1. Introduction

Nanocrystalline spinel ferrites are technologically important because of their wide applications, and it is believed that the production of ferrites will increase year by year as their applications become more and more diverse. Even though the saturation magnetization of ferrites is less than half that of ferromagnetic alloys, they have advantages like applicability at higher frequencies, lower price, very high electrical resistivity, greater heat resistance and high corrosion resistance. Unlike many other materials, they possess both high permeability and moderate permittivity at high frequencies. Due to their low eddy current losses, there exists no other material with such a wide range of applications in electronics in terms of power generation, conditioning and conversion. Besides the conventional applications such as transformer cores in high frequency power supplies, EMI shielding, microwave devices, high density magnetic recording etc, applications of nanoferrites are diverging to new fields like medical diagnostics, site specific drug delivery, magnetic refrigeration, ferrofluids and gas sensing.

The most important advantage of ferrites is their very high degree of compositional variability. Most of the original intrinsic properties on ferrites are made on the simple ferrites such as MnFe$_2$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$. However, most commercially important ferrites are of the mixed variety and actually consist of solid solutions of the various simple ferrites with infinite number of combinations possible. Depending on the requirements of the ultimate application, various combinations of different properties can be obtained by blending a judicious choice of the simple ferrites in an appropriate ratio [1].

Distribution of cations over A and B sites has a profound effect on the electrical and magnetic properties of spinel ferrites. Factors like ionic radius, electronic configuration, madelung energy, lattice energy and crystal field stabilization effects influence the metal ion distribution. Another factor which determines the occupancy of cations is the site preference energy. For example nickel and cobalt have a strong preference to octahedral sites, while zinc and cadmium have strong tetrahedral site preference. Thus with knowledge of site preference energy and other factors affecting cation distribution, we can manipulate the synthesis of ferrites with optimum properties in the micro regime. The rules regarding cationic distribution are no longer valid in the nano regime. For instance, in zinc ferrite nanoparticles, a small percentage of Zn$^{2+}$ ions are found to occupy octahedral sites and in case of nickel ferrite nanoparticles, some of the Ni$^{2+}$ ions are occupying tetrahedral sites [2]. Owing to the changes in cationic distribution and surface effects like core-shell structure, broken exchange bonds and canting of spins on the surface etc, the properties of ferrite nanoparticles deviate from that of the bulk.
Nickel ferrite and nickel based mixed ferrite nanoparticles are of technical importance due to numerous applications in electronics [3]. These are promising materials for use in telecommunication equipments, computer peripherals, and other electronic and microwave devices. Nickel ferrites have low eddy current losses and good magnetic properties, which make them suitable for the core material of power transformers [4, 5]. Nickel ferrite nanoparticles are widely used for improving the quality of MRI, targeted drug delivery, ferrofluids and gas sensors. Nickel ferrite adopts an inverse spinel structure with Ni$^{2+}$ in octahedral sites and Fe$^{3+}$ equally distributed between octahedral and tetrahedral sites. However, as we have already seen, deviation in cation distribution is observed in nickel ferrite, when the particle size is in the nano range.

It is well known that the desired electrical and magnetic properties of soft ferrites can be tailored by the addition of suitable divalent, trivalent or tetravalent cations in to the spinel lattice. Incorporation of small amount of rare earth metal ions into the spinel ferrites may lead to structural distortion due to their large ionic radius and to induce strain and significantly modify the microstructural, electrical and magnetic properties. Rare earth ions play an important role in determining the magnetocrystalline anisotropy in the 4f-3d intermetallic compounds [6]. Thus, from the application point of view, the properties of ferrite nanoparticles can be tuned by the inclusion of suitable rare earth ions.

The properties of nanoferrites are influenced by the composition and microstructure, which are sensitive to the preparation methodology used in the synthesis and to the sintering conditions. Ferrite nanoparticles are usually prepared by various physical and chemical methods like high energy milling, plasma deposition, inert gas condensation, citrate precursor technique, reverse micelle technique, microemulsion, hydrothermal reaction, polymer pyrolysis, sol-gel technique, chemical co-precipitation etc [7-12]. Among the available chemical methods, sol-gel and coprecipitation are two simple techniques without much complicated procedure and give ferrite nanoparticles of high purity at low cost. Sol-gel technique is a combination of combustion and chemical gelation process and has the advantage of good stoichiometric control and the production of ultra fine particles with a narrow size distribution. Advantages of coprecipitation are the high production rate, very small particle size, low synthesis temperature etc.

