 emu/g at 15 kOe. The coercivity of the NiFe$_2$O$_4$ nanopowders changed from 65.58 to 148.8 Oe according to the change in the ratio between glycine and nitrates.

The effect of nanostructures on the magnetic properties like the specific saturation magnetization ($\sigma_s$) and the coercivity ($H_c$) for
Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ ferrite prepared by the co-precipitation method has been investigated by Preeti Mathur et al (2008). They found that the average size of the nanoparticles of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ mixed ferrite ranging from 19.3 to 36.4 nm could be controlled efficiently by modifying the sintering temperature from 500 to 900°C. The nanostructures were single domain up to a diameter of 25.8 nm, after which they showed an incipient domain structure. A good agreement in the value of the diameter $D_{cr}$, that resulted from the calculation with the experimental values was obtained after taking into consideration the surface effects, particle shape and interactions between nanocrystallites. The magnetic properties of the powder ferrite were strongly dependent on the average size of the nanostructures.

Dielectric properties of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ ferrites synthesized by co-precipitation method have been investigated by Thakur et al (2007) as a function of frequency (up to 30 MHz) at different temperatures. They reported that their dielectric constant and the loss factor decreased rapidly with an increase in frequency and then reached a constant value. Dispersion in dielectric constant has been observed between temperatures 450 to 500 K. DC resistivity was found to increase up to 100 times greater than those for the samples prepared by the conventional ceramic methods. Resistivity variation with temperature was also reported by them. The particle size was calculated using Scherrer equation for Lorentzian peak, which varied between 9 and 19 nm.

Magnetic nanoparticles of Ni-doped cobalt ferrite [Co$_{1-x}$Ni$_x$Fe$_2$O$_4$ ($0 \leq x \leq 1$)] synthesized by co-precipitation route have been studied by Maaz et al (2009) as a function of doping concentration ($x$) and particle size. The size of the particles as determined by XRD and TEM analyses and they found it in the range 12 to 48 nm. The coercivity ($H_c$) and saturation magnetization ($M_s$) showed a decreasing behaviour with
increasing Ni concentration. $M_S$ of all the samples annealed at 600°C was found to be in the range 65.8 - 13.7 emu/gm. Field-cooled (FC) studies of the samples showed horizontal shift (exchange bias) and vertical shift in the magnetization loop. Strong decrease in exchange bias ($H_B$) and vertical shift ($\delta M$) was found for low Ni concentrations while negligible decrease was found at higher concentrations. The presence of exchange bias in the low Ni-concentration region has been explained with reference to the interface spins interaction between a surface region (with structural and spin disorder) and a ferrimagnetic core region. The decrease of blocking temperature ($T_B$) with increasing Ni concentration has been attributed to the lower anisotropy energy of Ni$^{2+}$ ions as compared to Co$^{2+}$ that increases the probability of the jump across the anisotropy barrier which in turn decreases the blocking temperature of the system.

Nanocrystalline manganese zinc ferrite particles $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for $x = 0$ to 1 were prepared by Veena Gopalan et al (2009) using the wet chemical co-precipitation technique. They reported that the particles were found to be exhibiting a spinel structure with sizes varying from 7 to 29 nm. The decrease in particle size and the lattice contraction with increasing zinc concentration in the nanoparticles were due to the occurrence of a metastable cation distribution different from their bulk counterpart. The compositional analysis also confirmed the stiochiometry of the samples. The deviations in the case of magnetization with zinc concentration along with the lower magnetization values compared to the bulk were additional evidences for the existence of the metastable cation distribution. Enhanced curie temperature ($T_C$) values obtained were indicative of a non-equilibrium cation distribution in the different compositions. The magnetic moment at zero Kelvin was estimated from
the temperature dependence of magnetization and a tentative cation distribution for manganese ferrite was proposed by them.

NiFe\textsubscript{2}O\textsubscript{4} powders were synthesized by Miroslaw M. Bücko & Krzysztof Haberko (2007) by co-precipitation with ammonia solution using aqueous solution of NiCl\textsubscript{2} and FeCl\textsubscript{3} followed by hydrothermal treatment of the precipitate. It was found that crystallization in water led to nanometric size and isometric shape crystallites, whereas crystallization in sodium hydroxide solution results in particles with well defined walls. Generally, particles crystallized in water were smaller and their particle size distribution was narrower than those crystallized in NaOH solution. Behaviour of the powders under dry compaction and sintering strongly depended on the powder morphology. The powder crystallized in NaOH solution gave compacts of higher density and the sintered density of this powder was also higher than that of the powder processed in water.

Nanocrystalline particles of Mn\textsubscript{x}Zn\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} were prepared by Nalbandian et al (2008) by chemical precipitation of hydroxides, followed by hydrothermal processing and freeze-drying. The synthesis involved the hydrolysis of aqueous metal precursors by using ammonia as the precipitating agent. The chlorine ion concentration in the solution and the pH of the precipitation, are shown to play a crucial role in retaining the initial stoichiometry of the solution to the nanoparticles. The researchers identified that the obtained products exhibited some interesting and unique features: they consisted of nanoparticles with sizes ranging from 5 to 25 nm, they had surface areas between 60 and 110 m\textsuperscript{2} g\textsuperscript{-1} and pore sizes in the mesopore region (i.e. 8 - 20 nm). The researchers were examined the materials by powder XRD for crystalline phase identification, SEM for grain morphology, high resolution TEM for particle size distribution and
Nanophase $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.5, 1.0$) samples were prepared by Chandan Upadhyay et al (2003) by chemically precipitating hydroxides followed by hydrothermal processing. They were characterized the products by XRD and Mossbauer spectroscopy. Ferrite formation was found to be quite sensitive to the procedures adopted for preparing the hydroxide slurry prior to hydrothermal treatment. Nickel ferrite could be prepared in pure phase by co-precipitation as well as by mixing separately precipitated hydroxides. However, $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ could only be prepared by co-precipitation. Leaving a small amount of sodium in the slurry seems to obstruct pure phase formation of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and results in partial formation of $\alpha$-$\text{Fe}_2\text{O}_3$ which is observed from their study. A similar effect was also observed by them in zinc ferrite.

