1. Introduction

Ferrites are one of the most useful magnetic materials, which find a wide range of technological applications. In the past few decades, the technology of ferrites has assumed a new importance. With the advent of developments in computer applications and satellite communications, there is high demand for ferrite with novel properties. The biocompatible ferro-fluids based on ferrites are promising for biomedical applications like cell separation, purification and magneto hyperthermia of tumor cells [1].

Nanotechnology is a highly diverse and multidisciplinary field, ranging from novel extensions of conventional device physics to completely new approaches based on molecular self assembly. Magnetic properties of materials in nano level are different from that of bulk materials. In recent years, a lot of studies have been done on nano crystalline magnetic materials because of their extraordinary properties compared to that of bulk materials. When the particle size is reduced to a few tens of nanometers, ferrite materials exhibit high coercive field, high Curie temperature and low saturation magnetization when compared to their bulk counterparts.

Several research groups are involved in the investigations of spinel oxide nanoparticles because of their potential applications in magnetic devices, microwave technology and high density magnetic recording media [2 - 5]. Cobalt ferrite nano particles have been of research interest due to their diverse technological and biomedical applications. They exhibit an inverse spinel structure and have inherent properties of high coercivity, moderate saturation magnetization, high electrical resistivity and good mechanical stability. Owing to these characteristics, cobalt ferrite is a potential candidate for magnetic storage devices, magnetic hyperthermia, bactericides and high frequency applications [6 - 8].

Cobalt ferrite is one of the most important ferrites with a partially inverse spinel structure whose degree of inversion is sensitive to the method of preparation. Magnetic properties of cobalt ferrite nanoparticles are strongly dependent on their chemical compositions and substitutions. Apart from its magnetic application in the area of memory and switching circuits in digital computers and microwave devices, cobalt ferrite can find important applications in biomedical field. The ability to be functionalized with drug and coatings makes it a good carrier in drug delivery applications [9, 10].
The properties of ferrites can be changed dramatically by the addition of small amount of rare earth ions. Several researchers have investigated the influence of different rare earth ion doping in modifying the properties of ferrites [11-15]. These studies revealed that the substitution of small percentage of Fe$^{3+}$ ions by rare earth ion induces strain and results in structural distortion which modifies its magnetic and electrical properties. Therefore, rare earth ions will be a promising candidate for doping cobalt ferrite in order to tune its properties. Systematic investigations on structural, magnetic and electrical properties of rare earth doped cobalt ferrite nanoparticles are only few. So in the present study, influence of rare earth ions (samarium, neodymium and dysprosium) in cobalt ferrite nanoparticles is explored.

It has been reported that zinc ions have a strong preference to tetrahedral sites in the spinel ferrite lattice [16]. Hence the substitution of magnetic ions in ferrite by non-magnetic zinc ions can lead to an improvement in magnetic properties. In order to optimize magnetic as well as electrical properties, Co-Zn mixed ferrites are synthesized by sol-gel technique and structural, magnetic as well as electrical properties are investigated. A small amount of Dy$^{3+}$ ions is incorporated in to these mixed ferrites and the resulting improvements in properties are evaluated.

Nanoparticles with antibacterial activity can find immense applications in biomedical devices, food processing and packaging, textile industry and water disinfection. Previous studies have shown that antimicrobial formulation in the form of nanoparticles can be used as effective bactericidal agents [17, 18]. Therefore, in the present study, attempts have been carried out to synthesize silver doped cobalt ferrite nanoparticles, hoping to achieve improvement in the antibacterial activity of cobalt ferrite. The biocidal activity was tested on Gram negative (Escherichia coli, Pseudomonas aeruginosa, and Serratia marcescens) and Gram positive (Staphylococcus aureus) bacterial strains.