2. Objectives of the Work

The main objectives of the present work can be summarized as follows,

- Preparation of NiFe$_2$O$_4$ nanoparticles by sol-gel and co-precipitation techniques.
Structural characterization of the samples using XRD.

Magnetic and electrical characterization of the samples and the comparison of properties of nano ferrites obtained by the two methods.

Partial replacement of Fe$^{3+}$ ions in sol-gel derived nano crystalline NiFe$_2$O$_4$ by rare earth ions Tb$^{3+}$, Gd$^{3+}$ and Sm$^{3+}$ and to study the modifications in structural, magnetic and electrical properties in each case.

Preparation of Tb$^{3+}$ doped mixed Ni-Zn ferrite nanoparticles and the structural, magnetic and electrical characterization.

Synthesis of Ni-Cd mixed ferrite nanoparticles by sol-gel technique and to investigate its properties.

Substitution of Fe$^{3+}$ ions in Ni-Cd mixed ferrite by Gd$^{3+}$ ions and to evaluate the effect of doping on its structural, magnetic and electrical properties.

3. Summary of the Research Work

3.1. Influence of preparation methods on structural, magnetic and electrical properties of nanocrystalline nickel ferrite.

Nickel ferrite nanoparticles were prepared using sol-gel as well as co-precipitation techniques. In sol-gel technique, stoichiometric ratios of AR grade Ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O) and Nickel nitrate (Ni(NO$_3$)$_2$.6H$_2$O) (99.9% pure MERK) were dissolved in minimum amount of ethylene glycol at room temperature. The solution was then heated at 60°C to form a wet gel. Then the gel was dried at 120°C for 6 hours and as a result of which, it ignited to form NiFe$_2$O$_4$ powder. The obtained powder was ground well and three different portions were sintered for two hours in a muffle furnace at 400°C, 600°C and 800°C respectively.

In co-precipitation, appropriate amount of ferric nitrate and nickel nitrate were dissolved in sufficient amount of de-ionized water. In order to control the pH, three molar sodium hydroxide, which acts as the precipitating agent was added to the solution kept under constant stirring. When the pH is maintained at 10, brown colored precipitate was formed. The precipitate was then filtered and washed several times using de-ionized water until it becomes neutral and dried at 200°C for one hour. The product was then milled in an agate mortar and three different portions were sintered at 400°C, 600°C and 800°C respectively for two hours to form fine Ni-ferrite nanoparticles.
For dielectric and resistivity measurements, cylindrical disc shaped pellets (10mm diameter and 2-3mm thickness) were made by applying a uniform pressure of 5 ton using a hydraulic press. Silver paste was used as the electrode material.

Structural characterization was carried out using X-ray diffraction technique. The XRD patterns were compared with standard data (JCPDS PDF card No.074-2081) and the formation of single phase cubic NiFe$_2$O$_4$ nanoparticles in all the samples was confirmed. Sol-gel derived samples sintered at 600°C and 800°C show some extra peaks, indicating the formation of Hematite (Fe$_2$O$_3$) at this temperature. In sol-gel as well as co-precipitation, the crystallite size is observed to be increasing with temperature. Compositional analysis of the samples using EDX technique confirmed expected stoichiometry.

![X-ray diffraction pattern](image)

Figure 3.1.1.X-ray diffraction pattern of Ni-ferrite nanoparticles prepared by (a) co-precipitation and (b) sol-gel technique, sintered at (i) 400°C (ii) 600°C and (iii) 800°C.