Nanocrystalline nickel ferrite powder was prepared by the co-precipitation method from Ni and Fe chlorides by Masoud Salavati-Niasari et al (2009). The as-prepared samples were characterized by powder XRD, TEM, SEM, FT-IR and VSM. SEM and TEM indicated that the particles were spherical with particle sizes in the range $25 \pm 5$ nm. They reported that the sample exhibited typical ferromagnetic behaviour at room temperature, while a finite coercivity of $245.5$ Oe was present at $300$ K. The saturation magnetization of the sample ($23.13$ emu/g) was significantly lower than that for the reported multi domain bulk particles ($55$ emu/g), reflecting the ultrafine nature of the sample.

The reverse micelle synthesis of nanocrystalline nickel-zinc ferrites has been carried out by Vuk Uskoković et al (2004). They have followed a multi-microemulsion approach at pH $> 8$ with an acidic solution.
of sulphate salts of precursor cations in one and an aqueous 0.5 M solution of (CH$_3$)$_4$ NOH in the other, precipitating microemulsion. The average particle size was found to increase with the pH of the precipitation, with a particularly noticeable increase between pH values of 10 and 11. The magnetization measured at magnetic field of 12 kOe was also found to increase with the increase in the precipitating pH values from 9 to 13.5, with a pronounced increase also between pH values of 10 and 11. The TEM images revealed the partly acicular nature of the synthesized particles at lower pH values, close to pH = 10. On the other hand, particles synthesized at higher pH values, close to 13, were spherical and of uniform size. This was explained by the existence of worm-like reverse micelles, together with the spherical micelles, so that the former gave rise to acicular particles, while the latter micelles induced the formation of spherical particles. The non-completion of the chemical route, which eventually leads to the formation of ferrite particles at higher pH values, might be taken into account to occur within the powder preparations performed at medium pH values. Thermal analysis revealed curie transition at around 390°C and two exothermic peaks at 260°C and 310°C, which were attributed to an amorphous-to-crystalline phase transition. The crystallinity of the spinel samples was found to improve with the heat treatment, with the largest increase in XRD determined average particle size for the samples annealed at 600°C and 800°C. The saturation magnetization and remanence were also found to increase with annealing. TEM investigation of the sample annealed at 800°C revealed a coral-like structure of larger and relatively uniform-sized rounded particles.

Nanocrystallites of six mixed ternary transition metal ferrite (MTTMF) were prepared by Gurdip Singh et al (2008) by co-precipitation method and characterized by XRD and BET equation. XRD patterns gave
average particle size for NiZnFe$_2$O$_4$ (NZF), CuCoFe$_2$O$_4$(CuCoF), NiCuFe$_2$O$_4$(NCuF), CuZnFe$_2$O$_4$(CuZF), CoNiFe$_2$O$_4$(CoNF) and CoZnFe$_2$O$_4$(CoZF) as 7.2, 3.0, 3.0, 6.8, 3.9 and 5.8 nm respectively. Further, catalytic activities of the MTTMF nanocrystallites on thermal decomposition of Ammonium Perchlorate (AP) were investigated using TG, Differential Scanning Calorimetry (DSC) and ignition delay measurements. IR-active internal mode of cation and anion of ammonium perchlorate changes with temperature in the presence of MTTMF nanocrystallites. The catalytic activity was found to be in the order: CoZF > CoNF > CuZF > CuCoF > NCuF > NZF. Nanocrystals of MTTMF have been proposed to play a significant role in the decomposition of Ammonium perchlorate.

Ni-Cu-Zn ferrites have been synthesized by Ghodake et al (2006) by employing co-precipitation technique using oxalate precursors. X-ray diffractograms did not show impurity phases, indicating single-phase formation of the ferrites. The diffractograms of oxalate complex decomposed at 650°C showed that ferritization was complete up to 650°C. Lattice parameter a (Å) was found to decrease with the addition of Ni$^{2+}$ which was attributed to ionic sizes of Ni$^{2+}$ (0.69 Å), which replaces Cu$^{2+}$ (0.72 Å). Initial permeability ($\mu_i$) showed increase when Ni$^{2+}$ was added up to $x = 0.15$ while for $x > 0.15$, it decreased. The increase in initial permeability ($\mu_i$) was attributed to monotonic increase in $M_s$ and $K_1$ on addition of Ni$^{2+}$. However, the microstructure and density (porosity) also influence $\mu_i$ variations. The decrease in $\mu_i$ was attributable to increase of $K_1$. The composition with density 91.14% exhibits large $\mu_i$ which also tends to increase with temperature up to 60°C. Thus its usable range extended up to 60°C and this sample has $T_c$ nearly equal to 160°C.
Ghodake et al (2009) have synthesized nanocrystalline Ni-Co-Zn ferrites by chemical co-precipitation method, using oxalate precursors. Usually, the phase formation of the sintered ferrite was confirmed by them using XRD study. The lattice parameter ‘a’ increased with the addition of Co$^{2+}$ content in the Ni-Zn ferrites. The electrical resistivity ($\rho$) of mixed Ni-Zn ferrites has been studied as a function of varying Co$^{2+}$ compositions. The resistivity was found to increase with the addition Co content in the Ni-Zn ferrite matrix. The variation of dc resistivity as a function of temperature was almost linear up to the curie temperature and thereafter a break occurs indicating a change of magnetic ordering from ferrimagnetism to paramagnetism. The values of activation energy in the paramagnetic region were found to be greater than those in ferromagnetic region, which suggested that the process of conduction was affected by the change in magnetic ordering. The dielectric properties were studied as a function of frequency by using an LCR precision meter bridge. It was observed that the dielectric constant ($\varepsilon'$) and dielectric loss tangent (tan $\delta$) decrease with the substitution of Co$^{2+}$ content in the Ni-Zn ferrites.

NiCuZn ferrite nanocrystalline powders with composition of (Ni$_{0.25}$Cu$_{0.25}$Zn$_{0.5}$)O(Fe$_2$O$_3$)$_{0.98}$ were synthesized by Zhenxing Yue et al (2004) using a sol-gel auto-catalytic combustion process. The influence of pH value of the precursor solution on the gel morphology, combustion behavior and crystallite size of synthesized powders were investigated with the help of SEM observations, thermal analysis, FT-IR spectra and XRD technique. Their experiments showed that the pH value of the mixed precursor solutions has a significant influence on the morphology of dried gels. The highly porous precursors with network structure could be formed at high pH values after the solutions were dried at 135°C. The as-burnt
powders became uniform in size and the crystallites size increased from 26 to 48 nm with pH value increasing from 2 to 7.