2. Objectives of the work

Polycrystalline ferrites are important magnetic nano-material and they exhibit interesting magnetic, electrical and antibacterial properties. Their applications in diverse fields such as information storage, electronics, catalysis, medical diagnostic, drug delivery, bactericides etc. shows its importance in research. The main objectives of the present work are as follows,

- Synthesize a series of rare earth doped cobalt ferrite nanoparticles – CoR$_x$Fe$_2$$_x$O$_4$ where R= Sm, Nd, Dy and x=0, 0.05, 0.1, 0.15, 0.2, 0.25 by sol-gel method.
Study the modifications in structural, magnetic and electrical properties due to the partial replacement of Fe$^{3+}$ ions in CoFe$_2$O$_4$ by rare earth ions Nd$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$.

Investigate the effect of dysprosium substitution on the structural, magnetic and electrical properties of Co-Zn mixed ferrite nanoparticles.

Study the influence of dopant concentration and particle size on the magnetic properties of the samples.

Analyze the effect of silver substitution on the structural and magnetic properties of cobalt ferrite nanoparticles.

To test the efficacy of silver doped cobalt ferrite nanoparticles against Gram negative (Escherichia coli, Pseudomonas aeruginosa, and Serratia marcescens) and Gram positive (Staphylococcus aureus) bacterial strains.

3. Summary of the Research Work

3.1 Sample Preparation and Characterization

The modern applications of nano science and nanotechnology demand novel preparation techniques for ensuring purity and controlling the size of the nanoparticles. Proper characterization using modern analytical tools is a prerequisite before the implementation of these materials in technological applications. Hence, the selection of proper synthesis method and analysis plays crucial role in material science research. Several chemical synthesis techniques such as sol-gel, co-precipitation, micro-emulsion, hydrothermal and reverse micelle method can be employed for producing nano magnetic materials [11-13, 19, 20]. To ensure the material to be single phase, the choice of technique for the preparation of nano ferrites and composites is very vital.

In the present study, sol-gel method was used for the preparation of cobalt ferrite nanoparticles. It is a widely used technique that has incredible potential in nano manufacturing. Due to good stoichiometric control and production of ultrafine particles in nano-range at relatively low temperature, sol-gel technique is an attractive method for the preparation of nano-ferrites [3, 21]. AR grade cobalt nitrate, rare earth nitrate, zinc nitrate, silver nitrate and ferric nitrate were used as chemical precursors. Metal nitrates in the required stoichiometric ratio were
dissolved in minimum amount of ethylene glycol at room temperature and the sol was heated at 60°C, to obtain a wet gel. Further heating of the gel at higher temperatures led to the self ignition. The obtained dry powder was ground well using agate mortar to form ultrafine particles of cobalt ferrite. The following series of samples were prepared using the above procedure.

1. CoR_{x}Fe_{2-x}O_{4} (x=0 to 0.025 at step size 0.05; R= Sm, Dy, Nd)
2. Co_{0.9}Zn_{0.1}Fe_{2-x}Dy_{x}O_{4} (x=0 to 1 at step size 0.02)
3. Co_{1-x}Ag_{x}Fe_{2}O_{4} (x=0 to 0.1 at step size 0.025)

The proper analysis of properties using various characterization techniques can lead to the design of nano materials for different applications. Hence the prepared materials were analyzed using various analytical instruments like X-ray Diffractometer (XRD), Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Wavelength Dispersive X-ray Fluorescence spectroscopy (WD-XRF), Fourier Transform Infrared spectrometer (FTIR), Vibrating Sample Magnetometer (VSM), Impedance analyzer (Wayne Kerr 6500 B) and Keithley 6221 DC and AC Current source and 2182A nano voltmeter.

The structural, magnetic and electrical characterizations of the prepared samples were investigated. Also attempts have been carried out to examine the antibacterial activity of silver doped cobalt ferrite nanoparticles against the Gram negative (Escherichia coli, Pseudomonas aeruginosa, and Serratia marcescens) and Gram positive (Staphylococcus aureus) bacterial strains.

3.2 Results and discussion

The proposed thesis is captioned “Characterization of Nano Cobalt Ferrites and Studies on Their Antibacterial Activity” and it consists of eight chapters.

Chapter one gives a general introduction on nano materials and nanotechnology, magnetic properties of macroscopic and nanoscopic magnetic materials, structure of spinel ferrites, magnetic and electrical properties of ferrite nanoparticles and its application as antibacterial agents. Chapter two discusses the synthesis method used in the present study, characterization techniques and their basic theories.
Chapter three and four discuss the characterization of samarium and neodymium substituted cobalt ferrite nanoparticles synthesized by sol-gel technique and heat treated at 673K. The effect of these rare earth ions on the properties of cobalt ferrite is investigated in detail. Structural analysis is performed using XRD technique and the samarium and neodymium induced changes are investigated in terms of lattice constant, grain size, X-ray density, apparent density and porosity with the help of Hall-Williamson plots [22]. Figure depicts the X-ray diffraction pattern of Samarium substituted cobalt ferrite nanoparticles. FTIR analysis of samples confirmed the presence of two characteristic absorption peaks [23]. TEM is used to evaluate the morphology and particle size of the nanoparticles. Compositional evaluation of samarium substituted sample was done by using EDX technique while WD-XRF technique is used to estimate the elemental composition of neodymium doped samples. Magnetic parameters of the ferrimagnetic ferrite samples are obtained from the hysteresis loops measured at room temperature. The temperature and compositional variation of DC resistivity of the ferrite samples are analyzed. Dielectric parameters like dielectric constant, dielectric loss and ac conductivity are investigated and presented as a function of temperature, frequency and rare earth concentration.

![Figure 1. XRD pattern of CoFe$_{2-x}$Sm$_x$O$_4$](image)

Chapter five discusses characterization of dysprosium substituted cobalt ferrite nanoparticles synthesized by sol-gel technique. The synthesized samples were heat treated at
773 K in order to improve the crystallinity. The dielectric dispersion observed in the samples with frequency is depicted in Figure 2. The effect of the dysprosium ion on the structural, electrical and magnetic properties of cobalt ferrite is investigated and presented.

Figure 2. Relative dielectric permittivity as a function of log f for CoFe$_{2-x}$Dy$_x$O$_4$ samples

Chapter six deals with the synthesis of dysprosium doped Co-Zn mixed ferrite nanoparticles. The effect of the rare earth ions on the structural, electrical and magnetic properties of cobalt zinc mixed ferrite is investigated and presented in detail. Figure 3 shows the magnetic characterization of the samples using vibrating sample magnetometer.

Figure 3. Room temperature hysteresis curves of Co$_{0.9}$Zn$_{0.1}$Fe$_{2-x}$Dy$_x$O$_4$ samples
Chapter seven presents the synthesis of silver doped cobalt ferrite nanoparticles. The structural and magnetic characterizations of the as prepared samples were done. The antibacterial activity against the Gram negative (Escherichia coli, Pseudomonas aeruginosa, and Serratia marcescens) and Gram positive (Staphylococcus aureus) bacterial strains were investigated as a function of the amount of silver in the samples. The optical density measurements of the bacterial strains in the culture media were examined as a function of silver content and the results are depicted in Figure 4.

![Figure 4. Optical density measurements of Co\(_{1-x}\)Ag\(_x\)Fe\(_2\)O\(_4\)](image)

Chapter eight gives a brief outline of important results and major findings of the study and scope and suggestion for future work.

The work presented in this thesis has either been published in or communicated to international journals or conference proceedings.

### 3.3 Conclusions

In the present study all the samples were successfully synthesized by sol-gel method. The structural analysis indicates the formation of single phase spinel structure in all the samples. The substitution of small concentrations of rare earth ions (samarium, neodymium and dysprosium) in cobalt ferrite has resulted in an increase in lattice parameter and crystallite size. However, for
higher concentrations of rare earth ions, lattice contraction and reduction in the crystallite size of cobalt ferrite nanoparticles are observed. This may be attributed to the difficulty in the rare earth ions with higher ionic radius to dissolve into the spinel lattice.

In the case of Co-Zn mixed ferrites, the analysis of XRD data revealed that the increase in Dy content decreases the crystallite size of the samples. The lattice parameter is found to increase with Dy$^{3+}$ addition up to $x=0.04$, suggesting the expansion of the unit cell and for further increase a contraction is observed. The prepared nanoparticles have spherical morphology, narrow size distribution and are slightly agglomerated as evident from TEM analysis. The expected stoichiometry of the sample was confirmed by the WD-XRF analysis. The absorption bands in FTIR spectra of all the samples are found in the expected range. The observed shift in the band frequencies suggests the occupancy of rare earth ions on the octahedral sites.

The saturation magnetization decreased with an increase in rare earth amount and this is explained based on the decrease in the net magnetic moment due to the substitution of non-magnetic ion in the octahedral site. Variation of coercivity with particle size depends on the domain nature of the ferrite nanoparticles [24, 25]. The electrical resistivity of the cobalt ferrite has been improved by doping rare earth content while the dielectric constant and dielectric loss have been reduced by doping. The improvement in the activation energy is a direct consequence of the enhanced electrical resistivity. The decrease in electrical resistivity with temperature is due to the higher mobility of the charge carriers at elevated temperatures.

The dielectric dispersion with frequency is explained on the basis of Maxwell - Wagner interfacial polarization and electron hopping mechanism which is responsible for conduction and polarization [26, 27]. The dielectric constant and dielectric loss of doped cobalt ferrites were decreased by increasing the frequency of the applied AC field, representing the typical behaviour of ferrites, caused by the lagging of hopping electron behind the changing frequency of applied AC field. AC conductivity increases with temperature and the linear increase observed at high frequencies suggest that the conduction is due to small polaron hopping.

The silver substituted cobalt ferrite nanoparticles exhibit a spinel structure with sizes varying from 15 to 20 nm. The saturation magnetization initially decreases and then increases with silver concentration. The decrease is attributed to the non-magnetic silver substitution on octahedral site while the increase may be due to the presence of metallic silver phase on the grain.
boundaries. The antibacterial efficacy was tested against Gram negative and Gram positive bacterial strains and the results show an enhancement in the activity with the addition of silver into cobalt ferrite. However for higher concentrations of silver ion, a decline in the antibacterial behaviour is observed. The improvement in the biocidal activity is attributed to the increase in the surface to volume ratio of the nanoparticles which enhances the contact area with the microbes.

These results suggest that the properties of cobalt ferrite nanoparticles can be tuned by the substitution of appropriate amount of rare earth ions and make it suitable for technological applications. Moderate saturation magnetization values, reasonable remnant ratio and high coercivity in combination with high electrical resistivity makes them a better choice for high density recording media and high frequency applications. Further, the silver substituted cobalt ferrite nanoparticles with good magnetic and antibacterial properties can offer great promises in biomedical and pharmaceutical applications.

3.4 Proposed plan of Thesis

Chapter 1: General Introduction

Chapter 2: Experimental Techniques
Chapter 3: Samarium substitution induced changes on structural, magnetic and electrical properties of cobalt ferrite nanoparticles
Chapter 4: Effect of neodymium substitution on structural, magnetic and electrical properties of cobalt ferrite nanoparticles
Chapter 5: Influence of dysprosium substitution on structural, magnetic and electrical properties of cobalt ferrite nanoparticles
Chapter 6: On the structural, magnetic and electrical properties of dysprosium doped Co-Zn mixed ferrite nanoparticles
Chapter 7: Synthesis, characterization and antibacterial activity of silver substituted cobalt ferrite nanoparticles
Chapter 8: Summary and Scope for Future Work