HRTEM analysis infer a particle size of 20-30nm for sol-gel derived and 10-25nm for co-precipitation derived particles. Co-precipitation technique produced nanoparticles of very small size with a wide size distribution and super paramagnetic in nature. Ni-ferrite samples prepared by sol-gel technique are of comparatively larger size with narrow size distribution and are ferrimagnetic. Magnetic properties including saturation magnetization, coercivity and remanence are observed to be increasing with increase in sintering temperature in both the methods and this can be attributed to the increase in particle size. The temperature variation of dc resistivity of the samples reflects usual semiconducting nature. Sol-gel synthesized NiFe$_2$O$_4$ samples are found to be more resistive than the corresponding samples prepared by co-precipitation technique. Dielectric measurements were done in the frequency range 100Hz to 20MHz from room temperature to 563K. All the samples demonstrate normal dielectric behaviour.
3.2. Effect of Tb$^{3+}$ Doping on the Structural, Electrical and Magnetic Properties of Nanocrystalline Nickel Ferrite

Terbium doped nickel ferrite samples with general formula NiTb$_x$Fe$_{2-x}$O$_4$ ($x=0, 0.1, 0.2$ and $0.3$) were prepared by the sol-gel technique. Structural characterization was done using XRD technique. Increase in Tb$^{3+}$ concentration has made an increase in the lattice parameter, indicating an expansion of the unit cell. FTIR analysis confirmed the formation of spinel structure in all the samples. Tb$^{3+}$ substitution has resulted in a decrease in the magnetization of nickel ferrite nanoparticles. The temperature variation of dc resistivity of the samples reflects semiconducting nature and the room temperature resistivity values are found to increase (from $10^7 \Omega \text{cm}$ to $10^8 \Omega \text{cm}$) with terbium content. Frequency and temperature variation of the dielectric properties and ac conductivity of the samples were investigated in detail. Observed dielectric dispersion with frequency is explained on the basis of Maxwell - Wagner two-layer model and electron hopping mechanism which is responsible for conduction and polarization.

3.3. Gadolinium substitution induced changes in the dielectric and magnetic behaviour of nickel ferrite nanoparticles

Using sol-gel technique, gadolinium ions are successfully incorporated in to NiFe$_2$O$_4$, keeping its spinel structure. Samples are characterized by XRD and FTIR techniques. Grain size of Ni-Gd ferrite samples is found to decrease with gadolinium concentration. Magnetic characterization using VSM technique revealed decrease in saturation magnetization and increase in coercivity by the doping. The observed increase in ac conductivity and dielectric constant with temperature is explained in terms of increase in drift mobility of charge carriers. Gadolinium doping is found to decrease dielectric loss of nickel ferrite.
3.4. Sol-gel Synthesis and Characterization of Sm\textsuperscript{3+} Substituted Nanocrystalline Nickel Ferrite

Samarium substituted NiFe\textsubscript{2}O\textsubscript{4} nanoparticles are successfully synthesized by the sol-gel technique. Properties of nickel ferrite are found to affect considerably by the substitution. Lattice constant of the samples is observed to decrease with samarium concentration. Like other studied rare earth metals, samarium substitution has resulted in a decrease in the saturation magnetization and the mixed Ni-Sm ferrite samples exhibited very high hysteresis loss. Temperature dependence of dc resistivity study using Keithley electrometer indicates usual semiconducting nature. Samarium substituted samples exhibited increased resistivity compared with pure nickel ferrite. Dielectric behaviour and ac conductivity of the synthesized samples are evaluated. The observed decrease in dielectric loss by samarium doping is explained in terms of the increase in resistivity of the samples. Ac conductivity is observed to increase with temperature, while decrease with samarium concentration.
3.5. On the Structural, Magnetic and Electrical Properties of Terbium Substituted Ni-Zn Mixed Ferrite Nanoparticles

A series of five samples with general formula \( \text{Ni}_{0.4}\text{Zn}_{0.6}\text{Tb}_{x}\text{Fe}_{2-x}\text{O}_4 \) (\( x = 0, 0.05, 0.1, 0.15 \) and 0.2) was prepared by the sol-gel technique. XRD analysis confirmed the formation of single phase FCC spinel structure. Terbium doping has resulted in an increase in lattice parameter and a decrease in particle size of Ni-Zn ferrite. The decrease in lattice parameter due to increased doping (\( x > 0.15 \)) indicated a possible cationic redistribution. Figure 3.5.1 shows Transmission Electron Micrograph of \( \text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 \) sample. Size of the particles obtained from TEM analysis (28±5 nm) is in reasonable agreement with that obtained from XRD analysis.