Hai-Bo Wang et al (2008) have investigated the structural, dynamic magnetic and dielectric properties of Ni$_{0.15}$Cu$_{0.2}$Zn$_{0.65}$Fe$_2$O$_4$ ferrite produced by NaOH co-precipitation method. The effect of calcining as well as sintering temperature variation on the grain size, structural, dynamic magnetic and dielectric properties were investigated by them. XRD measurements confirmed the formation of cubic spinel structure at all the temperatures for calcinations and sintering in this work. The microstructures were valued by SEM. The high frequency performance of the ferrite was estimated by measuring the frequency dispersion of the permeability, dielectric constant, dielectric loss and ac electrical resistivity. Compared with originally reported spinel ferrite, small liquid-like particles were found filling the grain boundaries of this copper-substituted NiZn ferrite, which has lower dielectric constant and dielectric loss. This could be an advantage for improving the penetration depth by weakening the skin effect for high frequency applications.

Magnetic nanoparticles of nickel ferrite (NiFe$_2$O$_4$) have been synthesized by Maaz et al (2009) by the co-precipitation route using stable ferric and nickel salts with sodium hydroxide as the precipitating agent and oleic acid as the surfactant. XRD and TEM analyses confirmed the formation of single-phase nickel ferrite nanoparticles in the range 8-28 nm depending upon the annealing temperature of the samples during the synthesis. The size of the particles (d) was observed to increase linearly with annealing temperature of the sample while the coercivity with particle size goes through a maximum, peaking at ~11 nm and then decreases for larger particles. Typical blocking effects were observed below ~ 225 K for all the prepared samples. The superparamagnetic blocking temperature ($T_B$)
was found to increase with increasing particle size that has been attributed to the increased effective anisotropy energy of the nanoparticles. The saturation moment values of all the samples were found to be much below the bulk value of nickel ferrite and this has been attributed to the disordered surface spins or dead/ inert layer in these nanoparticles.

Vaidyanathan et al (2007) have investigated the structural and magnetic properties of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles by co-precipitation method with $x$ varying from 0 to 1.0. The powder samples were characterized by XRD, VSM and FTIR. X-ray analysis showed that the samples were cubic spinel. The average crystallite size ($D_{\text{aveXR}}$) of the particles precipitated was found to vary from 6.92 to 12.02 nm decreasing with the increase in zinc substitution. The lattice constant ($a_0$) increased with increase in zinc substitution. The specific saturation magnetization ($M_S$) of the particles was measured at room temperature. The magnetic parameters such as $M_S$, $H_c$ and $M_r$ were found to decrease with an increase in zinc substitution. FT-IR spectra of the Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ with $x$ varying from 0 to 1.0 in the range 400 - 4000 cm$^{-1}$ were reported. The spinel structure and the crystalline water adsorption of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles were studied by using FT-IR.

Morphological and magnetic characteristics of cobalt ferrite nanoparticles synthesized by Toksha et al (2008) by sol-gel auto combustion method using nitrates of the respective metal ions. XRD pattern was indexed by the Rietveld program to calculate accurate unit cell dimension. A TEM study confirmed the formation of single phase cobalt ferrite nanoparticles in the range 11 - 40 nm depending on the annealing temperature and time. The size of the particles increased with annealing temperature and time, while the coercivity goes through a maximum, peaking at around 25 nm. They reported that the high field moment was
observed to be small for smaller particles and approaches the bulk value for large particles.

\[ \text{Ni}_x\text{Cu}_y\text{Zn}_{1-x-y}\text{Fe}_2\text{O}_4 \] nanoparticles (where \( x = 0.15 - 0.5 \) and \( y = 0 - 0.35 \)) were prepared by Wei-Chih Hsu et al (2004) using the chemical co-precipitation method at various reaction temperatures with a final pH value of 12. From the analysis of XRD patterns, they predicted the ferrite particles at pH equal to 12 and reaction temperature between 30 and 90°C with a reaction time of 6 hrs. The particle size ranged from 2 to 60 nm as observed them using TEM. Uniform size of cubic crystalline particles with particle size of about 30 nm was obtained at a reaction temperature of 70°C. The ferrite powders were compressed and sintered at various temperatures between 800 and 1000°C for 2 hrs. According to experimental results, the NiCuZn ferrite powders with high Cu content could be sintered at about 800°C. The density of the sintered \( \text{Ni}_{0.18}\text{Cu}_{0.31}\text{Zn}_{0.51}\text{Fe}_2\text{O}_4 \) ferrite was 5.01 g/cm\(^3\) after sintering at 900°C. The initial permeability \( \mu \) of this sintered sample was about 390 at a frequency of 1 MHz. Its \( H_c \) value was about 0.7 Oe and \( B_s \approx 3100 \) G. They found that Cu substitution for Ni in NiZn ferrite would enhance the densification of the ferrite and subsequently increase the \( \mu \) value as well as \( B_s \) value, and decrease the \( H_c \) value of the sintered ferrite.

Zhang et al (2009) have investigated the effects of co-doping on the structural and magnetic properties of Mn-Zn ferrite nanoparticles, prepared by the co-precipitation method. It was found that Co-ions were easily incorporated into the lattice of the ferrites and did not induce crystal-structure changes. All the co-doped ferrite nanoparticles exhibit superparamagnetism at room temperature and the crystallite size was between 24.5 and 27.0 nm. The saturation magnetization \( M_s \) increases with increasing Co content, reaching a maximum value of approximately
73 emu/g for Co content 1.0 (at %) and decreases with further increasing Co content.

Magnetic nanoparticles of nickel substituted cobalt ferrite (Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ : 0 $\leq x \leq$ 1) have been synthesized by Maaz et al (2009) by the co-precipitation route. Particles from XRD peak and TEM techniques were found in the range 18-28 ± 4 nm. Energy dispersive X-ray (EDX) analysis confirmed the presence of Co, Ni, Fe and oxygen as well as the desired phases in the prepared nanoparticles. SAED analysis confirmed the crystalline nature of the prepared nanoparticles. They were reported that the coercivity and saturation magnetization were found to decrease linearly with increasing Ni concentration in cobalt ferrite and this has been attributed to the lower magneto-crystalline anisotropy of Ni ions as compared to cobalt. The larger coercivity in case of nanoparticles has been attributed to the increased effective anisotropy constant ($K_{\text{eff}}$) due to the enhanced role of the surface and its associated anisotropies in these nanoparticles. The superparamagnetic blocking temperature has been found to decrease linearly with increasing Ni concentration which has been understood to be due to the lower magnetocrystalline anisotropy of Ni ions as compared to Co ions that increased the chance of a jump across the anisotropy energy barrier. This in turn decreased the blocking temperature of the system with increasing Ni concentration in these nanoparticles.

The mixing of (Ni$_{0.38}$Cu$_{0.12}$Zn$_{0.50}$)Fe$_2$O$_4$ powders with Bi$_2$O$_3$ was carried out by Sea-Fue Wang et al (2000) using the solid-state mixing as well as wet chemical coating processes such as ammonia precipitation coating, urea precipitation coating and solution coating. Ferrites prepared from the wet chemical coating processes could be densified at a lower sintering temperature without significant impact on the microstructural evolution compared with that prepared by solid-state mixing. In addition,
samples prepared from the wet chemical coating process have a higher $B_r$ and $B_s$ and a lower $H_c$ compared with that from solid-state mixing. Considering both the effects of sintering temperature and sintered density (> 95% T.D.), ferrites with 1.5 wt% Bi$_2$O$_3$ added by ammonia precipitation coating sintered at 900°C have the best permeability and quality factor (191 and 68.2 respectively) among all the cases studied.

The cobalt ferrite nanoparticles of average size 4 nm with narrow size distribution range have been synthesized by Subhasis Rana et al (2010) using reverse micelle technique. The cations distribution and phase transformation were found to be sensitive to the thermal history of samples. The FT-IR results confirmed the migration of the cations between octahedral and tetrahedral sites in the inverse spinel structure of the CoFe$_2$O$_4$ nanoparticles. The peak intensity of the tetrahedral sites increased at the expense of the octahedral sites due to the migration of cations from the octahedral to the tetrahedral sites during thermal treatment. The TGA / DTA analysis also confirmed the isochemical transformation during heat treatment.

Cobalt ferrite nanoparticles were prepared by Yue Zhang et al (2010) using the co-precipitation method followed by annealing treatment. The formation of nanoparticles with different composition, microstructure and sizes were confirmed by X-ray diffraction, Raman spectroscopy, TG / DTA and TEM. The magnetic hysteresis loops measured at room temperature revealed smaller effective magnetic anisotropy constant, coercivity and remanence ratio for the samples prepared by adding the NaOH solutions into the mixed solutions of Co$^{2+}$ and Fe$^{3+}$ ions due to the formation of Co$^{3+}$ ions. A small saturation magnetization and an enhanced coercivity were observed for the nanoparticles prepared by adding the mixed solutions of Co$^{2+}$ and Fe$^{3+}$ ions into the NaOH solutions, which was
related to the formation of outer layers with poor crystallization on the surfaces of the cobalt ferrite nanocrystals. Also they reported that the existence of these outer layers induced the oxidation of Co$^{2+}$ ions in cobalt ferrite nanocrystals at 200$^\circ$C and 300$^\circ$C and led to a large change on the composition and magnetic properties.

Copper ferrite nanopowders were successfully synthesized by a microwave-induced combustion process using copper nitrate, iron nitrate and urea by Yen-Chun Liu & Yen-Pei Fu (2010). The resultant powders were investigated by XRD, SEM, VSM and surface area measurement. The results revealed that for the CuFe$_2$O$_4$ powder the average particle size ranged from 300 to 600 nm. Moreover, the copper ferrite with Fe / Cu ratio of 2 - 12 possessed a saturation magnetization of 21.16 to 5.04 emu/g and an intrinsic coercive force of 600.84 to 267.25 Oe. In short as the Fe : Cu ratio increases, there was a reduction in magnetic strength due to the formation of Fe$_2$O$_3$. According to the experimental results, it was observed that it was very helpful to the catalytic reaction to add copper ferrite nanopowders, wherein copper ion reacts with 2,3,6-trimethyl-phenol first, then the -OH on the 2,3,6-trimethylphenol was attacked by copper ion and the free radical on -O forms and reacts with oxidant to form 2,3,5-trimethyl-1,4-benzoquinone.

Cobalt doped lithium ferrite nanoparticles were synthesized by Manish Srivastava et al (2010) at different pH values by sol-gel method. The effect of pH value on the physical properties of cobalt doped lithium ferrite nanoparticles has been investigated. The XRD patterns were analyzed to determine the crystal phase of cobalt doped lithium ferrites nanoparticles synthesized at different pH values. The XRD results showed the formation of impurity free cobalt doped lithium ferrites having ordered phase spinel structure. SEM micrographs showed that the structural
morphology of the nanoparticles was highly sensitive to the pH during the synthesis process. The magnetic properties such as saturation magnetization ($M_s$), remanent magnetization ($M_r$) and coercivity ($H_c$) have been also investigated and found to be different for the nanoparticles synthesized at different pH values.

The effects of milling time and annealing temperature on phase formation, microstructure and magnetic properties of nickel-cobalt ferrite synthesized from oxide precursors by mechanical alloying were studied by Amin Azizi et al (2010). The study of milling time effects on phase formation of milled materials showed that if milling continues up to 55 hrs, single phase nanosized nickel-cobalt ferrite was obtained. Also, magnetic properties of powders versus milling time and annealing at different temperatures extensively changed, so that annealing at 1200 C increased the magnetization saturation of the as-milled powder from 15.1 to 53.6 emu/g. XRD, SEM and TEM were also used to determine the morphology and size of the particles. The magnetic properties were measured by a VSM. Coercivity of annealed powders was reduced due to particle growth and strain recovery of milled particles. Magnetization saturation was increased with annealing temperature as a result of relaxation from the non-equilibrium cation distribution and the canted spin arrangement formed by the mechanical alloying synthesis route.

Aluminum substituted cobalt ferrite nanoparticles $\text{CoFe}_2\times\text{Al}_x\text{O}_4$ (for $x = 0.00, 0.25, 0.50$) have been synthesized by Gul et al (2010) by the chemical co-precipitation route. The average crystallite size was calculated using the Scherrer formula and found to be within the 17 to 27 nm range. The optical absorption spectra of all the samples showed two clear electronic transitions, the first was around 0.75 eV while the second at about 0.84 eV. The later was identified by means of $^4\text{A}_2 \rightarrow ^4\text{T}_1(4\text{F})$
transition while the former was attributed to the overlapping of the
$^4A_2 \rightarrow ^4T_1(4F)$ transition of the tetrahedral $\text{Co}^{2+}$ ions and the $\text{Co}^{2+}+\text{Fe}^{3+} \rightarrow \text{Co}^{3+} + \text{Fe}^{2+}$ metal-metal charge transfer transition. The saturation magnetization at room temperatures was found to be 61.50 emu/g for pure $\text{CoFe}_2\text{O}_4$ nanoparticles, while it decreased with increasing $\text{Al}^{3+}$ concentration up to 52.00 emu/g (for $x = 0.50$). Activation energy and drift mobility have been calculated from the temperature dependent DC electrical resistivity measurements for all the samples. The variation of dielectric constant, dielectric loss and tangent loss factor for all the samples have been studied as a function of frequency in the range 600 Hz to 1 MHz at room temperature.

Nickel zinc ferrite nanoparticles $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.1, 0.3, 0.5$) have been synthesized by Shahane et al (2010) using a chemical co-precipitation method. The samples were characterized by XRD, FT-IR, electron paramagnetic resonance, DC magnetization and AC susceptibility measurements. The XRD pattern of their samples reported that the lattice parameters decreased with increase in Ni content resulting in a reduction in lattice strain. The magnetic measurements showed the superparamagnetic nature of the samples for $x = 0.1$ and 0.3 whereas for $x = 0.5$ the material was ferromagnetic. The saturation magnetization was 23.95 emu/g and increases with increase in Ni content. The superparamagnetic nature of the samples was supported by the Electron Paramagnetic Resonance (EPR) and ac susceptibility measurement studies. The increase in blocking temperature for Ni concentration was explained by the redistribution of the cations on tetrahedral (A) and octahedral (B) sites.

$\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ ferrites were synthesized by Xue Cao et al (2010) by co-precipitation method. The crystal structure, size and magnetic properties of the synthesized nanoparticles were characterized by XRD,
SEM and VSM. The factors which influence the morphology and size of the products were investigated by them with the help of SEM. The saturation magnetization of the synthesized $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ octahedra was 51 emu/g, which was much lower than that of spheroidal nanoparticles. This investigation provided the guidance for the shape-controlled synthesis of $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ crystals and their application in hyperthermia for tumor therapy.

Nanoparticles of $\text{Mn}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3$) have been synthesized by Venkataraju et al (2010) by chemical co-precipitation method. They confirmed the lattice constant and distribution of cations in the tetrahedral and octahedral sites through XRD data analysis. They found that magnetization decreased with increasing Ni concentration except for $x = 0.3$. This was due to migration of $\text{Fe}^{3+}$ ions from B-site to A-site, which reduced the B-B coupling and thereby the spin canting in the B sublattice. The Curie temperature was found to decrease with increase in nickel concentration except for $x = 0.3$, where it showed a rise. Coercivity was very low and found to be inversely proportional to the grain size.

Hankare et al (2010) have synthesized Zn-substituted copper ferrite powders by oxalate co-precipitation method. Their XRD patterns revealed the single cubic structure of all the samples. Scanning electron micrographs indicated the increase in grain size up to $x = 0.5$ and later on it decreased with Zn content. The contents of the metals in the resulting spinel ferrites were confirmed by them using EDX measurements. The saturation magnetization increased with Zn content up to $x = 0.5$ and then it decreased due to Yafet and Kittel spin arrangement on the B-site.
Nanocrystalline Co-Ni samples were prepared by Mathe & Sheikh (2010) using the co-precipitation technique. XRD technique was used by them to check the phase purity of the samples. Surface morphology was studied by them using Atomic Force Microscopy (AFM) and SEM techniques. Nanosized grains of the samples were seen in AFM images of ultrasonicated powders. The nanocrystalline powders were shaped into pellets of desired size and used to record magnetostriction in the samples. The strain gauge method was used to record magnetostriction as a function of magnetic field in the range 0 - 10 kOe. The parallel and perpendicular magnetostrictions were of opposite signs. The maximum value of magnetostriction varied systematically with change in Co-Ni content. Magnetic Hysteresis (M-H) curves were recorded using the VSM technique.

Cobalt ferrite Co$_x$Ni$_{1-x}$Fe$_2$O$_4$ ($x = 0, 0.5, 1$) particles with controllable magnetic properties have been prepared by Yonglian Qi et al (2010) by calcination of co-substituted NiFe$^{2+}$Fe$^{3+}$ layered double hydroxide (NiFe$^{2+}$Fe$^{3+}$-LDH) precursors prepared via a scalable method involving separate nucleation and aging steps (SNAS). The LDH precursor-based product obtained by calcination of a mixture of CoFe$^{2+}$Fe$^{3+}$-LDH and NiFe$^{2+}$Fe$^{3+}$-LDH powders with a Co / Ni molar ratio of 1:1, exhibited a moderate value of $M_s$ and an increased value of $H_c$ compared to the corresponding values for an Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ material prepared by calcination of a Co$_{0.5}$Ni$_{0.5}$Fe$^{2+}$Fe$^{3+}$-LDH precursor, and a physical mixture of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ with a Co/Ni molar ratio of 1:1. These results might provide a way to regulate magnetic anisotropy of ferrite spinels by varying the composition of the LDH precursors.

Ni$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ with $x = 0.0, 0.25, 0.5, 0.75, 1$ were pressed immediately after preparation by the co-precipitation method without any
drying to simulate a humid environment by Saafan et al (2010). The nanoparticles were characterized by XRD and FT-IR. The AC and DC conductivity of the samples have been investigated immediately after preparation (the as-prepared samples). Then, the samples were dried at 200°C for about 12 hrs and reinvestigated. The behaviour of conductivity differed significantly in the two cases showing a noticeable effect due to humidity. Also, the magnetic induction of the as-prepared samples was investigated by using the VSM and the samples showed superparamagnetic behaviour.

Zinc substituted cobalt ferrite nanoparticles (Co_{0.5}Zn_{0.5}Fe_2O_4) have been synthesized by Mozaffari et al (2010) by the co-precipitation method, using stable ferric, zinc and cobalt salts with sodium hydroxide, at different solution temperatures, from room temperature to 363 K. The cobalt-zinc ferrite crystalline phase, the particle size and the morphology of the resulting nanoparticles were studied by XRD and TEM. The average crystallite size of each sample was calculated from the broadening of the most intense peak (311), using Scherrer’s formula and the results showed that the crystallite sizes increased from 6 to 8 nm on increasing the solution temperature from room temperature to 363 K. Room temperature VSM measurements showed that the prepared nanoparticles have superparamagnetic behaviour and did not saturate at maximum field of 800 kA/m. The variation of AC-susceptibility of the samples with respect to temperature was measured and it was found that the blocking temperature increased from 198 to 270 K on increasing the solution temperature from room temperature to 363 K respectively. FT-IR spectra of the samples have been analyzed in the frequency range 400 cm^{-1} - 4000 cm^{-1}, which also confirmed the results of XRD.
Nickel zinc ferrites, $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, nanoparticles have been synthesized by Rashad et al (2009) using the chemical co-precipitation technique. Effects of synthesis conditions on the crystal structure, crystallite size, lattice parameter, microstructure and magnetic properties of the produced spinel ferrites were investigated by XRD analysis, SEM and VSM. The results showed that a highly crystalline single cubic structure of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ phase was formed through precipitation precursors at pH 10 and annealing for 2 hrs at 1000°C, using sodium carbonate to adjust the pH. With the use of NaOH to adjust the pH, a mixture of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Fe}_2\text{O}_3$ phases was obtained. However, the addition of hydrogen peroxide, to the sodium hydroxide during precipitation, improved the formation of the single phase of Ni-Zn spinel ferrites. Moreover, the additions of two types of surfactants were found to enhance the formation of the spinel crystal structure of the ferrites. The change of the Ni molar ratio content ($x$) from 0.2 to 0.9 had strongly affected the properties of the formed ferrites powders. The lattice parameters were found to decline gradually with increasing nickel content and the crystallite size was in the range between 27 and 155 nm. Maximum saturation magnetization (85.4 emu/g) was achieved for the prepared $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ phase annealed at 1200°C for 2 hrs using $\text{Na}_2\text{CO}_3$ as alkali.

$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals with average diameter in the range of 1 - 2 nm have been synthesized by Sanjeev Kumar et al (2010) by reverse microemulsion. The nanocrystalline $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite exhibited characteristics of superparamagnetism at room temperature. The saturation magnetization of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals was less than that of those prepared by chemical co-precipitation and their bulk counter parts. This has been discussed in terms of the core shell morphology of the nanocrystals consisting of ferrimagnetically aligned
core spins and a spin-glass like surface layer. The magnetization curves for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite nanocrystals annealed at 600°C showed a superparamagnetic behaviour at 300 K. At low temperature (100 K) the samples showed a hysteresis loop characteristic of a superparamagnetic to ferromagnetic transition.

Nanoparticles of Li$_{0.1}$(Ni$_{1-x}$Zn$_x$)$_{0.8}$Fe$_{2.1}$O$_4$ ($x = 0 - 1.0$) were prepared by a chemical co-precipitation method by El Nimr et al (2010). A part of the precipitated powders was sintered at 1473 K for 2 hrs to obtain bulk samples via increasing the particle sizes. The particle size distribution, dc conductivity and magnetic permeability were investigated for the nanostructured samples and their bulk counterparts. The permeability as a function of temperature revealed the size effect of nanostructure in agreement with the literature. In some of the samples the permeability was almost constant over a considerable range of temperature, which may be useful in practical applications that require stability. Moreover, the nanosize structure caused a significant decrease in dc conductivity values.

Single phase nanosized nickel-ferrite powder was synthesized by Azizi & Sadrnezhaad (2010) by 30 hrs ball milling and annealing at 600 C. Annealing of the as-milled powder freed strain induced by milling, improved the crystallinity of the powder and promoted particle growth. Magnetic properties of the powders extensively changed with annealing temperature. Coercivity of the annealed powder changed due to the transformation of magnetic single-domain into magnetic multi-domain of the particles. Magnetization saturation increased with annealing temperature because of relaxation from the non-equilibrium cation distribution and the canted spin arrangement resulting from the mechanical alloying synthesis.
Ball milling (BM) of bulk CoFe$_2$O$_4$ powder material has been carried out by Richard Perez Moyet al (2010) in order to study its structural stability and attendant property changes with respect to coercivity enhancements and superparamagnetic behaviours, showing that drastic crystallite size reduction occurred within the first 1 hr of ball milling. Crystallite size dropped from 74 nm for the as-received material to a value of 11.6 nm for 600 min of ball milling. Combined XRD and SEM analyses confirmed crystallite size reduction with corresponding increase in interparticle agglomeration/pores with increasing milling time. The maximum coercivity of 0.46 T and the crystallite size of 15.6 nm were recorded for 20 min, while peak residual strain of 0.0066 mm/mm was for 180 min of BM. Material with peak coercivity value did not have peak residual strain, or minimum crystallite size, thereby suggesting that other structural defects contributed to coercivity enhancement. The saturation magnetization ($M_s$) value decreased continuously with increasing milling time, while remanence ($M_r$) and coercivity decreased with increasing BM time, after an initial increase. Mössbauer Spectroscopy (MS) measurements confirmed particle size distribution and decomposition/disordering of the material together with superparamagnetism as BM time increased. The degree of inversion ranged from 41% to 71.7% at different milled states from MS. The internal magnetic fields of the Fe sites associated with the tetrahedral and octahedral sites were 507.4 kOe and 492 kOe respectively in the unmilled state, while 484 kOe and 468.5 kOe in the 600 min milled state correspondingly.

Cobalt-zinc ferrite (Co$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$) was prepared by combustion method by Yousefi et al (2010), using cobalt, zinc and iron nitrates. The crystallinity of the as-burnt powder was developed by annealing at 700°C. Using Williamson-Hall method, the average crystallite
sizes for nanoparticles were determined to be about 27 nm before and 37 nm after annealing and residual stresses for annealed particles were omitted. The morphology of the annealed sample was investigated by TEM and the mean particle size was determined to be about 30 nm. The final stoichiometry of the sample after annealing showed good agreement with the initial stoichiometry using atomic absorption spectrometry. Magnetic properties of the annealed sample such as saturation magnetization, remanence and coercivity measured at room temperature were 70 emu/g, 14 emu/g and 270 Oe respectively. The Curie temperature of the sample was determined to be 350°C using AC-susceptibility technique.

Polycrystalline NiCuZn soft ferrites with stoichiometric iron were prepared by a novel microwave sintering method by Penchal Reddy et al (2010). The powders were calcined, compacted and sintered at 950°C for 30 min in a microwave sintering furnace. XRD patterns confirmed the formation of single phase cubic spinel structure. The grain size was estimated using SEM micrographs. The lattice constant was found to increase with increase in zinc concentration. The sintered ferrites have been investigated for their physical, magnetic and electrical properties such as bulk density, X-ray density, porosity, anisotropy constant, initial permeability, saturation magnetization, DC resistivity, dielectric constant and dielectric loss as a function of zinc concentration. Permeability, saturation magnetization, dielectric constant and dielectric loss were found to increase while DC resistivity was found to decrease with the replacement of Zn with Ni. The present series of ferrites were found to posses properties that are suitable for the core materials in multilayer chip inductors.

Krishnaveni et al (2006) have synthesized Ni-Cu-Zn ferrite nanopowders by co-precipitation method using microwave-hydrothermal
(M-H) reaction system. The ferrite formation conditions such as pH, temperature and time were determined in detail according to the reaction conditions. The phase identification, crystallinity and morphology of the prepared samples were characterized by XRD and TEM. Nanocrystalline ferrites with high surface area were synthesized at temperatures as low as 165°C in a short time (30 min). The nanoferrite powders were sintered at different sintering temperatures from 800°C to 950°C for 6 hrs using the conventional sintering method. The performance of the sintered Ni-Cu-Zn ferrites has been estimated from the studies of dependence of permeability spectra on the frequency and temperature. Multilayer chip inductors were fabricated from the ferrite using the screen-printing method. Inductance and quality factor of the prepared inductors were measured over a wide frequency range.

Co-Cu-Zn doped Fe$_3$O$_4$ nanoparticles with tunable particle size and morphology have been successfully prepared by Yuan Pu et al (2010) using the hydrothermal method by varying the metal ionic concentration (MIC) of the original reagents. The structure, composition, morphology, magnetic property and microwave absorbing properties of Co-Cu-Zn doped Fe$_3$O$_4$ nanoparticles were found to be size-dependent. Ultra-fine single-crystal Co-Cu-Zn doped Fe$_3$O$_4$ nanoparticles were obtained and every product has a typical spinel structure. Also, decreases in particle size led to a lower saturation magnetization and the Co-Cu-Zn doped Fe$_3$O$_4$ nanoparticles had a better magnetic property than Fe$_3$O$_4$. The 360 nm Co-Cu-Zn doped Fe$_3$O$_4$ nanoparticles showed a better dielectric loss at high frequencies. The as-synthesized Co-Cu-Zn doped Fe$_3$O$_4$ nanoparticles were expected to be applied in magnetic, biomedical and microwave absorption fields.
Shaikh et al (2010) have studied the structural, magnetic and electrical properties of Co$_{1-x}$Ni$_x$Fe$_{1.9}$Mn$_{0.1}$O$_4$ ($x = 0.2, 0.4, 0.6$ and $0.8$) ferrites synthesized by co-precipitation method. XRD analysis confirmed the cubic spinel phase formation and broadness of (311) plane indicated the smaller particle formation. FT-IR spectra showed shifting of the absorption bands towards lower frequency with the addition of Ni$^{2+}$ in Co$_{1-x}$Ni$_x$Fe$_{1.9}$Mn$_{0.1}$O$_4$. SEM analysis revealed the highly agglomerated particles. Magnetic measurements revealed that the increase of Ni$^{2+}$ ion concentration yields a monotonic decrease of magnetization at 6 kOe. A reduction in coercivity was observed by them which showed that the studied system might be suitable for magnetic recording media applications with some improvements. Doping with nickel was found to enhance the resistivity.

Nanoparticles of Li$_{0.1}$(Ni$_{1-x}$Zn$_x$)$_{0.8}$Fe$_{2.1}$O$_4$ with $x$ varying from 0.0 to 1.0 were prepared by chemical co-precipitation method by Saafan et al (2010). A part of these samples was sintered at 1200°C for 2 hrs to obtain bulk samples via increase in particle sizes; the other part was left as prepared. Structural and magnetic properties comparison studies were carried out between the as-prepared nanoparticle samples and their bulk counterparts. XRD and infrared spectroscopy were used to characterize the samples. It was observed that porosity of bulk samples was lower than their nano counterparts as a result of sintering at 1200°C and particle growth. IR spectra showed the two main absorption bands characteristic of ferrites ($\nu_1$ and $\nu_2$) at about 600 and 400 cm$^{-1}$, respectively in all samples, whereas the band at $\nu_3$ appears only in two samples believed to contain Fe$^{2+}$ ions more pronounced than other samples because of expected cationic distribution. Moreover, the fourth absorption band characteristic of ferrites ($\nu_4$) appears only in nanosamples at approximately the same value and
disappeared in bulk samples. This may be attributed to lattice vibrations of the tetrahedral metal ions i.e. Fe$^{3+}$ - O$^{2-}$ in nanoparticles. The presence of broad absorption bands of water was observed in the nanostructured samples, while they were completely absent in their bulk counterparts. Reduction in saturation magnetization of nanosamples in comparison to their bulk counterparts has been attributed to the large surface-to-volume ratio, crystal imperfection on the surface layer, reduction in super-exchange interactions and non-collinear magnetic structure in nanosamples.

Venkataraju et al (2010) have synthesized nanoparticles of Mn$_{0.5}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x = 0.0, 0.1, 0.2, 0.3 and 0.5) by chemical co-precipitation method. The lattice constant for all Mn / Ni concentration was found to be less than that for the corresponding bulk values. The X-ray intensity of the (440) plane increases with increasing Ni$^{2+}$ concentration indicating the occupation of Ni$^{2+}$ ions on octahedral sites. The dielectric constant decreased with the increase in Ni concentration except for x = 0.3. The resistivity was found to increase with increase in Ni concentration and decreases with increase in temperature.

Deraz (2010) has synthesized copper ferrite nanocrystals by a combustion route depending upon the glycine-nitrate process and also by ceramic method. In order to investigate the effect of degree of crystallinity and crystallite size of copper ferrite system on its magnetic properties, a series of Cu-ferrite samples with different degrees of crystallinity and crystallite size were produced by varying the preparation temperatures via changing the ratio between the glycine and nitrates. FT-IR and XRD patterns confirmed the single-phase spinel structure for the synthesized materials. TEM analysis revealed needle-like tubular nanostructures containing polygon particles. The magnetization values of the samples
increased with the increase of the particle sizes. The combustion method
displayed magnetic copper ferrite in the range of nanoscale comparing to
the bulk ferrite prepared by ceramic route.

The sensitivity to some reducing gases (acetone, ethanol, methane and Liquefied Petroleum Gas (LPG)) of calcia doped nickel ferrite
(NiFe$_2$O$_4$+1%CaO) and cobalt and manganese doped nickel ferrite,
Ni$_{0.99}$Co$_{0.01}$Mn$_x$Fe$_2$O$_{4-x}$ (x = 0.01 and 0.02) was investigated by Rezlescu
et al (2006). The nanosized powders were obtained by quick combustion.
After 30 min heat treatment at 1273 K of the compacted powder were
carried out by XRD, SEM and measurements of the electrical resistivity
sensitivity to the four test gases. The gas sensitivity largely depends on the
composition, temperature and the test gas species. The ferrite compounds
doped with Co and Mn were selective to detect reducing gases at low
operating temperatures. The mixed ferrites with Ni$_{0.99}$Co$_{0.01}$Mn$_{0.02}$Fe$_{1.98}$O$_{4.5}$
composition were sensitive and selective to acetone gas.

Simultaneous treatment of two industrial wastes, i.e. the
electroplating sludge and the spent pickling liquor, to produce valuable
spinel ferrite with high crystallinity and high saturation magnetization
through the hydrothermal process has been investigated by Dan Chen et al
(2010). After the hydrothermal treatment, the electroplating sludge could
only produce poorly crystallized ferrite with a high content of impurities.
However, co-hydrothermal treatment of the electroplating sludge and the
spent pickle liquor in a suitable mixing ratio resulted in a well crystallized
ferrite product, with all heavy metals being fixed into the ferrite lattice.
In order for the ferrite product to have a maximum saturation
magnetization (41.42 emu/g in this research), the response surface
methodology (RSM) has been employed to derive the optimal experiment
condition, e.g. hydrothermal treatment at 300℃ for 6 hrs with the initial
pH adjusted to 10. This optimal experimental condition has been further proven valid when applied to a different kind of electroplating sludge. In addition, the magnetization of ferrite products could be further enhanced to 58.34 emu/g by acid washing to remove the impurity (calcite). This research thus showed an effective way to transfer two common industrial wastes into valuable ferrite materials.

\[ \text{Ni}_{0.5-x}\text{Cu}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4(0.0 \leq x \leq 0.5) \] ferrite nanofibers with diameters of 80 - 160 nm have been prepared by Jun Xiang et al (2010) by electrospinning and subsequent heat treatment. Both the average grain size and lattice parameter were found to increase with the addition of copper. Fourier transform infrared spectra indicated that the portion of \( \text{Fe}^{3+} \) ions at the tetrahedral sites moved to the octahedral sites as some of the substituted \( \text{Cu}^{2+} \) ions get into the tetrahedral sites. VSM measurements showed that the coercivity of these ferrite nanofibers decreased with increasing Cu concentration, whereas the specific saturation magnetization initially increased, reaches a maximum value at \( x = 0.2 \) and then decreased with a further increase of Cu content.

Hankare et al (2009) have synthesized polycrystalline magnesium ferrite (\( \text{MgFe}_2\text{O}_4 \)) by the co-precipitation method. Conductance responses of the (\( \text{MgFe}_2\text{O}_4 \)) were measured towards gases like hydrogen sulfide (\( \text{H}_2\text{S} \)), LPG, ethanol vapours (\( \text{C}_2\text{H}_5\text{OH} \)), \( \text{SO}_x \), H\(_2\), NO\(_x\), NH\(_3\), methanol, acetone and petrol. The gas sensing characteristics were obtained by measuring the sensitivity as a function of various controlling factors like operating temperatures and concentrations of gases. It was found that the sensor exhibited various responses towards these gases at different operating temperatures. The \( \text{MgFe}_2\text{O}_4 \) based sensor exhibited a fast response and a good recovery towards petrol at temperature 250°C. The results of the response towards petrol reveal that (\( \text{MgFe}_2\text{O}_4 \))
synthesized by a simple co-precipitation method, would be a suitable material for the fabrication of the petrol sensor.

2.3 OBJECTIVE OF THE WORK

The synthesis of spinel ferrite nanoparticles has been investigated intensively in recent years because of their potential applications in high density magnetic recording microwave devices and magnetic fluids. The interesting physical and chemical properties of spinel ferrites arise from the distribution of transition metal cations having various oxidation states among the available tetrahedral and octahedral sites.

Among spinel ferrites, cobalt ferrite is especially interesting because of the high cubic magnetic crystalline anisotropy, high coercivity and moderate saturation magnetization. In the case of nickel ferrite, the inverse type is particularly interesting due to its high magneto crystalline anisotropy, high saturation magnetization from a typical crystal and magnetic structure.

The substitution of Cu brings about a structural phase transition accompanied by the reduction in the crystal symmetry due to cooperative Jahn-Teller effect which ultimately results in some interesting electrical and magnetic properties. A novel idea of using Cu as an additive element to cobalt ferrite and nickel ferrite is proposed in this work. As the properties of the synthesized materials are influenced by the composition and microstructure which are sensitive to the preparation methodology, cobalt-copper ferrite \( \text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \) [where \( x = 0.2, 0.4, 0.6 \)], nickel-copper ferrite \( \text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \) [where \( x = 0.2, 0.4, 0.6 \)], Co-Ni-Cu mixed ferrite \( \text{Co}_{0.4}\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4 \) and Ni-Mn-Cu mixed ferrite...
(Ni$_{0.4}$Mn$_{0.4}$Cu$_{0.2}$Fe$_2$O$_4$) are synthesized using co-precipitation method. The magnetic and dielectric properties of these mixed ferrites are studied and their significance is discussed in this work. The humidity sensing and electro catalytic properties of Co-Ni-Cu and Ni-Mn-Cu mixed ferrites are also studied.