![Figure 3.5.1. Transmission Electron Micrograph of the sample with \( x = 0 \)](image)

Magnetic characterization showed decrease in saturation magnetization as well as coercivity of Ni-Zn ferrite by terbium doping. Resistivity of the samples is found to increase with terbium content up to \( x = 0.15 \). Ac conductivity as well as dielectric constant is found to increase with temperature, which is due to thermally enhanced drift mobility of charge carriers. The observed decrease in dielectric loss with terbium content up to \( x = 0.15 \) is due to increase in resistivity.

3.6. Magnetic Properties, Ac conductivity and Dielectric Behaviour of Ni-Cd Mixed Ferrites and Gd\(^{3+}\) Substitution Induced Changes

Ni-Cd and Ni-Cd-Gd mixed ferrites were synthesized and characterized using various techniques like XRD, FTIR, WD-XRF, VSM etc. X-ray diffraction study indicated the formation of single phase spinel structure in both Ni-Cd as well as Ni-Cd-Gd ferrite systems. Average particle size obtained from TEM analysis is in the nanometer range and are in close agreement with that obtained
from XRD analysis. Increase in saturation magnetization and coercivity is observed in Ni-Cd mixed ferrites with cadmium content. Gadolinium doping is found to decrease saturation magnetization and to increase coercivity of Ni-Cd ferrite.

Resistivity of Ni-Cd ferrites is observed to increase by gadolinium doping up to $x = 0.2$. Dielectric properties and ac conductivity were studied as a function of frequency, temperature and composition. Minor cadmium and gadolinium doping is observed to decrease the dielectric loss of nickel ferrite. Ac conductivity study supports the findings in the dc resistivity as well as dielectric measurements.

4. Conclusions

- The synthesis and structural, magnetic and electrical characterization of nickel ferrite, a typical inverse spinel ferrite, substituted by divalent transition metal and trivalent rare earth metal ions has been investigated.
- The sol-gel derived nickel ferrite particles are of comparatively bigger size, multi domain in nature, ferromagnetic and more resistive, can be used in high frequency applications.
- Co-precipitation derived particles are of smaller size, single domain in nature and super paramagnetic useful in biomedical applications like targeted drug delivery, MRI contrast agents, treatment of cancer etc.
- Expansion of the unit cell is observed by the substitution of terbium as well as gadolinium, whereas samarium doping has decreased the lattice parameter of nickel ferrite.
- Gadolinium and samarium doping is found to inhibit the grain growth in nickel ferrite, while it was enhanced by terbium doping.
• The magnetization of nickel ferrite could be reduced by the doping of all the studied rare earth metal ions.
• Coercivity and hence hysteresis loss is found to decrease by terbium substitution, while gadolinium and samarium doping has resulted in increased coercivity.
• Magnetic characterization and FTIR analysis suggested the occupation of rare earth metal ions on the octahedral sites; however this has to be verified using Mossbauer analysis.
• Dielectric loss of nickel ferrite can be decreased by the rare earth metal ion doping.
• Particle size Ni-Zn ferrites is found to decrease by terbium substitution. Magnetization as well as coercivity of Ni-Zn ferrite is decreased by terbium doping. Maximum resistivity, least dielectric loss and small hysteresis loss is observed for Ni_{0.4}Zn_{0.6}Tb_{0.15}Fe_{1.85}O_{4} ferrite.
• Cadmium doping is found to increase the lattice constant of nickel ferrite. Unit cell of Ni-Cd mixed ferrite is observed to expand by gadolinium substitution and for higher gadolinium concentration it decreased.
• Magnetization as well as coercivity of nickel ferrite can be improved by cadmium substitution. However this increase is limited by the secondary CdO phase formation.
• Coercivity of Ni-Cd ferrite can be further increased by gadolinium doping but at the same time magnetization will be reduced.
• Investigations on electrical and dielectric properties infer that dielectric loss of Ni-Cd mixed ferrite can be reduced but resistivity can be increased by gadolinium doping.

Reference: