

**SYNTHESIS, CHARACTERIZATION AND SOLID STATE
PROPERTIES OF PURE AND SUBSTITUTED NICKEL-
COBALT FERRITES AND THEIR APPLICATIONS**

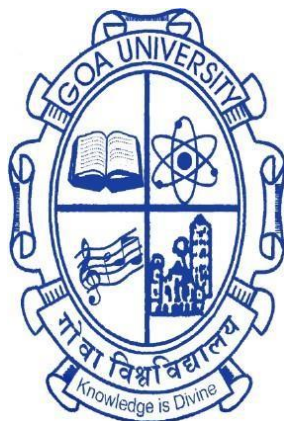
A THESIS SUBMITTED IN THE PARTIAL FULFILLMENT FOR THE DEGREE OF
DOCTOR OF PHILOSOPY

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CHEMISTRY

IN THE SCHOOL OF CHEMICAL SCIENCES,

GOA UNIVERSITY



BY

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FEBRUARY 2025

DECLARATION

I, Miss Mangala Ulhas Sawal hereby declare that this thesis represents the work which has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

Place: Taleigao Plateau

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CERTIFICATE

I hereby certify that the above Declaration of the candidate Miss Mangala Ulhas Sawal is true and the work was carried out under my supervision.



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...Ms. Mangala U. Sawal

*Dedicated to
my family and
friends*

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Chapter 1

*Introduction, literature review,
aims and objectives*

1.1 Introduction of ferrites

In the recent years, many researchers have shown interest in the synthesis of nanomaterials. Nanomaterials are found to show interesting properties which their bulk counterparts do not exhibit because of their larger sizes. One among such promising nanomaterials are nano spinel ferrites which due to their amazing structural, electric, dielectric and magnetic properties [1-2] are attracting more and more materials researchers. The use of nano scale magnetic devices for the technological application purely depends on the homogeneity, composition magnetic and structural properties of the nanoparticles. The crucial parameters which control the performances of the devices are the particle size, particle size distribution, uniform morphology and compositions [3]. Thus, the increase in particle sizes of the nanoparticles is not desirable for their application [4], as the nanomaterial properties are different from their bulk counterparts in various aspects [5].

The rudimentary knowledge and the applications of the nanomaterials are considerably investigated in broad research area like the hard magnetic nanoparticles in applications such as organic synthesis catalytic [6], microphone [7], photochemical [8], supercapacitor [9], etc. Numerous methods have been used for synthesizing the nano ferrites like the solution combustion synthesis method [7], wet chemical co-precipitation [10], micro-emulsion based method [11], precursor-combustion synthesis [12], sol-gel method [13], a hydrothermal technique [14] etc.

1.1.1 Brief history of ferrites

The history of the magnetic properties of ferrites and their applications has been known few centuries ago. Magnetite or loadstone (Fe_3O_4): a natural non-metallic solid could attract iron was first known around 800 B.C. Magnetite is a hard ferrite which appears in nature. The earliest scientific study of magnetism was the publication named ‘De Magnete’ which was published by William Gilbert in 1600. Besides, Hans Christian Oersted, Ander Marie Ampere, Micheal Faraday, Pierre Curie and others explained the fundamentals of electromagnetic theory in general and for the crystal structures. J. Snoek of the Phillips Research Laboratories in the Netherlands synthesized soft ferrites for commercial applications in 1945. Later in 1947, he published a book ‘New developments in Ferromagnetic materials’.

In 1952, C.L. Hogan from Bell Labs made the first non-reciprocal microwave which was operating at a frequency of 9 GHz that was based on Faraday rotation effect.

1.1.2 Classification of ferrites

The five different crystal structures in which the ferrites have been classified are as under

1. Hexagonal Ferrites:

These are a family of ferrites with hexagonal and rhombohedral symmetry. They construct an extensive variety of solid solutions. These types of ferrites show greater coercivity values.

2. Garnets:

These are ferrites having general formula $R_3Fe_5O_{12}$ where $R = Yt$ or mostly rare earth metal ions like Dy, Gd, La, etc. The crystal structure is basically cubic and is relatively very complex. Garnets have three kinds of cation sites namely, dodecahedral (8 fold), octahedral (6 fold) and tetrahedral (4 fold) sites. Fe^{+3} can distribute amongst three tetrahedral and octahedral sites while the rare earth elements can preferentially occupy the largest, dodecahedral sites.

3. Perovskites:

Perovskites have cubic structure with general formula ABO_3 . In this structure the A site ion on corner of the lattice is rare earth element or alkaline earth metal element. The B site ions in the centres of lattice can be 3d, 4d and 5d transition metals. The perovskites show submetallic to metallic lustre and are usually brittle.

4. Orthoferrites:

These are a class of rare-earth iron oxide compounds having general formula $RFeO_3$, wherein $R =$ rare element or Yttrium, that has orthorhombic perovskite structure. Orthoferrites have unusual electrical, optical and magnetic properties due to interaction between Fe^{3+} ions and rare earth (R^{3+}) ions.

5. Spinel Ferrites:

These ferrites are explained by the formula MFe_2O_4 in which M stands for divalent metal ions. The crystal structure of spinel ferrite exhibit two interstitial sites namely tetrahedral (A-site) and octahedral [B-site]. Various cations can accommodate at tetrahedral site and at octahedral site which can facilitate number of changes in the properties of the ferrites.

M is a divalent metal ions and thus forms a number of spinel ferrites. Fe^{3+} ions in ferrites can also be partially substituted by other trivalent ions like Al^{3+} , Cr^{3+} , etc.

There are three types of spinel ferrites based on distribution of cations on tetrahedral and octahedral sites viz.

- (1) Normal spinel ferrites,
- (2) Inverse spinel ferrites and
- (3) Random spinel ferrites.

1. Normal spinel ferrite:

Normal spinel has only one kind of cation on octahedral (B) sites in the ferrite. In these ferrites the divalent cations occupy the tetrahedral (A) sites while the trivalent cations are on the octahedral [B] sites. The normal spinel have been represented by the formula $(\text{M}^{2+})[\text{Me}^{3+}]_2\text{O}_4$, where M represent divalent ions and Me represent trivalent ions. An example of such a ferrite is ZnFe_2O_4 .

2. Inverse spinel ferrite:

In these types of ferrites, half of the trivalent ions occupy the tetrahedral (A) sites and the remaining half occupies the octahedral (B) sites; the remaining cations are randomly distributed among the octahedral (B) sites. These ferrites are represented by the formula $(\text{Me}^{3+})[\text{M}^{2+}\text{Me}^{3+}]\text{O}_4$, where M represent divalent ions and Me represent trivalent ions. An example of such ferrite is Fe_3O_4 .

3. Random spinel ferrite:

The spinel which have distribution of ions between normal and inverse are called as Random spinel. Their general formula may be written as $(\text{M}^{+2}\text{Me}^{+3})(\text{M}^{+2}\text{Me}^{+3})\text{O}_4$, where M represent divalent ions and Me represent trivalent ions.

The smallest unit cell of the spinel structure exhibits cubic symmetry and contains eight formula units of MFe_2O_4 , where M denotes a divalent transition metal ion such as Fe^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and so on. Each unit cell comprises of 32 oxygen anions and 24 metal cations, totalling to 56 atoms. As can be seen from Fig. 1.1, the large oxygen ions make a face centered cubic (FCC) lattice; two types of interstitial site arrangement is possible in such cubic closed-packed structure i.e., tetrahedral (A) sites coordinated by 4 oxygen ions and the octahedral (B) sites surrounded by six oxygen ions. A cubic unit cell comprises of 64 tetrahedral and 32 octahedral interstitial sites. However, only $1/8^{\text{th}}$ of the

tetrahedral sites and $\frac{1}{2}$ of the octahedral sites are occupied which implies that only 8 tetrahedral and 16 octahedral sites per unit cell are filled by the metal ions.

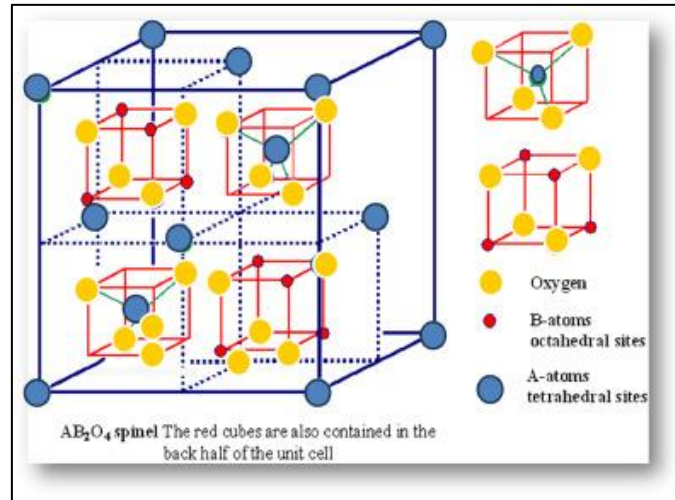


Fig. 1.1 Crystal structure of spinel ferrites

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1.2 Literature review

The perception of the literature review endows numerous ferrite synthesis routes and their impact after substituting with different elements on the structural, magnetic, electric properties of the ferrites as well as their applications in everyday life. The present research work is restricted to the study of Ni-Co ferrites and Zn^{2+} and Mg^{2+} substituted Ni-Co ferrite system to be investigated for their structural, electric, dielectric, morphological and surface properties along with their thorough application studies as gas sensors and supercapacitors. Thus, this chapter mainly focusses on the literature survey of Ni-Co ferrites ($\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ where $x = 0.0-1.0$) followed by the research survey of substituted Ni-Co ferrites, viz. $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) and $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites and ultimately discussing their applications.

1.2.1 Literature review of Ni-Co ferrites

Baykal et al. [15] synthesized a series of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.4, 0.6, 0.8$, and 1.0) by microwave induced combustion using glycine as fuel. The characterization techniques such as the powder XRD, IR, SEM were used for structure and the morphology investigations, respectively. All the ferrite samples had porous, cubic spinel structure with particle size in the range of 60-67 nm. The lattice parameter decreased with nickel concentration because of smaller ionic radius of nickel. The magnetization studies

showed that coercivity decreases with increase in nickel content. Some other researchers [16] did an environment friendly synthesis of the nickel substituted cobalt ferrites by self-combustion method as no external oxidizing agents were used to change the pH of the precursor. The powder XRD, VSM and impedance analyser techniques were used to determine the structural, magnetic and electrical characteristics of the nano ferrites, respectively. The magnetic and the electrical properties were tuned from hard magnetic and low resistivity cobalt ferrite to the soft magnetic and high resistivity nickel ferrite.

Kumar et al. [17] synthesized $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0.02, 0.04, \text{ and } 0.06$ M) by sol-gel auto-combustion method. The powder XRD studies indicated the decrease in the crystallite size from 31 to 27 nm with an increase in nickel concentration thus indicating the incorporation of the Ni^{+2} ions in cobalt ferrite lattice. The two most intense characteristic Raman bands vibrational modes of the spinel ferrites were observed at 486.87 cm^{-1} (E_g) and 696.96 cm^{-1} (A_{1g}). The VSM studies revealed the variation in saturation magnetization and coercivity with an increase in nickel concentration. The SEM studies showed spherical shaped particles with pores. Pubby et al. [18] synthesized $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0-1, \Delta = 0.15$) via Pechini's sol-gel citrate route. The Raman spectroscopy, XRD, SEM and EDS were used to examine the structural purity of the prepared ferrites. The studies showed that doping of cobalt increases the lattice constant and decreases the density and porosity. The Mössbauer spectral studies revealed strong sextets indicating ordered magnetism in the magnetic domain and iron in +3 vacancies. Doping of cobalt for nickel increased the complex permittivity and complex permeability. The electromagnetic and shielding properties of these Ni-Co ferrites were also studied. The dielectric properties and complex impedance spectroscopy studies of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ (where $x = 0.0, 0.2, 0.4, 0.6$ and 0.8) were done by some researchers [19] by synthesizing the ferrites by double sintering ceramic technique. The IR confirmed the spinel structure because of presence of two peaks at around 600 cm^{-1} and 400 cm^{-1} for tetrahedral and octahedral stretching vibrations, respectively while the SEM micrographs showed an increase in the grain size with the addition of cobalt to the nickel ferrite. The results obtained showed that with an increase in the cobalt concentration, the total complex impedances decreases, while the dielectric permittivity showed usual dielectric dispersion and with increase in nickel concentration the dielectric permittivity also increases.

R.C. Kambale and co-workers [20] studied the effect of cobalt substitution on magnetic, structural and electric properties of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ which was synthesized by standard

ceramic technique. The powder XRD technique was used to confirm the single phase formation and also carried out structural analysis. The DC resistivity studies were done by two probe method and the measurements indicated a decrease in resistivity with an increase in cobalt concentration. The hysteresis studies showed that with an increase in cobalt concentration, there was increase in saturation magnetization and decrease in the coercivity, thus making the ferrites suitable to be used in magnetic recording media. Nickel doped cobalt ferrite was also synthesized by some researchers [21] by solid state reaction route. They studied the doping effect on structural, vibrational and dielectric properties. The Rietveld analysis was carried out for refinement of the cell parameter thus inferring the $Fd3m$ space group. The Cell parameter variation with nickel substitution confirmed the partial substitution of Co^{+3} by Ni^{+3} in the spinel $CoFe_2O_4$. They observed a blue shift in the Raman spectra of Ni-doped cobalt ferrite compared to pure $CoFe_2O_4$. The dielectric constant and loss tangent values were also investigated as a function of composition and frequency.

The co-precipitation synthesis of $Ni_{1-x}Co_xFe_2O_4$ ($x=0.3, 0.5, 0.7$) nanoparticles was done by using citrate as chelating agent. The synthesized powders after calcining for 400 °C, 600 °C and 800 °C were characterized by powder XRD technique affirming that the nanoparticles belonged to the spinel type lattice having space group $Fd3m$. The FE-SEM and HR-TEM with SAED techniques were used to identify the cubic shape of the prepared nanoferrite [22]. Some researchers [23] also investigated the structural analysis of nickel doped cobalt ferrites prepared by co-precipitation route and estimated the particle size in the range of 18-24 nm. The superparamagnetic blocking temperature decreased linearly with an increase in nickel concentration that was attributed to lower magneto-crystalline anisotropy of nickel compared to cobalt which increased the chance of jump across the anisotropy energy barrier.

Joshi et al. [24] prepared nanosized $Ni_{1-x}Co_xFe_2O_4$ ($x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) by wet chemical co-precipitation method. From the powder XRD, the single phase spinel formation was confirmed and the increase in the lattice parameter was observed as cobalt content was increased. The dielectric measurements showed usual dielectric dispersion because of the Maxwell-Wagner type of interfacial polarization. The temperature dependent dielectric constant studies showed that with increase in temperature, the dielectric permittivity also increases. $Ni_xCo_{1-x}Fe_2O_4$ ($x=0.0, 0.2, 0.3$) was synthesized by precursor-combustion technique by Gonsalves et al. [25]. The research group used novel

precursors of metal fumarato-hydrazinate for the synthesis. The TG-DTA was employed for studying the thermal decompositions pattern of the precursors. The major features of the precursors were they autocatalytically decomposed after the ignition to yield nanocrystalline monophasic ferrite. Coutinho et al. [26] synthesized the single phase nanosized $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ by precursor-combustion technique from hexahydrazine nickel cobalt ferrous succinate precursor at a relatively lower temperature. The characterization of the precursor was done by IR, CHNS analysis, chemical analysis, TG-DTA and mass loss studies. The precursor autocatalytically decomposes on ignition to yield the ‘as-prepared’ ferrite. The powder XRD revealed single cubic phase spinel and SEM results depicted nanosized nature of ferrite. The loss tangent showed the relaxation peaks which were explained on the basis of Maxwell–Wagner two-layer model and Koops phenomenological theory, whereas the DC conductivity results indicate the semiconductor nature of the ferrite.

Some researchers have synthesized the $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) by the hydrothermal synthesis technique at a relatively low temperature (160°C) for 15 h and subsequently annealing at 300°C for 3 h. All the samples were found to have the cubic spinel structure determined from the powder XRD studies. The morphological variations were studied by SEM and the results obtained showed average particle sizes between 30–35 nm. From the ESR results a core shell type structure formation was proposed wherein the core is composed of the undoped CoFe_2O_4 and the shell is Ni^{+2} doped CoFe_2O_4 [27].

Mozaffari et al. [28] synthesized ($\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$, $x = 0.1, 0.3, 0.5, 0.7$ and 0.9) by sol gel method. The magnetic measurements showed that the increase in nickel content led to an increase in the saturation magnetization and decrease in the coercivity values which was explained on the basis of magnetocrystalline anisotropy. Besides, Curie temperatures of the samples was found to increase with increasing nickel content which was justified by the change in the superexchange interactions after substituting with the magnetic Ni ions in Co ferrites. Nandan et al. [29] examined the synthesis of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.4, 0.5, 0.6, 1.0$) using sol gel method and their characterizations was done. Different ligand parameters such as the bond length, force constant and effective mass were associated with a shift and broadening in the Raman spectra with change in Co^{2+} content. The A_{1g} peak in Raman estimated $\text{Co}^{2+}/\text{Ni}^{2+}$ and Fe^{3+} ion distribution amongst the two interstitial sites.

Majid et al. [30] focussed on synthesizing $\text{Ni}_x\text{Co}_{x-1}\text{Fe}_2\text{O}_4$ nanoparticles ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) using the hydrothermal synthesis method. They studied the impact of doping using IR, powder XRD, Raman and Impedance analyser. Raman spectroscopy exposed the two intense optical peaks at E_g and T_{2g} which were reported to increase with increasing nickel substitution. They also reported improved dielectric properties with doping and found that the dielectric constant and the dielectric loss tangent decreased with increase in frequencies. Moreover, AC conductivity was found to increase as the frequency was increased. Torkian et al. [31] employed sol gel auto combustion method for synthesis of $\text{Co}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ferrites ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1). They characterized the samples by powder XRD, IR, FE-SEM and EDAX. Further, magnetic investigations (by VSM) confirmed an increase in coercivity (H_c) and saturation magnetization (M_s) values after substituting Co^{2+} ions in nickel. They reported M_s and H_c values to be 93 emu/g and 420 Oe respectively for composition $\text{Co}_{0.8}\text{Ni}_{0.2}\text{Fe}_2\text{O}_4$. The investigations of the reflection loss properties were done in the frequency range of $8\text{-}12 \text{ GHz}$ by vector network analyser (VNA) and the maximum reflection loss was found to be $\sim -26 \text{ dB}$ (i.e. over 99% absorption) at 9.7 GHz with bandwidth of 4 GHz ($\text{RL} < -10 \text{ dB}$).

Tanbir et al. [32] scrutinized the effect of rare earth (Gd^{3+} , Sm^{3+} , Eu^{3+}) doping on the properties of nickel cobalt ferrites which are synthesized via co-precipitation triggered route. The characterization of the ferrite samples was done by powder XRD and the morphology was determined by HR-TEM micrographs and it was seen that the results obtained for mean particle size were in close agreement with the crystallite sizes. The room temperature and 60 K VSM measurements displayed the paramagnetic nature of the rare-earth ions that impairs the superexchange interactions in between the sublattices. Upon substitution of the rare earth metals, the H_c , M_s and Curie temperature T_c values were found to decrease as compared to the pure samples. The optical properties recorded by UV visible spectrometer from $200\text{-}700 \text{ nm}$ displayed an indirect allowed optical band gap (E_g) for all the ferrites. The obtained E_g values for the samples were 1.91 eV , 1.88 eV , 1.71 eV and 1.92 eV .

Ati et al. [33] used gel method to synthesized cobalt substituted nickel ferrites with compositions $\text{Ni}_{(1-x)}\text{Co}_{(x)}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$). The room temperature magnetic measurements by VSM explained that saturation magnetization, remnant magnetization and coercivity were found to show improved values after Co^{2+} ions

substitution. Sontu et al. [34] synthesized the cobalt nickel ferrite nanoparticles using auto-combustion method and stated the impact of temperature and the applied external magnetic field strength on the magnetic behavior of these ferrites. The effect on the optical properties of the cobalt ferrite was perceived by diffuse reflectance spectroscopy (DRS) and the thermomagnetic studies were performed by employing SQUID technique from 5 K to 400 K temperature range. For ZFC-FC studies, the fields of 1 kOe was used and 5 kOe and 50 kOe fields were used for the M-H hysteresis loop for studying their magnetic properties. They also reported increased values of blocking temperatures as suggested in the literature.

The nanocrystalline $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ (where $x = 0.0, 0.25, 0.50, 0.75, 1$) were synthesized by citrate-nitrate precursor sol gel technique by Hankare et al. [35]. These researchers stated an increase in the crystallite with decreasing lattice parameter values upon increasing nickel substitution. The surface morphological studies from SEM depict that the grains are uniform in size and are in the nano range and the average grain size was found to increase with increase in the nickel substitution which lies between $0.63\ \mu\text{m}$ and $3.18\ \mu\text{m}$. Further because of increase in drift mobility of the charge carriers in the samples with increase in temperature, a decrease in the resistivity was observed. Also, a decrease in the activation energy in the ferromagnetic region was seen with disorientation of spins. The thermoelectric power measurement (TEP) curves demonstrated negative slope indicating that the samples are n-type semiconductors except for NiFe_2O_4 which showed p-type semiconducting property.

Dysprosium doped nickel-cobalt spinel ferrite with composition, $\text{Ni}_{0.8}\text{Co}_{0.2}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4$, was synthesized by the simple ceramic method by some scientists [36]. It was observed that there was a decrease in dielectric constant and the loss tangent with the increase in frequency and Dy content. The dc resistivity variation with temperature confirmed the semiconducting nature of the ferrite samples. The synthesized samples exhibited usual dielectric dispersion having Maxwell Wagner interfacial polarization. Semicircles which ascribes to high resistance were seen in the complex impedance analysis at lower frequencies. Duan et al. [37] synthesized hollow microspheres of Ce^{+3} doped nickel cobalt ferrite by template based deposition and surface reaction method with high microwave absorbance performances. The results depicted the saturation magnetization and coercivity decreased eventually with the increasing content of Cerium. The microwave absorbing properties were studied in the frequency range of 1 to 6000 MHz

and it was observed that on doping of 0.2 the ferrite hollow microspheres exhibit maximum absorption peak, and minimum reflectivity was -18.8 dB near 5500 MHz frequency.

Abbas et al. [38] reported the synthesis of nanorods series and nanoflakes of Co/Ni ferrite spinel by hydrothermal method and using NH_4F as a surfactant. The Maxwell Wagner model explained the increase in dielectric response with increase in nickel content. Besides, the impedance studies showed the activation of various electro-active regions in various frequency ranges. The estimation of the potential functional nanostructures for energy storage was done using their ferroelectric behaviour data and carrying out calculations for energy density. Bhasker et al. [39] monitored the transitions in the magnetic interactions, core shell structure and Hopkinson's peak in chromium substituted nickel cobalt ferrite ($\text{Ni}_{0.75}\text{Co}_{0.25}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$; $x = 0, 0.10, 0.15$) synthesized via auto-combustion route. Powder XRD affirmed the phase purity of the samples and TEM analysis confirmed nanosized particle nature. The magnetic measurements were performed by VSM study and the results showed that all samples have hysteresis and exhibit reduction in the magnetic properties as Cr content was found to increase. The thermomagnetic study displays Hopkinson peak in the magnetization against temperature plot which further implies changes in the Hopkinson peak with increasing Cr content.

The structural and magnetic properties of the nickel doped cobalt ferrite nanoparticles $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.75, 0.9$) ferrites synthesized by chemical co-precipitation method were investigated by Kumar et al. [40]. Electron paramagnetic resonance (EPR) Studies investigated the magnetic properties of the samples at X- band. The resonance EPR peak to peak line width and the resonance field was found to decrease with increasing nickel substitution. The broad signal ascribed to ferromagnetic nature of the nanoparticles as well as the increase in the $\text{Ni}^{2+}\text{--O--Co}^{2+}$ interactions assists resonance value shifts to a comparatively lower field. The blocking temperature was found to increase with Ni^{2+} content which could be attributed to low magnetocrystalline anisotropy of the Ni ions in comparison to the Co ions. The coil method was employed to find out the magnetization values and the results show a linear decrease in M_s , H_c and M_r with increase in Ni content.

Das et al. [41] employed simple hydrothermal method for the synthesis of ($\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$) nanoparticles. From Mössbauer spectroscopy it was seen that the two

sextet patterns are formed at Fe^{3+} tetrahedral and Fe^{3+} octahedral sites which express that the alteration time of magnetization direction is more than 10 ns in the nano ferrites. Besides, a small increase in the quadrupole splitting displays little disorders of lattices while exchange of $\text{Ni}^{2+}/\text{Co}^{2+}$ and Fe^{3+} in tetrahedral and octahedral sites.

1.2.2 Literature review of Ni-Co-Zn ferrites

The $\text{Zn}_{0.35}\text{Ni}_{0.57}\text{Co}_{0.03}\text{Fe}_{2.05}\text{O}_4$ ferrite which was synthesized by the chemical combustion route was studied for its initial permeability [42]. The formation of the single phase cubic spinel structure was confirmed by powder XRD. With increasing sintering temperature, the grain size as well as the average crystallite size increased. The results showed that the real part of the initial permeability increased while the loss factor of the ferrites decreased with increasing sintering temperature. The $\text{Co}_{0.5-x}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 0.25 in steps of 0.05) were synthesized by combustion method [43] using citric acid as fuel by few researchers. They observed that with increase in the nickel concentration, there is an increase in experimental density and a decrease in porosity. The morphological and surface studies were done by them using SEM and the results observed showed well developed spherical grains as the nickel concentration was increased. The EDS analysis for all samples depicted stoichiometric amounts of ions in samples as per the chemical composition. There was a slight variation in initial permeability with an increase in nickel concentration and it nearly remained constant with frequency up to 3 MHz while the dielectric constant and dielectric losses of all samples exhibited low values compared to the conventional ferrites.

The structural and magnetization characterization studies of $\text{Ni}_{0.2}\text{Co}_x\text{Zn}_{0.8-x}\text{Fe}_2\text{O}_4$ synthesized by Mohit et al. [44] by the auto-combustion method were studied for antenna applications. The cubic spinel structure of the ferrite was confirmed by powder XRD analysis. The dielectric constant was found to decrease and temperature coefficient of the resonant frequency was increased and thus relatively permeability increased with an increase in cobalt content. $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ were synthesized by the solid state reaction method and their structural and magnetic properties were found out [45]. The lattice parameter was found to decrease upon the introduction of the cobalt into the Ni-Zn ferrite. The coercivity of the synthesized samples was found to be much more than the bulk sample and it increased with an increase in cobalt content. In contrast, the values of saturation magnetization obtained were less than the bulk ferrites.

One research group [46] synthesized $\text{Zn}_{1-x}\text{Co}_{0.5x}\text{Ni}_{0.5x}\text{Fe}_2\text{O}_4$, by the co-precipitation technique and their powder XRD studies confirmed the formation of the single phase spinel structure and the lattice constant was found to decrease with an increase in nickel and cobalt content. The saturation magnetization increased for the concentration $x=0.60$ and later decreased for $x=0.75$. The dielectric parameters were found to decrease with an increase in the Ni-Co content. The co-precipitation synthesis of $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ was done by Dalal et al. [47] and its studies on the magnetic, Mössbauer spectroscopy, microwave absorption was done. The synthesized nanoparticles were incorporated in the multiwall carbon nanotubes matrix to improve the microwave absorption. The powder XRD studies confirmed their desired phases and cation distributions in A- and B- sites. The HRTEM showed nanoparticles having almost spherical shape with particle size of 2-22 nm. The magnetic and hyperfine behaviour showed high magnetization at room temperature. The AC induction heating studies for Ni-Co-Zn ferrite for hyperthermia applications in the treatment of cancer was done followed by comparative study for $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Co}_{0.2}\text{Cu}_{0.1}\text{Fe}_2\text{O}_4$.

The ferrite phase having the composition $\text{Co}_{0.5-x}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was synthesized by the co-precipitation technique [48]. The powder XRD analysis indicated the formation of single phase ferrite with particle size of up to 12 nm which closely matched the TEM results having particle size 15 nm. The lattice constant of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ obtained was 8.38 Å, however it was found to decrease with the replacement of cobalt by nickel up to $x=0.2$. The lattice constant for $x=0.3$ was increased due to formation of Fe^{+2} in octahedral site. With an increase in nickel concentration, Fe^{+3} migrations from octahedral to tetrahedral site decreased the dielectric constant. Sinfrônio et al. [49] and others did the microwave assisted hydrothermal synthesis of the cobalt and zinc substituted nickel ferrite and their structural and magnetic properties were studied. The crystallinity and single phase partially inverse spinel structure were revealed by powder XRD studies which were confirmed subsequently by IR and Raman technique. The synthesized samples showed spherical morphology and a little agglomeration. The DC magnetic measurements showed magnetically soft behaviour of materials at 300 K.

Gawas et al. [50] performed the precursor combustion synthesis of cobalt-substituted nickel zinc ferrite having the composition $\text{Co}_x\text{Ni}_{0.6-x}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ($x=0.1$ and 0.4) from the hydrazinated mixed metal fumarates. The precursor complexes formed, $\text{Co}_x\text{Ni}_{0.6-x}\text{Zn}_{0.4}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x=0.1$ and 0.4) were subjected to TG–DTG–DTA and patterns of both

the formed precursor complexes revealed multistep decomposition, i.e., dehydrazination followed by oxidative decarboxylation. The IR showed elimination of the organic moieties from decomposed precursors. The AC magnetization studies depicted the presence of single domain and superparamagnetic particles. P. Mathur and others [51] employed Citrate precursor method for the synthesis of $\text{Ni}_{0.49}\text{Zn}_{0.49}\text{Co}_{0.02}\text{Fe}_2\text{O}_4$. The size, structure and morphology of the nanoferrite were confirmed by XRD, TEM and SEM. The material showed almost constant complex permeability and permittivity in 10-200 MHz frequency range. The low loss tangent values were attributed to homogeneity and uniformity at structural level. These properties made the nanoferrites useful for high frequency applications.

Some scientists synthesized hydrazinated nickel cobalt zinc ferrous fumarate precursor and the precursor was decomposed autocatalytically to yield $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ [52]. The formation of $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Zn}_{0.4}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ was confirmed by chemical analysis, IR and mass loss studies. The higher dielectric values at low frequencies were because of the nanosized nature of the ‘as prepared’ ferrites. Also, Curie temperature of the ‘as prepared’ ferrite determined by AC susceptibility measurements was 380 °C.

A few other researchers [53] studied the effect of zinc-substitution on structural and magnetic properties of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ synthesized by citrate based sol-gel method in which with the increase in zinc content, the lattice parameter was increased. The SEM and EDS were utilized to determine the surface morphology and stoichiometric ratios of compositional elements, respectively. Increase in the saturation magnetization was observed with an increase in the Zn concentration up to $x=0.3$ and thereafter it decreased. Kumar et al. [54] studied the enhanced saturation magnetization in Co doped Ni-Zn ferrite nanoparticles synthesized by the sol-gel method. The ferrites synthesized had composition $\text{Ni}_{0.6-x}\text{Zn}_{0.4}\text{Co}_x\text{Fe}_2\text{O}_4$ where ($x=0, 0.03, 0.09, 0.27$). The XRD and FE-SEM examined the influence of cobalt doping on structural properties of Ni-Zn ferrites and the stoichiometry of the synthesized samples were determined by energy dispersive X-ray spectroscopy. The saturation magnetization values initially decreased with Co doping and later increased as obtained from VSM. This effect was explained on the basis of spin canting effect which was due to prominent secondary phase found in the ferrite sample.

Rashad et al. [55] studied the effect of Co^{2+} and Y^{3+} substitution on $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrites synthesized by co-precipitation method. $\text{Ni}_{0.5}\text{Zn}_{0.5x}\text{Co}_x\text{Fe}_{2z}\text{Y}_z\text{O}_4$ powders ($x=0$ –

0.3 and z from 0 to 0.3) were prepared and were characterized by powder XRD, IR, and SEM. VSM measurements studied the magnetization of the samples and it was noted that there was suppression in the grain size upon Y^{3+} substitution while Co^{2+} addition was found to improve the grain growth. The magnetic properties showed an increase in M_s values with increasing Co and Y substitutions. Rani et al. [56] used co-precipitation method for synthesizing $(Zn_xCo_{0.005-x}Ni_{0.005}Fe_2O_4)$, where $x=0, 0.002, 0.004$. Techniques such as powder XRD and SEM determined the respective phase purity and morphology of the samples. The Raman spectra showed all the phonon vibrations T_{2g} (1), T_{2g} (2) and E_g for cubic system. The transition mechanism $^3A_2(^3F) \rightarrow ^1T_2(^1D)$ and $3d^5 \rightarrow 3d^4 4s$ was seen at 493 nm and 521 nm affirmed by the photoluminescence (PL) studies. The incorporation of the cation was studied by virtue of electrochemical behaviour and the specific capacitance was obtained to be 183 F/g for $Zn_{0.002}Co_{0.003}Ni_{0.005}Fe_2O_4$ at a scan rate of 5 mV/s. Huili et al. [57] synthesized $Co_xNi_{0.5-x}Zn_{0.5}Fe_2O_4$ ($x= 0.0, 0.2, 0.4$) nanoparticles by polyol method and later sintered at 700 °C for 4 h. The resistivity studies of the samples were done and the results showed a decrease in resistivity with increasing temperature displaying semiconducting behaviour. Moreover, the DC conductivity followed Arrhenius law having slope at the critical temperature. The dielectric constant and dielectric loss tangent properties with regards to frequency and temperature were determined. They reported that the sintered nanoparticles showed superparamagnetic nature at room temperature magnetic studies. Besides M_s , Curie temperature also was found to increase from $x= 0.0$ to $x= 0.2$ which was ascribed to changes in the superexchange interactions.

Song et al. [58] synthesized $3Ni_{0.2}Ni_{3/2}Co_{1/2}ZnO_4$ hollow multicomponent transition metal oxide nanocomposite having porous nanostructures. These nanocomposites were characterized by powder XRD to find the phase purity, XPS spectroscopy to find out the oxidation states. The thermogravimetric analysis and N_2 adsorption- desorption isotherm were also done. The BET specific surface area was found to be 171.17 m^2/g and 47.6 m^2/g for $3Ni_{0.2}Ni_{3/2}Co_{1/2}ZnO_4$ -HD and $ZnO/ZnCo_2O_4$ -HD, respectively. When these nano-composites were made as anode material for lithium-ion batteries, a specific capacitance of 1337 $mAhg^{-1}$ was observed after 100 cycles. Mallapur et al. [59] investigated the electrical and structural properties of the system $Ni_{0.7-x}Co_xZn_{0.3}Fe_2O_4$ ($x = 0.0-0.7$) prepared by chemical route using sucrose as fuel and PVA as the chelating agent. The two-probe DC resistivity against temperature confirmed the semiconducting

behaviour as with increase in temperature the resistivity was found to decrease. The room temperature dielectric properties were measured in the frequency range of 100 Hz to 1 MHz and the samples showed standard behaviour which was attributed to the Maxwell Wagner type interfacial polarizations. Variation in the AC conductivity as a function of frequency was found to be linear suggestive of conduction as a result of hopping of polarons.

Gawas et al. [60] synthesized $\text{Co}_x\text{Ni}_{0.6-x}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 0.6) by precursor-combustion method. They reported the average crystallite sizes to be in the range of 10-30 nm which was calculated by Scherrer's formula and TEM analysis. The main focus was to study the magnetic properties of the synthesized ferrites and hence they observed a considerable impact of Co addition on the properties like M_s , H_c and M_r well as the Curie temperature (T_c). Due to the higher magnetocrystalline anisotropy of cobalt ions than the nickel ions the coercivity values were found to be more for the higher concentrations of cobalt. The single domain particle nature was observed for the cobalt substituted samples as opposed to the superparamagnetic particles for the non-substituted nickel zinc ferrites.

Atif et al. [61] synthesized cobalt substituted nickel zinc nanoparticles $\text{Ni}_{0.5-x}\text{Co}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.5$) by sol gel method. ^{57}Fe Mössbauer measurements showed that iron is present in Fe^{3+} states that are distributed randomly over the octahedral and the tetrahedral sites. Besides, an improvement in the resistive properties was found with increasing Co^{2+} substitution and the acquired values were approximately 104 times more than the reported for their bulk analogues. They also reported the colossal resistivity and lower tangent loss for the sample $x = 0.2$ thus making the composition eligible for high frequency applications. Kumar et al. [62] synthesized $\text{Ni}_{0.6-x}\text{Zn}_{0.4}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.0165, 0.033, 0.264$ and 0.528) ferrites. The structural and magnetic data correlated with each other with respect to Co^{2+} doping. The samples were found to exhibit moderate saturation magnetization and lower values of coercivity which were ascribed to the use of these materials in magnetic recording devices.

1.2.3 Literature review of Ni-Co-Mg ferrites

Nano crystalline Co-Ni-Mg ferrites of composition $\text{Co}_{0.5}\text{Ni}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ were successfully synthesized by some researchers [63] by the co-precipitation technique. The reported particle sizes of the ferrites were in the range of 32-36 nm and they observed an increase in the lattice constant with an increase in Mg^{+2} content. The maximum

magnetization and coercivity increased with an increase in Mg^{+2} substitutions, thus implying the materials having applications in high frequency devices and core materials wherein low eddy currents are necessary.

Zhao et al. [64] synthesized nanocrystals of $\text{Ni}_{0.2}\text{Mg}_x\text{Co}_{0.8-x}\text{Fe}_2\text{O}_4$ by the co-precipitation method. The characterization methods used were XRD to confirm the formation of single phase spinel and to calculate lattice constant which was found to decrease with an increase in Mg^{+2} content. The TEM showed cubic spherical microcrystals in the samples. The saturation magnetization, coercivity and remanent magnetization were found to decrease as the Mg^{+2} content increased. Because of these significant parameters, studies indicated that the materials have applications in low eddy current loss core materials and high-frequency devices.

Ni-Co doped MgFe_2O_4 nanostructures were fabricated by the micro-emulsion method by some researchers, having the composition $\text{Mg}_{1-x}\text{Ni}_x\text{Co}_y\text{Fe}_{2-y}\text{O}_4$ [65]. They observed that the real and imaginary parts of the dielectric constants and dielectric loss indicate peaking behaviour. Thus, they explained these dielectric properties with the help of Debye-type relaxation phenomenon according to the Koop's phenomenological theory. Ni-Co substitution in MgFe_2O_4 increased saturation magnetization and coercivity.

Patil et al. [66] synthesized $\text{Ni}_{0.5-x}\text{Mg}_{x-0.01}\text{Zn}_{0.5-y}\text{Co}_{y+0.01}\text{Fe}_2\text{O}_4$ ($x = 0.1, 0.2, 0.3, 0.4$ and $y = 0.1, 0.2, 0.3, 0.4$) by using ceramic method and their temperature and frequency dependent dielectric properties were studied. The powder XRD revealed the formation of single phase cubic spinel structure. The decrease in resistivity up to composition $x = 0.3$ was attributed to formation of excess Fe^{+2} ions. The decrease in dielectric constant was due to low concentration of Fe^{+2} ions, high porosity and low density. The AC resistivity variation with frequency for all samples showed a decreasing trend with an increase in frequency, which is a normal behaviour of ferrites.

The ceramic method synthesis of cobalt substituted Ni-Zn-Mg ferrite of composition $\text{Ni}_{0.57-y}\text{Co}_y\text{Zn}_{0.35}\text{Mg}_{0.08}\text{Fe}_2\text{O}_4$ ($y = 0.00-0.20$ in the step of 0.04) was done by some researchers [67]. An unusual increase in the magnetic permeability with increasing Co-concentration was observed. Also a simultaneous fall in the saturation magnetization and Curie temperature was reported as coercivity increased. The observed increase in initial permeability in Ni-Zn-Mg ferrite with Co content, was inferred from lower magnetic anisotropy, decrease in exchange interactions and an increase in grain size.

Some researchers [68] had investigated $\text{NiMg}_{0.1}\text{M}_x\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Mn}, \text{Co}$) by using the citrate precursor method with calcining temperature of 1100 °C. The powder XRD studies with Rietveld refinement indicated the crystallite sizes between 0.576 and 0.626 μm . The presence of clustered particles smaller than 1 μm was depicted by SEM analysis. The composition having Mn, has lower magnetization value, that doesn't generate high microwave absorption, however 0.1 cobalt additions has high coercivity which optimizes the reflectivity results. Also, the magnetocrystalline anisotropy of the Co material was higher.

Jangam et al. [69] synthesized magnetically separable $\text{Zn}_{1-x}\text{Co}_{0.5x}\text{Mg}_{0.5x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.25, 0.50, 0.75, 1.0$) nanoferrites by sol gel auto-combustion method. The monophasic nature of the ferrites samples was determined by the Rietveld refinement and IR studies and the average crystallite size was found to be in the range of 34-57 nm. The magnetic investigations were performed on VSM at room temperature. It was understood that incorporation of Mg^{2+} and Co^{2+} ions in the Zn ferrites showed a transition from superparamagnetic to hard ferromagnetic behaviour. The photocatalytic activity of the ferrite sample was reported and it was observed that methylene blue dye was degraded under sunlight showed efficiency of 99.23 % degradation having a prompt 40 minutes irradiation period with greater reusability of up to four cycles.

1.2.4 Ferrites showing gas sensing properties

Synthesis of the $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 0.5$) thin films deposited on the quartz substrate was done by spray pyrolysis technique by Bagade et al. [70]. The various gases used were SO_2 , LPG, NH_3 , H_2S and NO_2 . The synthesized samples showed highest response towards NO_2 gas at moderately lower operating temperature of 150 °C for 100 ppm concentration of gas.

Kumar et al. [71] studied the gas sensing properties of $\text{Ni}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ prepared by employing the simple evaporation method using egg white as bio-template. The sample was annealed at three different temperatures 600 °C, 750 °C and 900 °C. The sample with the lowest crystallite size was found to exhibit the best gas sensing performance as a ferrite sensor for detection of LPG, H_2 , NH_3 and CO at an operating temperature of 250 °C. Gawas et al. [72] investigated the gas sensing response of Co-Ni-Zn ferrite thick film for oxidizing and reducing gases. They reported the synthesis of $\text{Co}_{0.3}\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ferrite by precursor-combustion method and later characterized for its phase purity by

powder XRD and Raman spectroscopy. The ferrite sample was fabricated to a thick film by screen printing and the gas sensing response of film towards oxidizing and reducing gases were examined. The ferrite thick film showed high activity towards oxidizing gases at 200 °C while negligible response was reported for the reducing gases at all temperatures.

Tudorache et al. [73] investigated the effect of Co^{2+} ion concentration on the gas sensing properties of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.25, 0.5, 0.75$) thin films deposited on glass substrates by spin coating method. They reported the sensitivity to some of the reducing gases like LPG, acetone, methanol and ethanol. It was seen that the film $x= 0.75$ showed greater sensitivity to ethanol and the film $x= 0.25$ showed sensitivity towards acetone. Dessai et al. [74] investigated the gas sensing properties of $\text{Ni}_{0.7-x}\text{Mn}_x\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ($x= 0.1-0.4$) ferrites which were synthesized by precursor-combustion method. The fabrication of the thick films was done on to a glass substrate for Cl_2 to be used as the test gas. Four different gases were tested for the response and it was seen that Cl_2 showed high gas sensing response towards $x= 0.3$ thick film of ferrite at operating temperature of 100 °C. The sensing response was found to vary from 115 to 212 % for gas concentration of 20-300 ppm of the Cl_2 gas. The response and recovery time was reported to be 10 seconds and 15 seconds respectively hence making the material a good gas sensor for Cl_2 gas.

Kamble et al. [75] synthesized NiFe_2O_4 by chemical co-precipitation method and tested this sample for its gas sensing properties. The resistance measurements were performed by exposing the sensor material to gases like O_2 , LPG, NH_3 and Cl_2 at room temperature in a closed chamber. The order of gas sensing response was $\text{Cl}_2 > \text{ammonia} > \text{LPG} > \text{O}_2$. The thick film showed the highest response towards Cl_2 and NH_3 which was 96 % and 68 %, respectively. Li et al. [76] reported the synthesis of ZnFe_2O_4 nanoparticles by hydrothermal synthesis method and investigated its gas sensing properties for NO_2 gas. The sensor was found to exhibit very high response ($R_{\text{gas}}/R_{\text{air}} = 247.7$), fast response time (6.5 s) and recovery time (11 s) towards 10 ppm of NO_2 gas at lower operating temperature of 125 °C. Dua et al. [77] deposited ultrathin tin oxide on flat hotplate using atomic layer deposition (ALD) method. The gas sensing response was then measured for this SnO -ALD at 300 °C for CO gas. The sensing response was found to increase between 15.9 Å and 26.2 Å thicknesses and was found to decrease with increasing thickness in between 26.2 Å and 58.7 Å.

Another research group synthesized $\text{NiFe}_2\text{O}_4 + 1 \text{ wt. \% CaO}$, $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_{0.01}\text{Fe}_{1.99}\text{O}_{4-\delta}$ and $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_{0.02}\text{Fe}_{1.98}\text{O}_{4-\delta}$ by sol gel auto-combustion method and the ferrite nanoparticles were tried for the gas sensing properties towards reducing gases like acetone, ethanol, methanol and LPG. It was seen that the sample $\text{Ni}_{0.99}\text{Co}_{0.01}\text{Mn}_{0.02}\text{Fe}_{1.98}\text{O}_{4-\delta}$ showed higher values of sensitivity towards acetone gas at 488 K showing a response time of 3 minutes [78].

Ma et al. [79] synthesized NiFe_2O_4 using the hydrothermal approach and was characterized using various techniques such as powder XRD, FESEM, TEM, EDAX. The gas sensing properties of the sample was determined for acetone gas. It was observed that the sensor shows a high gas sensing properties to 100 ppm acetone at low working temperature of 120 °C. Chu et al. [80] also synthesized ZnFe_2O_4 using hydrothermal synthesis method and tried for their gas sensing properties towards gases like CH_4 , CO, CH_3COCH_3 and $\text{C}_2\text{H}_5\text{OH}$. It was reported that the ferrite sample showed highest sensitivity and shorter response for $\text{C}_2\text{H}_5\text{OH}$ at a concentration of 100 ppm and it showed sensitivity as greater as 76. Kadu et al. [81] prepared $\text{Zn}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2$ and 0.4) by sol gel citrate method and studied the gas sensing properties. The samples were tested for their sensing properties towards reducing gases such as LPG, CH_4 , CO and ethanol and it was seen that Mn-Zn ferrite nanoparticles exhibited high response to ethanol at lower working temperature. The $\text{Zn}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ showed better ethanol sensitivity towards ethanol gas at 300 °C. Furthermore they also reported an enhanced sensitivity, selectivity and response time with insertion of 1.5 wt.% Pd as the temperature was reduced from 300 °C to 230 °C.

Madake et al. [82] deposited Cu-Ni-Zn ferrite thin films using the cost-efficient spray pyrolysis method and characterized the sample by structural, morphological properties. They also investigated their gas sensing properties and the deposited ferrite material was found to show good response for SO_2 gas at an operating temperature of 120 °C which was found to be lower than the earlier reports for SO_2 gas sensors. At an optimum temperature the ferrite deposit showed a linear response up to a concentration of 50 ppm of the gas exposure.

Mukherjee et al. [83] synthesized $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ using wet chemical synthesis and citrate-based Pechini process. The comparison in the gas sensing properties in both the samples implied that they got a good response for sample synthesized by Pechini process

as compared to that of the other method. They also stated that they could detect as low as 50 ppm concentration of H_2 gas with 44 % response. Raut et al. [84] synthesized $CoFe_2O_4$ nanoparticles using sol gel auto-combustion method and later irradiated with 2 and 5 kGy γ -doses. Gases such as methanol, ammonia, acetone, ethanol and toluene were studied to see their selectivity and sensitivity with pure and γ - irradiated $CoFe_2O_4$. 70 % gas response was observed for 5 kGy irradiated $CoFe_2O_4$ for ammonia at 100 ppm gas concentration having high selectivity.

Vignesh et al. [85] illustrated the synthesis of $MnFe_2O_4$ using combustion method. The ferromagnetic nature of the samples was determined by room temperature VSM analysis and BET surface area was found to be $33\text{ m}^2/\text{g}$ obtained from the N_2 -adsorption desorption isotherm. The sturdy ferrite sample showed 100 % sensitivity towards NH_3 gas. It showed 83.5 % selectivity for 10 ppm concentration for NH_3 over other gases such as $CHCl_3$.

Deepty et al. [86] prepared $Mn_xZn_{1-x}Fe_2O_4$ ($x = 0.5, 0.6, 0.7$) using co-precipitation and sol-gel auto-combustion method. Different gases were tested such as NH_3 , H_2 , LPG and CO and it was observed that the ferrite samples synthesized by sol gel method has operating temperature of 300 °C and 250 °C for co-precipitation technique. The ferrite sample $Mn_{0.7}Zn_{0.3}Fe_2O_4$ showed exceedingly high gas sensor response. It was concluded that the $Mn_{0.7}Zn_{0.3}Fe_2O_4$ sample synthesized by co-precipitation method was appropriate for the fabrication of gas sensors. Cao et al. [87] synthesized spinel ferrites MFe_2O_4 ($M = Fe, Co, Ni, Mg, Cd$ and Zn) using solid state chemical reactions in mild conditions and investigated the gas sensing properties. It was observed that all the ‘as prepared’ ferrite sensors showed high responses, swift response-recovery time and lower operating temperatures, selectivity and long-duration stability towards ethanol and methanol. In between all the ferrites $ZnFe_2O_4$ showed the best response of 37.3 for 100 ppm concentration of methanol at 260 °C and 29.1 for 100 ppm concentration of ethanol at 300 °C. Besides, the response-recovery time did not exceed 5 seconds and 26 seconds, respectively.

Zhou et al. [88] prepared $Zn_xFe_{3-x}O_4$ ($x = 0-0.6$) by facile solvothermal route and tested their gas sensing properties towards acetone gas. It was seen that the sensors exhibit highly sensitive dependence with Zn/Fe ratio variations. $Zn_{0.4}Fe_{2.6}O_4$ sample displayed the highest response (157) towards 100 ppm concentration of acetone and good selectivity

in comparison with the other ferrites. The ferrite sensors also show a clear signal for tracing acetone level in the breadth of a diabetic patient. Powar et al. [89] investigated the gas sensing properties of the Zn-substituted cobalt ferrite thick films along with their structural, morphological and electrical properties. Different gases like H₂, H₂S, CO₂, Cl₂, NH₃ and C₂H₅OH were tested on the ferrite thick film. It was reported that Zn_{0.25}Co_{0.75}Fe₂O₄ sensor had the highest room temperature resistance. Consequently, this ferrite achieved the highest gas sensing response and good selectivity to 100 ppm concentration of ethanol at 30 °C with outstanding long-duration stability.

Yin et al. [90] designed a facile strategy to controllably synthesize 2D single crystalline ZnCo₂O₄ nanosheet arrays on surface of the Ni foam. The sample exhibited surface area 94.1 m²/g with pore size distribution of 8 nm. Besides, methanol, ethanol formaldehyde and ammonia were also used as test gases. The sample also behaves as a gas sensor demonstrating brilliant sensitivity and selectivity towards methanol gas. Rao et al. [91] deposited nanocrystalline (Co, Cu, Ni, Zn) ferrite thin films on Si (100) and Al₂O₃ substrate using spray pyrolysis method. Various structural properties of the ferrites were examined using powder XRD, SEM and double beam UV-Vis spectrophotometer recorded the optical transmittance and reflectance measurements. The gas sensing properties towards LPG displayed that NiFe₂O₄ thin films are sensitive at high temperature while ZnFe₂O₄ films are sensitive at lower temperatures.

Sutka et al. [92] have synthesized Ni_{0.3}Zn_{0.7}Fe_{2+z}O₄ (z = 0 and 0.1) ferrites by sol gel auto-combustion method and have performed the gas sensing studies of the samples. They reported the gas sensing response towards 500 ppm concentration of acetone gas at working temperature of 200-323 °C. Higher response was reported for Fe-excess Ni-Zn ferrite at all the working temperature which was ascribed to the presence of Fe²⁺ in the non stoichiometric ferrites. Xiangfeng et al. [93] reported the gas sensing properties of CdSnO₃ thick film towards Cl₂ gas. The sample was synthesized by using co-precipitation method and characterized by powder XRD and morphology was revealed using SEM. The effect of the calcining temperature on the sensing properties, working temperature and sensitivity were examined. The research findings demonstrated that CdSnO₃ sample synthesized at 900 °C displayed high sensitivity to dilute Cl₂ at working temperature of 250 °C.

Patil et al. [94] prepared CuO modified ZnO thick films by screen printing technique. Pure white ZnO powder was found to be insensitive to chlorine gas. The modified thick film sensor was found to be sensitive to 300 ppm concentration of Cl₂ gas at room temperature. They reported the impact of operating temperature, calcination temperature, gas concentration and the amount of CuO in ZnO for the gas sensing response. The gas response, selectivity and recovery time of sensor were reported and it was found that the sensors had the prompt response of around 18 seconds and quick recovery of around 50 seconds. Patil et al. [95] reported the synthesis of MgFe₂O₄ by combustion synthesis method using glycine as fuel and examined their gas sensing properties using gases like LPG, acetone, ethanol and ammonia. The highest response of 71 % was observed for the concentration of 2000 ppm of LPG at 698 K.

Gadkari et al. [96] synthesized Mg_{1-x}Cd_xFe₂O₄ (x= 0, 0.2, 0.4, 0.6, 0.8 and 1) by oxalate co-precipitation method. The samples were characterized using powder XRD, SEM and IR. They reported a decrease in the gas sensing response with Cd²⁺ concentration for Chlorine, LPG while an increase in the response for ethanol. The response for Sm³⁺ added Mg-Cd ferrites was found to be higher than for Mg-Cd ferrites. The shorter response-recovery time was observed for Sm³⁺ added Cd ferrite sensor as compared to the other sensor. Yadav et al. [97] prepared lanthanum ferrite using citrate-nitrate auto-combustion route and investigated its gas sensing property for LPG. Various volume % of LPG concentration like 0.1, 0.2, 0.3, 0.4 and 0.5 were tried for the gas sensing response. The highest response of 394 was seen at 0.5 vol% LPG. Besides this, the response and the recovery times were 50-100 seconds and 350-400 seconds, respectively.

Chakraborty et al. [98] prepare bismuth ferrite by employing sol gel method and demonstrated a good CO sensing capacity. Bismuth ferrite was tested as a gas sensor towards CO gas in 5 ppm–30 ppm concentration range at temperatures between 270 °C to 450 °C. The gas sensors were found to show quick response and recovery time of 25 seconds and 13 seconds, respectively, for 30 ppm concentration of CO. Additionally, the sensors are highly reproducible, selective and were found to be stable for 150 days as required for application.

1.2.5 Electrochemical properties of Ferrites

Sen et al. [99] prepared NiFe₂O₄ conducting nanocomposites using sol gel method and investigated their electrochemical properties in order to find out whether the electrodes

are suitable for supercapacitors. Cyclic voltammetry (CV) was used at different scan rates from 2-20 mV/s and galvanostatic charge-discharge (GCD) measurements were carried out at current densities from 0.5 to 10 mA/cm². The highest value of specific capacitance of 251 F/g was seen for the nanocomposite. Nikam et al. [100] examined and compared the effect of substrate temperatures on pulsed layer deposited (PLD) CoFe₂O₄ thin films for their supercapacitive applications. The investigations implied enhanced electrochemical performances at room temperature as compared to the films deposited at 450 °C. The electrodes deposited at room temperature and at 450 °C demonstrated the specific capacitance values of 777.4 and 258.5 F/g, respectively at current densities of 0.5 mA/cm². Besides the film deposited at room temperature exhibit very good power density of 3277 W kg⁻¹ and energy density of 17 W hKg⁻¹.

Dang et al. [101] obtained the porous rod-like NiCo₂O₄ using water-glycol mixed solvothermal method. The high specific capacitance values of 417.1 Cg⁻¹ at 1 A g⁻¹ was reported for the 'as prepared' sample with 73.4 % retention range from 1 to 10 g⁻¹ and brilliant cyclic stability with 130 % of the initial capacitance after 10000 cycles. Ismail et al. [102] reported preparation of manganese zinc ferrite nano-needles by co-precipitation method and studied their electrochemical properties. They observed the specific capacitance of 783 F/g and the ferrite showed good columbic efficiency and better long term stability. The asymmetric fabricated supercapacitor based on these nanao-needles/ activated carbon gave 15.8 Wh kg⁻¹ energy density at a power density of 899.7 W kg⁻¹. Kharat et al. [103] synthesized Ni_{0.5}Zn_{0.5}Fe₂O₄ and tried them to be used in supercapacitors. Cyclic voltammetry investigations showed reversible and steady redox behaviour which was affirmed by the well-developed CV curve. The charge-discharge plateaus with stability showed that the nanoparticles were suitable for high rate applications. The Nyquist plot obtained focussed on the kinetics of charge transfer and the capacitive behaviour. All these findings pointed towards the use of these ferrite nanoparticles to be used in supercapacitors.

Malima et al. [104] synthesized Ni_{1-x}Co_xFe₂O₄ (0 ≤ x ≤ 1) solid solutions using the benign solventless synthesis route. The samples were then examined for their electrochemical performance towards energy storage and energy generation. Ni_{0.4}Co_{0.6}Fe₂O₄ showed the best supercapacitor performance which showed the specific capacitance of 237 F/g, energy density of 10.3 W hkg⁻¹ and higher power density peak value of 4208 W kg⁻¹. It was observed that 100 % of the charge storage capacity was conserved after 4000 cycles

with 97 % coulombic efficiency. The results implied to the ferrite solid solutions could be used as electrode material for supercapacitor and water splitting applications. Elkholy et al. [105] reported synthesis of $\text{MnCoFe}_2\text{O}_4$ by coprecipitation technique and it was found to exhibit the specific capacitance of 675 F/g at scan rate of 1 mV/s. The energy density and power density were found as 18.85 Whkg^{-1} and 337.50 W kg^{-1} , respectively, at current density of 1.5 Ag^{-1} . The GCD measurements and the electrochemical impedance spectroscopy (EIS) investigated the cyclic stability of the sample. They reported a 7.14 % decrease in the performance after 1000 GCD cycles which indicated brilliant long term stability.

Xiong et al. [106] developed and fabricated a ternary electrode which comprised of cobalt ferrite/graphene/polyaniline. The electrochemical measurements indicated that the specific capacitance values were found to be 113.3 F/g at a scan rate of 1 mV/s of current density 0.1 A/g. The specific capacitance of 767.7 F/g was observed for three-electrode system but for two-electrode system it showed C_{sp} value of 716.4 F/g and 392.3 F/g at the scan rate of 1 mV/s and current density of 0.1 A/g. Wang et al. [107] investigated the electrochemical properties of the MnFe_2O_4 colloidal nanocrystals in various aqueous electrolytic solutions. The techniques such as CV, GCD and EIS studies were performed. It was observed that when 2 M KOH, NaOH, LiOH and Na_2SO_4 were used as the electrolytic solutions, the working electrode showed the C_{sp} of 97.1, 93.9, 74.2 and 47.4 F/g, respectively at a current density of 0.1 A/g. Besides, when the KOH electrolyte concentration was increased from 0.5 to 6 M, the C_{sp} also increased from 56.9 to 152.5 F/g, respectively. They reported the best cycling stability for 6 M KOH electrolyte.

Liu et al. [108] prepared the NiFe_2O_4 ferrite using hydrothermal synthesis method to be made as an anode in lithium-ion battery. They investigated the effect of hydrogenation on the electrochemical properties of this ferrite sample. The octahedral morphology of the ferrite was reported to be distorted because of the hydrogenation and it resulted in the oxygen vacancies and formation of the metallic nickel. This was found to improve the electrochemical properties that showed 60 % retention of the capacity at the 50th cycle and also 3 times higher capacity was observed at current density of 1 A/g.

Zhang et al. [109] prepared three samples of copper-doped zinc ferrites having 0.5, 1 and 2 mmol of CuCl_2 using hydrothermal method. They investigated the gas sensing properties for gases like $\text{C}_2\text{H}_5\text{OH}$, H_2 , CH_4 , $\text{C}_2\text{H}_6\text{CO}$, HCHO and H_2S . The samples were

found to show highest response for H₂S gas with good selectivity and a better good reproducibility for 5 ppm of H₂S gas at room temperature. Kennaz et al. [110] synthesized cobalt ferrite using hydrothermal method and coprecipitation method using various precursors such as nitrates, chlorides and acetates at different concentrations and different conditions. The specific surface area of the sample was found to be around 34 m²g⁻¹. The three-electrode electrochemical performance with a 6 M KOH electrolyte gave the specific capacitance of 429 F/g at 0.5 A/g with a very good capacitance retention of 98.8 % after 6000 cycles at 10 A/g synthesized at 200 °C for 18 h. Mitchell et al. [111] synthesized the monodispersed iron oxide nanocrystals. These nanocrystals were characterized and subjected to electrochemical studies to determine their supercapacitive behaviour using cyclic voltammetry, galvanostatic charge discharge studies. The CV was performed in 3 M electrolytic solution and the specific capacitance of 185 F/g was observed at current of 1 mA with brilliant cyclic stability. They claimed that this could be proven as the method for synthesis of the nanostructured iron oxide for applications in the next generation energy storage.

1.3 Identified research gaps

❑ **Limited research of tartaric acid as a fuel in $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x= 0.0-1.0$) synthesis.**

Though the literature for synthesis of nickel substituted cobalt ferrites through various synthesis methods is substantial, use of DL-Tartaric acid as a fuel in the combustion synthesis is relatively unexplored. DL-Tartaric acid significantly influence the morphology, crystallite size, and surface properties of the resulting ferrite material. The lack of comprehensive studies in the areas like their applications presents an opportunity to evaluate how this alternative fuel can optimize or enhance functional characteristics, particularly for applications in sensors or energy storage devices.

❑ **Novel fuel-based synthesis of $\text{Ni}_x\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x= 0.0-0.5$) with no prior research studies.**

The second ferrite series under investigation, $\text{Ni}_x\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x= 0.0-0.5$) ferrites, has been synthesized using a novel, laboratory-prepared fuel viz. L-Tartaric acid dihydrazide, which has not been reported as a fuel in any previous studies. Since this novel fuel is introduced for the first time, there is no available literature that examines its effect on the synthesis and functional properties of this ferrite series. This represents a significant research gap, particularly in understanding how such a fuel can influence the performance of these ferrites in practical applications.

❑ **Underexplored synthesis and properties of $\text{Ni}_x\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x= 0.0-0.5$) using precursor combustion method.**

The third series, $\text{Ni}_x\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x= 0.0-0.5$) ferrites, has been synthesized using the precursor combustion method, which is known for producing nanostructured materials with better surface area and enhanced properties. Although this synthesis method has been used for numerous ferrites the correlation between synthesis conditions and the resulting structural, morphological, and electrochemical characteristics remains inadequately studied. A deeper understanding of how zinc substitution and combustion parameters affect the performance of these ferrites is necessary.

❑ Scarcity of studies on gas sensing and supercapacitive properties across all three ferrite series.

Regardless of promising characteristics of spinel ferrites for multifunctional applications, very limited research has been conducted on the gas sensing and supercapacitive properties of all three series. As per the literature, most existing studies highlight mainly on structural, magnetic, or catalytic aspects, with minimal attention given to their potential use in gas sensors or electrochemical energy storage. Considering the growing importance of materials that offer multifaceted nature, this lack of information limits both the scientific understanding and practical application of these ferrite systems.

❑ Complete absence of research on supercapacitive behaviour of $\text{Ni}_x\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites

A critical research gap exists for the $\text{Ni}_x\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites series, which, according to a thorough review of available literature, has not been explored at all for supercapacitor applications. The incorporation of Mg^{2+} ions, known for altering the electronic structure and conductivity of ferrites, could potentially enhance their charge storage capacity. However, in the absence of any prior studies, the supercapacitive potential of this material remains unknown. Investigating this unexplored system could lead to the discovery of a new class of efficient and low-cost electrode materials for energy storage devices.

1.4 Aims and objectives

❑ To identify the significance and multifaceted applications of ferrites

- Acknowledge the extensive interest in ferrites over recent decades due to their diverse properties and wide-scope uses in everyday life and industries.
- Review and investigate numerous literature sources which explain the magnetic, electrical, catalytic, supercapacitor and gas sensing properties of ferrites, highlighting the research gaps and areas requiring further research.

❑ To synthesize three different series of ferrite nanoparticles for exploring their exceptional properties

- Select three ferrite series for synthesis: pure Ni-Co ferrites, Ni-Co ferrites with zinc (Zn) substitution, and Ni-Co ferrites with magnesium (Mg) substitution.
- Examine how substituting Zn^{2+} and Mg^{2+} ions into the Ni-Co ferrite lattice affects the structural, magnetic, electrical, and sensing properties of the synthesized nanostructured ferrite material.
- Use precise chemical formulas and compositions, specifically:
- $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 1.0) for pure Ni-Co ferrites,
- $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 0.5) for zinc-substituted ferrites
- $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 0.5) for magnesium-substituted ferrites.

❑ Employing advanced synthesis procedures using novel and lesser investigated fuels to achieve controlled particle formation

- Use the combustion method with DL-Tartaric acid as a relatively less-explored fuel for synthesizing pure Ni-Co ferrites, aiming to investigate its efficacy and influence on the final properties of ferrites.
- Employ the precursor-combustion synthesis method to prepare zinc-substituted ferrites by developing mixed metal fumarato-hydrazinate precursors, facilitating autocatalytic decomposition for formation of uniform nanoparticle.
- Synthesize magnesium-substituted ferrites through a combustion-triggered route using laboratory-synthesize L-Tartaric acid dihydrazide as a novel fuel, characterizing the fuel before use to understand its role in the synthesis.

- Ensure all ferrite samples undergo sintering at 1000 °C for 10 h to achieve optimal crystallinity and phase formation.
- ❑ **Perform extensive and multi-technique characterization of the synthesized ferrites**
- Investigate thermal stability and decomposition behaviour through thermogravimetric-differential thermal analysis (TG-DTA) for the precursors for precursor-combustion method and the melt for combustion method.
 - Determine crystallographic structure, phase purity, and crystallite size via powder X-ray diffraction (XRD).
 - Assess elemental composition and concentration using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and microwave plasma-atomic emission spectroscopy (MP-AES).
 - Analyse vibrational modes and molecular bonding with infrared (IR) and Raman spectroscopy.
 - Examine surface chemical states and elemental composition through X-ray photoelectron spectroscopy (XPS).
 - Measure specific surface area by Brunauer–Emmett–Teller (BET) method and analyze surface acidity/basicity by NH₃ and CO₂ temperature-programmed desorption (TPD) study.
 - Study morphology, particle size, and microstructure with high-resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy combined with energy dispersive X-ray analysis (SEM-EDAX).
 - Measure magnetic properties such as saturation magnetization and coercivity at room temperature (300 K) and low temperature (60 K) using vibrating sample magnetometry (VSM).
 - Perform zero field cooled (ZFC) and field cooled (FC) magnetization studies under different magnetic fields to understand magnetic behaviour and phase transitions.
- ❑ **Correlate particle size and morphology with improved material applications**
- Scrutinize the impact of crystallite size and shape of nanoparticle on the surface area and surface-to-volume ratio.

- Relate enhanced surface area and reduced particle size to improved gas sensing performance and supercapacitor capabilities.
- Emphasize on the significance of controlling particle size for maximizing application performances.

❑ **Investigate electrochemical properties for energy storage applications**

- Evaluate the suitability of synthesized ferrite nanoparticles as electrode materials for supercapacitors and rechargeable batteries.
- Using cyclic voltammetry (CV) to analyse charge storage behaviour and electrochemical reversibility.
- Apply galvanostatic charge-discharge (GCD) techniques to evaluate charge/discharge efficiency and capacity retention.
- Employ electrochemical impedance spectroscopy (EIS) to investigate resistance and ion transport mechanisms in electrodes fabricated on nickel foam substrates.
- Address serious environmental and energy challenges by developing ferrite-based materials for clean, efficient energy storage solutions.

❑ **Contribute to environmental protection efforts by designing, fabricating, and evaluating ferrite-based gas sensors capable of detecting harmful atmospheric pollutants**

- Prepare thick films of pure and zinc-substituted Ni-Co ferrite nanoparticles by employing the screen printing technique, ensuring uniform and stable sensor films.
- Test ferrite sensor response, sensitivity, and selectivity toward toxic and hazardous gases such as chlorine (Cl₂), nitrogen dioxide (NO₂), liquefied petroleum gas (LPG), and ammonia (NH₃).
- Study gas sensing performance at varying operating temperatures (30 °C to 150 °C) and gas concentrations to determine optimal sensing conditions.

This thesis is organized into six chapters.

Chapter 1

This chapter includes the introduction of the ferrite samples, their brief history, and literature review of the ferrites along with their applications as gas sensors and supercapacitors. Chapter ends with aims and objectives of the current research work.

Chapter 2

This chapter briefly describes the methods of preparations of ferrites, various characterization techniques which were used for characterization of the precursors, ‘as prepared’ and ‘sintered’ ferrites and the instruments used for carrying out applications.

Chapter 3

This chapter describes the detailed characterization of ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites with their solid-state properties. The ‘as prepared’ samples were tested for applications such as gas sensing and supercapacitors.

Chapter 4

This chapter describes the detailed characterization ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites with their solid-state properties. The ‘as prepared’ samples were tested for applications such as supercapacitors.

Chapter 5

This chapter deals with characterization of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors along with ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites with their solid-state properties. The ‘as prepared’ samples were tested for supercapacitor applications.

Chapter 6

This chapter deals with summary and conclusions.

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Chapter 2

*Experimental procedures and
characterization techniques*

2.1 Introduction

Chapter 2 outlines the synthesis methods employed for synthesizing the ferrite samples and the characterization techniques utilized in order to characterize the synthesized ferrites. The technological significance of the spinel ferrite materials due to their extraordinary properties have made them feasible to be used in potential applications such as environmental monitoring, catalysis, high frequency devices, in smart materials and so on. These astounding applications of the ferrites motivated many materials chemistry researchers to devise several methods of synthesis. Significant modifications in the structural and the magnetic properties are performed in the nanomaterials by appropriately tuning the elemental compositions and improvising their routes of preparation [1-6]. All the synthesis methods are extensively categorized into two approaches; viz. bottom-up approach wherein there is a gathering of ions in chemical formation to obtain nanoparticles and the top-down method in which large particles are ground into smaller ones (breaking down and building up processes) [7].

In the present study, we have scrutinized three ferrites series viz. $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$), $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) and $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$). $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite series has been synthesized using precursor-combustion method by adding a non-magnetic constituent (zinc) in $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Fe}_2\text{O}_4$. While $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) has been synthesized by combustion method using a relatively unexplored fuel i.e. DL-tartaric acid. A novel $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) series has been synthesized by the combustion technique by employing the novel L-tartaric acid dihydrazide as a fuel which was synthesized in the laboratory and later characterized. In this case we examined the impact of adding a magnetically dilute constituent i.e. magnesium to $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite. The elaborated synthesis procedures for both the synthesis methods have been discussed in the succeeding sections. We preferred the precursor-combustion technique since it produces smaller, uniform particles with higher surface area, which is crucial for gas sensing and supercapacitive properties. However, the solid state reaction synthesis method gives larger and less active particles with lower surface area which limits the performances in these applications.

Characterizations of the synthesized ferrite compounds were later done by various techniques and the exact methods of characterization along with the software used for interpretation have been discussed in this chapter.

2.2 Optimization of $Ni_xCo_{1-x}Fe_2O_4$ ($x= 0.0-1.0$) ferrite series

2.2.1. Optimization of the synthesis method

The major purpose of optimization is to find out the sufficient heat required for the reaction and to control the exothermic nature of the reaction. To fix the amount of heat required for the combustion reaction, the fuel: metal nitrate ratio has to be fixed. Optimization also helps in getting the final monophasic ferrite compound by preventing its decomposition and agglomeration due to excessive heat.

$Ni_xCo_{1-x}Fe_2O_4$ ($x= 0.0-1.0$) ferrite series was prepared using combustion method employing DL-Tartaric acid as a fuel. The stoichiometric ratios of $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (all AR grades) were used as oxidizers and DL-Tartaric acid (fuel) as a reducer. Five fuel deficient ratios viz. 1:0.25, 1:0.375, 1:0.5, 1:0.625 and 1:0.75 and five fuel excess ratios: 1:0.875, 1:1, 1.125, 1:1.25 and 1:1.375 were examined for optimization. The optimization was done of the middle composition viz. $Ni_{0.5}Co_{0.5}Fe_2O_4$ as a representative sample. The metal nitrates were initially weighed in fixed stoichiometric amounts, mixed and thereafter heated on a hotplate to obtain a molten melt. To this melt, finely ground fuel (varying amounts) was added individually to various fuel ratios which was subsequently heated with continuous stirring on a hot plate until it triggers the reaction by igniting, undergoes combustion forming fine powdered nanosized ferrites nanoparticles. All the ratios were calcined at 500 °C for 5 h and later ground for 2 h. Various studies of different optimization ratios have been done such as the powder XRD, VSM, AC susceptibility, IR in order to find out the monophasic nature of the ferrites and the ratio to be used for further synthesis of the main series.

2.2.2. Synthesizing the main series of $Ni_xCo_{1-x}Fe_2O_4$ ($x= 0.0-1.0$) ferrites

From the optimization studies, it was concluded that the fuel ratio 1:0.75 has the lowest crystallite size and highest lattice parameter confirmed by powder XRD. Further this ratio also shows the single domain particle nature (A.C. susceptibility), hence it was chosen for synthesizing the main series. The detailed description for optimization has been discussed in section 3.2 of chapter 3.

Initially, the stoichiometric amounts of metal nitrates (for respective compositions) were taken into a clean and dry beaker and heated on a hot plate to obtain a melt. This melt was then cooled to room temperature and later fuel (DL-Tartaric acid) was added to it with

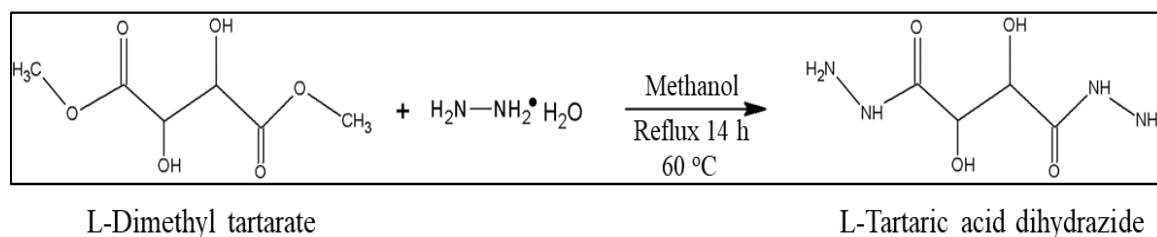
constant stirring for homogenizing the mixture and heated on a hotplate. Initially this mixture forms thick slurry and later combusted to form the ferrite powder. During the redox reaction, the mixture released a huge amount of nitrate gases to form the ferrite. The ferrite powder was then crushed using motor pestle, ground for around half an hour for homogenizing and then kept in furnace at 500 °C for calcination for 5 h and later ground for 2 h. This is called as the ‘as prepared’ ferrites. Calcination is done in order to eliminate any carbonaceous impurities or the unburnt fuel present in the sample. The ‘as prepared’ ferrites were then pelletized by using a hydraulic press and applying pressure of 5 tons for 5 minutes. These pellets were then pre-sintered at 800 °C for 5 h and later crushed for 2 h and again pellets were made and the ferrite samples were then sintered at 1000 °C for 10 h.

2.3 Optimization of $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x= 0.0-0.5$) ferrite series

2.3.1. Synthesis and characterization of L-tartaric acid dihydrazide (L-TADH)

Hydrazine based fuels such as mainly carbohydrazides like malonic dihydrazide, oxalyl dihydrazide have low ignition temperature and are combustible due to the presence of the N–N bond which can exothermically decompose to form the product are found to be apt for the synthesis of the metal oxides [7] Hence we have tried to explore the same principle for tartaric acid dihydrazide which is a novel fuel used for the synthesis of the $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x= 0.0-0.5$) ferrite series.

L-tartaric acid dihydrazide (L-TADH) has been used for the first time as a fuel in the combustion synthesis. L-TADH has been synthesized by refluxing L-dimethyl tartrate (AR grade) in methanol solvent with excess of hydrazine hydrate (AR grade) in the ratio 1:2. [8]. Thus, L-dimethyl tartrate (2 g) (dimethyl ester) was first dissolved in methanol (30 mL) and to it hydrazine hydrate (4 mL) (monohydrate) was added and this reaction was stirred for 2 h at room temperature. Later the reaction was refluxed at 60 °C for 14 h under nitrogen atmosphere. This resulted in the formation of white solid precipitate which was later filtered, washed with methanol (2×15 mL) and dried with diethyl ether (2×10) [8-10]. The white powder formed (L- tartaric acid dihydrazide) was then characterized by NMR, IR and CHNS analysis and its melting point was recorded. The melting point of the product was found to be 184 °C. The synthesis scheme has been shown in scheme 2.1.



Scheme 2.1 Synthesis of L-tartaric acid dihydrazide.

The Carbon hydrogen Nitrogen (CHN) analysis of L-tartaric acid dihydrazide (L-TADH) (synthesized fuel) was done and the data has been depicted in Table 2.1. The experimental CHN values are found to be in close agreement with the theoretical ones.

Table 2.1: The theoretical and experimental percentages of carbon (C), hydrogen (H) and nitrogen (N) in L-tartaric acid dihydrazide (L-TADH).

L-tartaric acid dihydrazide (L-TADH)	Nitrogen (%)	Carbon (%)	Hydrogen (%)
Theoretical	31.43	26.94	5.61
Experimental	31.28	27.66	5.43

The synthesized of the fuel has been also confirmed by IR spectroscopy and the IR plots of the reactant and the product are demonstrated in Fig. 2.1. The absorption band observed for the synthesized compound at approximately 3278 and 3398 cm^{-1} is due to the presence of N–H stretching vibrations which is found to be absent in the reactant. Besides, the frequency band approximately at 970 cm^{-1} is attributing to the N–N stretch present in the compound. The formation of the prepared new L-tartaric acid dihydrazide is confirmed by ^1H NMR and ^{13}C NMR.

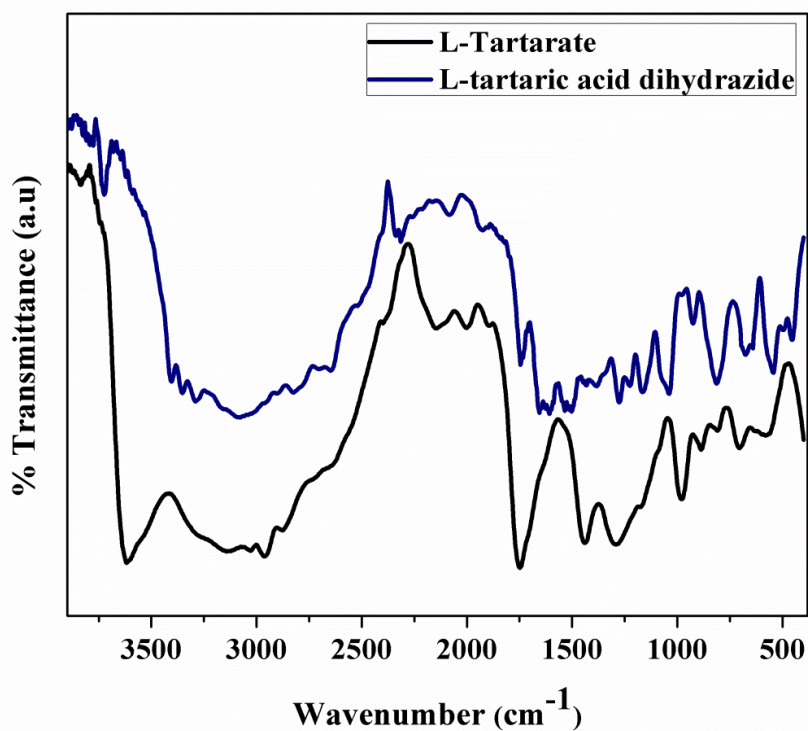


Fig. 2.1 The Infra red spectra of L-tartaric acid dihydrazide.

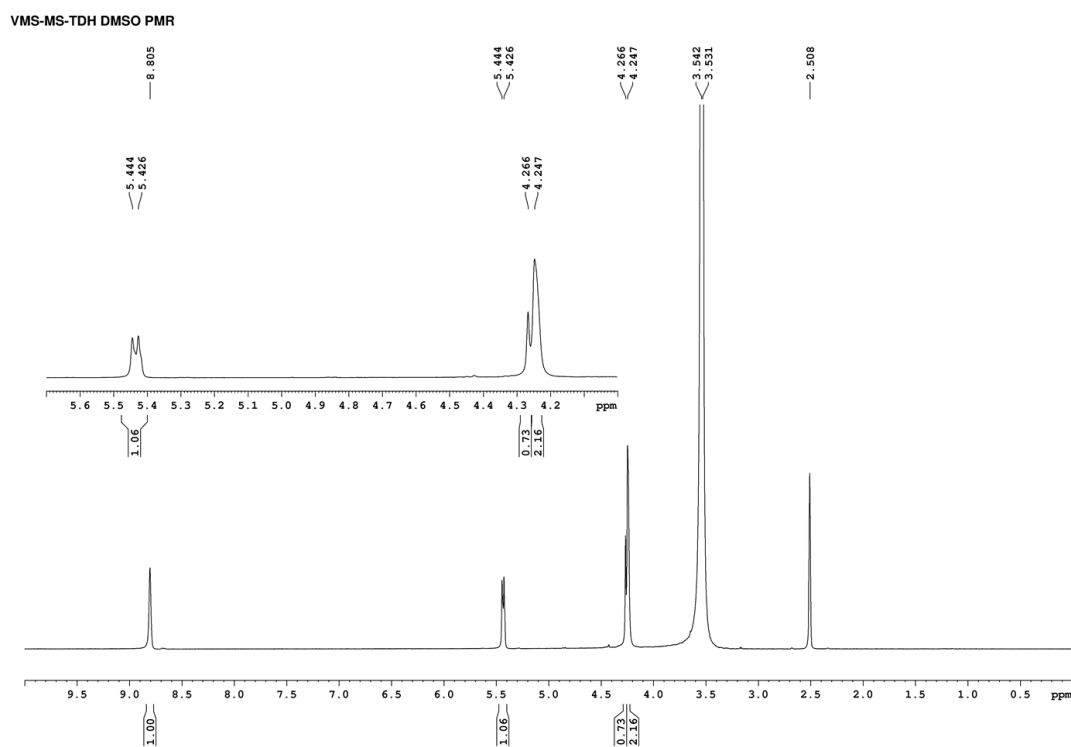


Fig. 2.2a The ^1H NMR of L-tartaric acid dihydrazide.

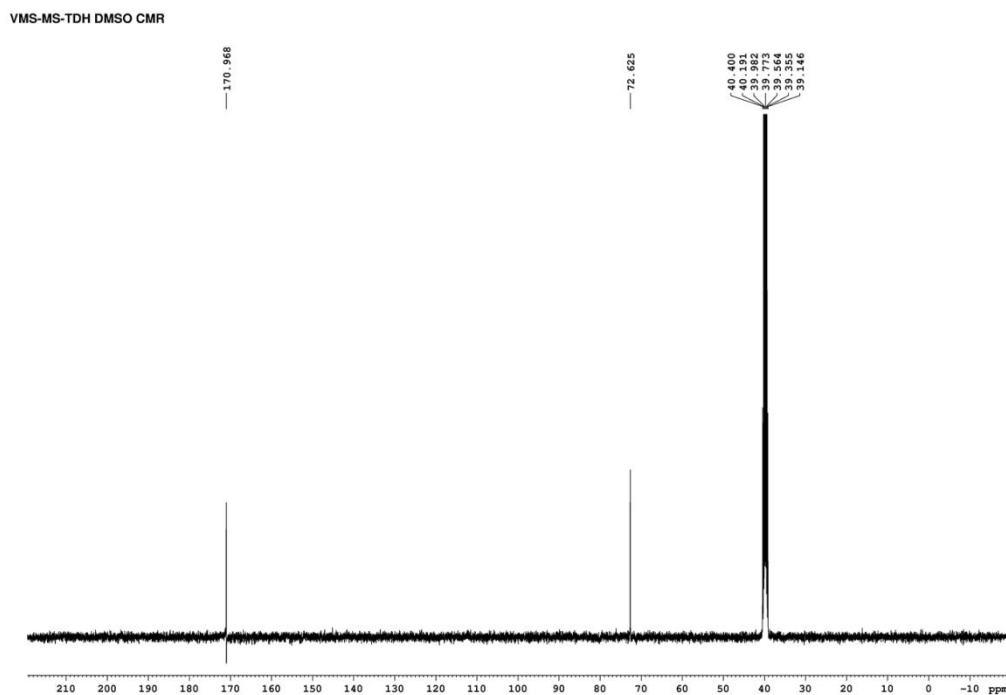


Fig. 2.2b The ^{13}C NMR of L-tartaric acid dihydrazide.

2.3.2 Optimization of the synthesis method

$\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite series was synthesized using combustion method by using the novel L-tartaric acid dihydrazide as a fuel. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (all AR grades) were taken in stoichiometry as oxidizers and the L-TADH was used as fuel (reducer). For this series, five fuel deficit ratios were investigated for optimization due to the high exothermic nature of the fuel. The fuel ratios used are 1: 0.075, 1:0.175, 1:0.25, 1: 0.375 and 1: 0.5. Optimization was done for one of the middle composition i.e. $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ as a representative sample. All the metal nitrates, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were taken in requisite amounts and were heated on a hotplate until a melt was obtained. Later, to this melt the synthesized fuel was added (L- tartaric acid dihydrazide) and mixed with heating to get the final ferrite powder. This procedure was repeated for individual ratios so as to form the ferrite nanoparticles. Further, the samples with these ratios were calcined at 500 °C for 5 h and then ground for 2 h. Studies such as powder XRD, IR and AC susceptibility was carried out of all these ratios to ascertain the single phasic nature of the ferrite to be used for synthesizing the main series.

2.3.3 Synthesizing the main series of $\text{Ni}_x\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0 - 1.0$) ferrites

The optimization studies deduce that the fuel ratio 1: 0.175 does not have any impurity and it possess the lower crystallite size and a higher lattice parameter value affirmed by powder XRD. Thus, this ratio was chosen for the synthesis of the main series. The optimization studies have been discussed thoroughly in chapter 4.

The required amounts of the metal nitrates (for corresponding compositions) were taken in to a beaker and heated on a hotplate. This led to the formation of melt which was then cooled at room temperature. To this mixture, fuel was added (L-tartaric acid) with constant stirring and heating on a hotplate which initially formed thick slurry and ultimately led to the ferrite powder formation. The ferrite powder was then crushed and ground for half an hour for homogenization and later kept in the furnace at 500 °C for 5 h (calcined) followed by grinding for 2 h giving the ‘as prepared’ ferrite. The ‘as prepared’ ferrites were then made into pellets using the hydraulic press using pressure of 5 tons for 5 minutes. These pellets were then pre-sintered at 800 °C for 5 h and then crushed for 2 h and again the ferrite samples were pelletized which was then sintered at 1000 °C for 10 h.

2.4 Synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite series by precursor-combustion method

2.4.1 Chemicals required

The materials required for the synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite by the precursor-combustion method were all AR grade chemicals which includes metals chloride salts, disodium fumarate and hydrazine hydrate.

2.4.2 Synthesis procedure

$\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were synthesized by precursor-combustion method. The requisite amounts of disodium fumarate in aqueous medium was taken and stirred with optimized quantity of hydrazine hydrate for 2 h in nitrogen atmosphere. This led to the formation of the fumarato-hydrazinate precursor (ligand solution). The freshly prepared ferrous chloride solution, along with the desired quantities of metal chloride solutions ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 , all from AR grades) were then added to this ligand solution with continuous stirring (in N_2 atmosphere). The obtained precipitate was then filtered, washed with ethanol and dried with diethyl ether. This precursor (mixed

metal fumarato-hydrazinate precursor) was then spread in the evaporating dish and small part of it was ignited with a burning matchstick. The precursor catches fire and the glow spreads over the entire volume decomposing the precursor autocatalytically thereby forming monophasic mixed metal ferrites. The synthesized ferrites were then calcined at 500 °C for 5 h to eliminate any unburnt carbon present and later ground for 2 h using motor and pestle. This ferrite powder is termed as the ‘as prepared’ ferrites. This synthesis method has been discussed in detail in previously published research articles from our group [3, 11]. These samples were then pelletized using a hydraulic press by applying a pressure of 5 tons for 5 minutes. The pellets were then pre-sintered at 800 °C for 5 h which gives strength to the pellets and takes care of any shrinkage during final sintering. The pre-sintered pellets were again broken by crushing and ground for 2 h and again pellets were made which were then sintered at 1000 °C for 10 h.

2.5 Characterization techniques

2.5.1 ICP-AES and MP-AES techniques

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and Microwave plasma-atomic emission spectroscopy (MP-AES) were employed to find out the stoichiometric composition of the respective elements in the ferrite samples. The quantitative analysis of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite series and ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites series was done by ICP-AES technique on ACROS simultaneous ICP spectrometer of R.F generator 1.6 kW at 27.12 MHz determined the chemical composition of the ferrites. The quantitative analysis of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites was performed on MP-AES technique of model Agilent 4210 MP-AES as it is a highly sensitive technique. This instrument uses microwave plasma and runs on air in place of combustible gases. The hydrazine estimation of the precursors was performed by volumetric titrations using Andrew’s conditions by using 0.025M KIO_3 as a titrant [12].

2.5.2 Carbon hydrogen nitrogen (CHN) analysis

The Elementar Vario Micro Cube CHNS analyser was employed to determine the carbon, hydrogen and nitrogen concentration of the mixed metal carboxylate-hydrazinate (fumarato-hydrazinate) precursors. Also the same technique was used to carry out the

carbon, hydrogen and nitrogen analysis of the newly synthesized fuel (L-Tartaric acid dihydrazide).

2.5.3 Thermal analysis

To anticipate the formula of the final product after decomposition of the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors, the isothermal weight loss analysis was done of all the precursors and simultaneously recording the IR at each step. These studies were executed at varying temperature set and concomitantly estimating the amount of hydrazine at that particular temperature. Additionally, the precursors were kept in the furnace at 500 °C for 3 h to determine the total mass loss of each of the precursors. The thermogravimetric (TG) properties with the differential thermal analysis (DTA) together with thermal differential analysis (TG-DTG) analysis of the precursors for the precursor-combustion synthesis methods were examined using the simultaneous Netzsch STA 409PC (Luxx) make TG-DTA-DTG thermal analyser in zero air atmosphere at a heating rate of 10 °C/min and from 30 °C to 800 °C by taking ~ 10 mg of the sample in alumina cups. Besides, analysis of the melt to find out the decomposition temperature for both the combustion series was performed on the same instrument.

The TG determines the change in the mass of a sample responding to the change in the temperature and the plot of mass loss against temperature is known as a thermal decomposition curve. On the contrary, DTA estimates the change in temperature amongst the reference and sample with respect to time or temperature. It associates the corresponding mass losses shown in TG by either depicting endo or exo peaks in accordance with the respective processes. Moreover, DTG appears as derivative of TG analysis and assists in the TG data interpretation precisely by detecting any minor mass loss as DTG peak.

2.5.4 Powder X-ray Diffraction studies

The characterization of all the ‘as prepared’ and the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite series was performed to find out their phase purity by powder XRD technique using the instrument Rigaku Miniflex X-Ray diffractometer having monochromatized Cu-K α radiations filtered through Ni absorber ($\lambda = 1.5418 \text{ \AA}$). The diffraction patterns are noted from 20 °C to 80 °C with step of 0.02°. Identification of the specific diffraction pattern gives proper understanding about the crystal structure of the crystalline material, presence of amorphous concentration in a material and phase purity with existing impurities. Besides, this

technique is of enormous use for determining numerous structural parameters such as lattice constant, crystallite sizes, X-ray density, porosity and so on.

The lattice parameter (a), crystallite size (D), measured density (d_m), theoretical density (d_x) and porosity (P) for all the samples is calculated using the powder XRD data. The lattice parameter (a) for all the samples was calculated using the equation 2.1 [11].

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (2.1)$$

In this equation ' a ' is the lattice parameter, d_{hkl} is the interplanar distance and ($h k l$) are the miller indices. The Debye Scherrer's relation assessed the average crystallite size of all the 'as prepared' and 'sintered' ferrite samples and the formula is given as [11].

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2.2)$$

' D ' is the crystallite size, ' β ' denotes the full width at half maxima (FWHM) in radians, ' λ ' is the wavelength incident of Cu-K α radiation of X-ray and ' θ ' is the Bragg's diffraction angle. Also, the measured density calculated using powder XRD is given as [13].

$$d_m = \frac{8M}{N_A a^3} \quad (2.3)$$

Wherein, ' d_m ' is the measured density, ' M ' is the molecular weight, a^3 is the volume of unit cell and N_A is the Avogadro's number and 8 is the number of formula units. The theoretical density of all the ferrites samples can be given as in the formula [11].

$$d_x = \frac{m}{\pi r^2 h} \quad (2.4)$$

Wherein, ' m ' is the mass, ' r ' is radius and ' h ' is the height of the sample pellet. The porosity can hence be calculated as

$$P (\%) = \frac{d_m}{d_x} \times 100 \quad (2.5)$$

2.5.5 Infrared spectroscopy (IR) studies

IR spectroscopy is a non-destructive technique which gives qualitative structural information with the electromagnetic radiation range of 400-4000 cm^{-1} . This mid-IR region is significant region for analysis since it provides knowledge about the molecular vibrations and thus about the molecular structure. Infra-red spectrum assists to affirm the presence or absence of any functional group in a particular molecule. The IR spectra of the precursors, isothermal IR for

precursors and their corresponding final ferrite samples for precursor series as well as combustion series were recorded on Shimadzu FTIR Prestige-21 spectrophotometer in the IR range 4000 cm^{-1} to 400 cm^{-1} . Sample preparation was done by combining the ferrite sample powder with potassium bromide (KBr) in the ratio of 1:100 and was recorded in the IR range 4000 cm^{-1} to 400 cm^{-1} .

2.5.6 Raman Spectroscopy Studies

The room temperature Raman spectroscopic measurements for all the ‘as prepared’ and ‘sintered’ ferrite samples was carried out in the range of $100\text{--}800\text{ cm}^{-1}$ on the Horiba LabRam HR Evolution Raman spectrometer. He–Cd LASER source of 532 nm with the power of 100 mW was used as an excitation source. The Raman effect is based on the light scattering process which means the monochromatic scattering of light when a source (LASER) passes through a sample. After interacting with the sample the frequency of the photon of monochromatic light changes in which the sample absorbs the photon of the LASER light and later reemits. This frequency of the re-emitted photons shifts either up or down with regards to original monochromatic frequency which is known as the Raman effect. Raman is a sensitive tool in case of ferrites as it is used in identification and cation distribution. This technique can be utilized in determining the extrinsic iron oxides phases such as magnetite or hematite and assisting in identifying the impurities if present.

2.5.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectrometer (XPS) is a surface characterization technique. A sufficiently high energy X-ray beam is incident on a material to overpower the binding energy of the core level electrons. This leads to the electron ejection from the core level. The kinetic energy of the ejected core level electron is measured as it is the characteristic of the orbital. We have used X-ray photoelectron spectrometer (XPS) of make PHI 5000 Versa Probe II by FEI, Inc. which affirmed the oxidation states of all the corresponding elements in the synthesized samples. After getting the raw data, XPSPEAK41 software was used to deconvolute the peaks and they were plotted individually using Origin Pro 8.5 software. All the peaks were corrected referring to binding energy of carbon 1s at 284.8 eV.

2.5.8 Surface area studies

2.5.8.1 The Brunauer–Emmett–Teller BET surface area studies

The specific surface area of all the ‘as prepared’ ferrite samples was determined using the Quantachrome Autosorb iQ-MP-C instrument. The degassing of the sample (~200 mg) was done on the instrument using liquid N₂ at 200 °C for 2 h. After degassing N₂-sorption (adsorption-desorption) studies at liquid nitrogen temperature (77 K) using the multipoint (20 point) BET measurements were done for all the ‘as prepared’ ferrite samples for all the series. The instrument gave the information about the specific surface area, BET isotherm, total pore volume and average pore sizes of the ferrite samples. The nature of the isotherm reveals the nature of the pores present in the porous ferrite material. Depending on the pores sizes, the material is microporous if the pore diameter is 2 nm, mesoporous if pore diameter lies between 2-50 nm and the material is macroporous if the pore diameter exceeds 50 nm. All the ferrite samples in our present study are found to be mesoporous with type IV isotherms according to the IUPAC classification.

2.5.8.2 Temperature programmed desorption (NH₃-TPD) and (CO₂-TPD)

NH₃-TPD and CO₂-TPD were done using the same Quantachrome Autosorb iQ-MP-C BET instrument. 50 mg of the ferrite powder of each composition was initially pre-heated at 200 °C for 30 minutes in helium flow. Later the acidic sites of the ferrite nanoparticles were saturated by flowing 20 % NH₃-He mixture for 40 minutes. After flushing away the physisorbed NH₃ by He-flow for around 20 minutes, desorption was performed by heating the sample till 800 °C with helium flow. Similar sequence was used to carry out the CO₂-TPD using the same instrument. In helium flow 50 mg of the ferrite sample was pre-heated at 200 °C for 30 minutes. The basic sites of the ferrite samples were saturated by flowing 5 % CO₂-N₂ for 40 minutes. After flushing away the physisorbed CO₂ by flowing helium for 20 minutes desorption was done by heating till 800 °C in helium flow. The similar sequence has been also followed by et al. Sartoretti [14].

2.5.9 Morphological studies

The surface morphology in combination with the elemental analysis of the synthesized ‘as prepared’ and ‘sintered’ ferrite samples were investigated using scanning electron microscope (SEM) with connected EDAX facility of Carl Zeiss make bearing Model No. EVO1. The particle shape and morphology of the nanoparticles of ‘as prepared’ samples which are less

than 50 nm are identified using high resolution transmission electron microscopy (HR-TEM) using JEOL-make field emission transmission electron microscope of model JEM 2100F.

2.5.10 DC Electrical Resistivity studies

The DC electrical resistivity measurements were performed using the two probe resistivity method in the temperature range of 30°C to 500°C. The pellets of diameter of roughly 1.0 cm and approximately 0.3 cm thickness were pressed between the two electrodes and then the measurements were made. By keeping the voltage constant (2 V) current of the pellet was measured and by applying the Ohm's law the resistance of the sample was measured.

$$R = \frac{V}{I} \quad (2.6)$$

'V' is the applied voltage, 'I' is the current and 'R' is the resistance of the pellet.

The resistivity can hence be calculating using the below equation

$$\rho = \frac{Rl}{A} \quad (2.7)$$

Wherein 'ρ' denotes the resistivity of the sample, 'R' is the resistance, 'l' is the pellet thickness and 'A' is the area of cross section.

The resistivity of the ferrites was measured and plot of $\log \rho$ v/s $1000/T$ (K^{-1}) is plotted for heating and cooling.

2.5.11 Dielectric Studies

The dielectric constant (ϵ') is the amount of energy stored in a dielectric material as polarization. The dielectric constant in spinel ferrites is because of four types of polarization effects viz. electronic, ionic, dipolar and space charge polarizations. The dielectric loss tangent ($\tan \delta$) measures the amount of energy lost in the ferrite sample. An electrical insulator which can be polarized by applying external electric field is called a dielectric material. The angle δ is the difference in phase between the applied electric field and the induced current.

The dielectric constant (ϵ') was calculated by using the formula:

$$\epsilon' = \frac{Ct}{\epsilon_0 A} \quad (2.8)$$

Wherein,

ϵ' = Dielectric constant

C = Capacitance of the sample in Farads

t = thickness of the sample in metres

ϵ_0 = permittivity of free space (8.854×10^{-12} F/m)

A = Area of cross section of the sample (m^2)

The dielectric loss of the ferrite samples was determined using the following equation

$$\tan \delta = D \text{ or } 1/Q \quad (2.9)$$

The dielectric measurements as a function of frequency was carried out with the help of Wayne Kerr LCQR meter (Model- 6500 P) in the frequency range of 20 Hz to 1 MHz. The same instrument was used to measure the record the dielectric measurements as a function of temperature from 30 °C to 500 °C at particular frequencies.

2.5.12. Magnetic Studies

2.5.12.1 AC Susceptibility Studies

One of the significant parameters one can determine from this technique is the Curie temperature. A transition from the ordered alignment of the magnetic spins to the random alignment is the Curie temperature (viz the transition from ferromagnetic to paramagnetic). Moreover, the particle nature whether it is Single domain (SD), multi-domain (MD) and super paramagnetic (SP) can also be determined using this technique. In case of SP particles there is a sharp fall in the magnetization with increase in temperature and usually nanoparticles with 10-25 nm size show this behaviour. The nanoparticles sizes between 25-50 nm show SD nature wherein the susceptibility plot shows increase in magnetization with increase in temperature accompanied by a continuous decrease at a particular temperature with further increase in temperature. MD particles initially show a constant susceptibility value and a sharp fall at the Curie temperature. In our present research work AC susceptibility of all the ferrites were investigated using ADEC Embedded Technology &

Solutions Pvt Ltd, Corlim-Goa, India from room temperature to 600 °C. The plots of χ_T/χ_{RT} against temperature were plotted and the Curie temperature was obtained.

2.5.12.2 Vibrating sample magnetometer (VSM)

Vibrating sample magnetometer (VSM) instrument was used to find out the DC magnetization of the samples. The Quantum design, cryogen-free Versa Lab (USA make) vibrating sample magnetometer with a magnet of 3 T was used to measure the magnetic properties of the ferrites. The magnetic hysteresis (M-H) studies were performed at two different temperatures of 300 K and at low temperature (60 K) from field of -3 Tesla to 3 Tesla. Similarly the zero field cooled field cooled (ZFC-FC) measurements (M-T studies) were done at different fields of 5000 Oe and 10000 Oe in the temperature range of 60-350 K for nickel substituted cobalt ferrite series and at fields of 2000 Oe and 3000 Oe (as prepared) and 3000 Oe and 5000 Oe (sintered) for zinc substituted nickel cobalt ferrite series. Roughly 5-7 mg of the sample was wrapped in Teflon and was attached to the VSM sample holder for measurements. The saturation magnetization, remnant magnetization and coercivity were determined by plotting magnetic field against magnetic moment at constant temperatures i.e. at 60 K and at 300 K. The magnetocrystalline anisotropy (K_{eff}) can be given as bellows [15]

$$H_c = \frac{0.985 K_{eff}}{M_s} \quad (2.10)$$

The blocking temperature was obtained from the M-T studies, after plotting magnetic moment against temperature at constant mentioned fields. The nanoparticles are initially cooled in zero field cooling measurements from 300 K to 60 K with no applied magnetic field and later on a constant external magnetic field was applied and sample heating was done from 60 K to 350 K and while heating the measurements were taken. For FC measurements again the ferrite nanoparticles were cooled from room 300 K to 60 K in presence of externally applied magnetic field later sample heating was done from 60 K to 350 K in presence of field by simultaneously evaluating the magnetization.

2.6 Applications of ferrites of synthesized ferrites

2.6.1 Gas sensing studies

The ‘as prepared’ ferrite samples were tested for their gas sensing properties to measure the response towards various gases and to check whether they are apt to be used as sensor materials. Gases such as (Cl_2), nitrogen dioxide (NO_2), ammonia (NH_3) and liquefied

petroleum gas (LPG) were tested at four different operating temperature of 30 °C, 50 °C, 100 °C and 150 °C. Sensing parameters like recovery, response, operating temperature, gas concentration (in ppm) were determined. LPG was used from the domestic LPG cylinder and the other gases were prepared in laboratory using conventional synthesis technique. Chlorine was synthesized by taking approximately 2 g of KMnO_4 with 20 mL of HCl in a clean and sealed three necked flask and by using a gas trap (CaCl_2 desiccant). Similarly, NO_2 was synthesized by reacting 2 g of Cu metal with 20 mL HNO_3 in a sealed flask using CaCl_2 as desiccant to absorb moisture. Synthesis of NH_3 was done by heating 1:2 ratio of Ca(OH)_2 : NH_4Cl in a closed flask using CaO as desiccant. The gases in all cases were collected in nitrogen bladder and used for testing. [16-17]

2.6.1.1 Fabrication of thick film

The thick films were fabricated by screen printing for scrutinizing the gas sensing properties of the ferrite samples. A thixotropic paste was made of the ferrite samples after mixing with binder ethyl cellulose in the ratio 70: 30 using butyl carbitol acetate as a solvent. Later, screen printing of this paste was done on clean glass substrate using nylon mesh of 200-mesh density. The raw thick film synthesized was then heated in at 60 °C in an oven for 1 h for removing moisture and then in tubular furnace for 20 minutes at 400 °C to remove any organic impurity. Silver paste (high temperature conducting) was then applied at both edges of the thick film to ascertain electric contacts.

2.6.1.2 Gas sensing instrument setup

The gas sensing response was measured at a predetermined temperature and concentration for numerous gases at various concentrations and temperatures by using the gas sensing instrument which is schematically represented in Fig. 2.3. It is composed of an air tight stainless steel gas chamber (250 mL) in which the sensor thick film was placed. The inbuilt DC power supply controlled the temperature of the gas sensing unit. The Keithley electrometer (Model 6514) was used for measuring resistance across the thick film. The measured known amounts of gases were injected into gas inlet and the changes in the resistance of the thick film were determined through computer by appropriate communication with the electrometer. The gas sensing response/recovery was then determined from resistance variation using the formula by measuring the resistance.

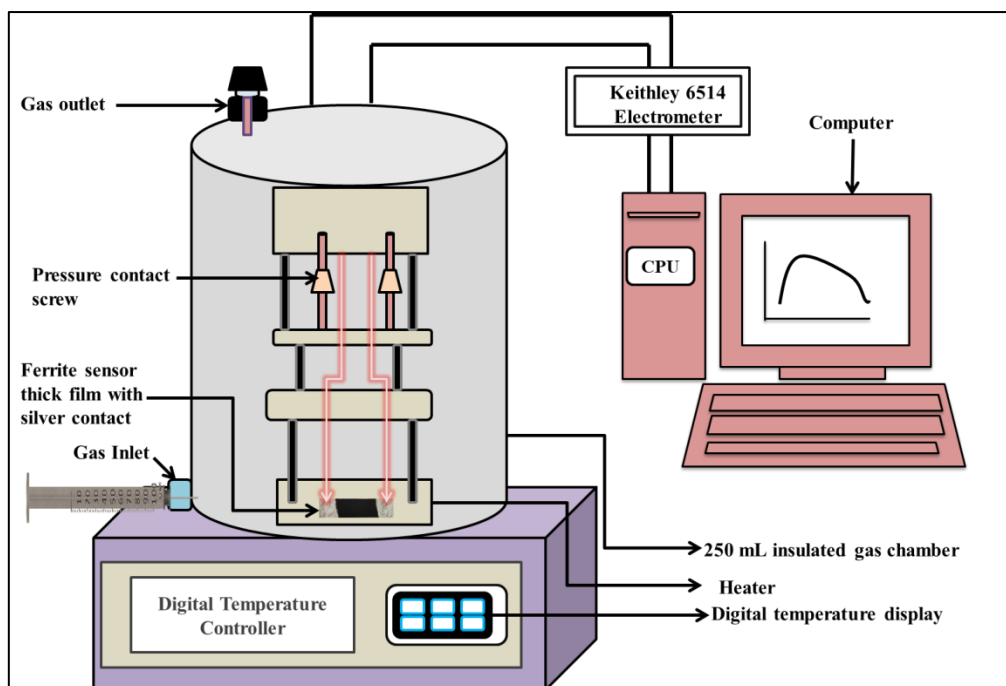


Fig. 2.3 Schematic illustration of the gas sensing setup.

2.6.1.3 Gas calibration and Sensor response

A known volume of the test gases (Cl_2), nitrogen dioxide (NO_2), ammonia (NH_3) and liquefied petroleum gas (LPG) were injected through the gas inlet by using a calibrated medical syringe. The gas sensing response is the change in the resistance of the thick film. The gas response obtained was calculated using the following equation [18].

$$\text{Gas response (\%)} = \frac{|R_a - R_g|}{R_g} \times 100 \quad (2.11)$$

Wherein, ' R_a ' is the thick film resistance in air (Ω) and ' R_g ' is the thick film resistance in the test gas (Ω).

2.6.2 Electrochemical properties of ferrites

An increased concern about environmental pollution and growing need for clean energy generation and storage, appliances like supercapacitors and rechargeable batteries have garnered attention in the past few years [19-20]. The energy storage is mainly possible due to devices like batteries and supercapacitors which are essential to store energy through electrochemical processes [21]. From the literature reports it is understood that ferrites have been used extensively as supercapacitors. Thus in our present research work we have tried to

fabricate the ‘as prepared’ ferrite samples into working electrode and to be used as supercapacitors.

2.6.2.1 Fabrication of the working electrode (three-electrode setup)

To prepare the working electrode a slurry of the ‘a prepared’ ferrite samples (active material) was made by mixing carbon black (conductive additive) and poly(vinylidene flouride) as binder using 1-Methyl-2-pyrrolidinone as solvent in the ratio of 80:10:10. The ‘as prepared’ ferrite samples (80 wt. %), poly(vinylidene flouride (10 wt. %) and conducting carbon black (10 wt. %) were mixed in this stoichiometric ratio and a slurry was made having ink like consistency. Subsequently, pre-cleaned and pre-weighed nickel foam of dimension 1 cm × 1 cm was taken as a substrate and this slurry was drop casted on the same Ni foam. This foam after drop casting the slurry was then dried in an oven at 120 °C for 14 h. to ensure total removal of the solvent. This was then pressed by applying 1/2 ton pressure for 1 minute in a hydraulic press and this was used as the working electrode. Ad/AgCl electrode was used as reference electrode and a platinum wire as counter electrode and 3 M KOH as electrolyte.

2.6.2.2 Electrochemical measurements

The eletrochemical measurements were done such as cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) by employing the Metrohm Autolab PGSTAT204 electrochemical workstation. The electrochemical impedance spectroscopy (EIS) measurements were performed by connecting the instrument to FRA32M- Impedance analyser. The CV measurements were investigated from 0.0-0.6 V with scan rates of 10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s, 50 mV/s, 60 mV/s, 70 mV/s, 80 mV/s, 90 mV/s, 100 mV/s, 150 and 200 mV/s. The GCD investigations were done from 0.0 to 0.4 V at current densities of 0.1 A/g, 0.25 A/g, 0.5 A/g, 0.75 A/g, 1.0 A/g and 2.0 A/g. The EIS measurements were done at AC amplitude of 20 mV in the range of 0.1 Hz 100 kHz. The specific capacitance by using CV was calculated using the following equation.

$$C_{sp} = \frac{S}{2mk\Delta V} \quad (2.12)$$

Where, ‘S’ is the area within the CV curve, ‘m’ is the mass of the material (in g), ‘k’ is the scan rate and ‘ΔV’ is the potential window [22].

Equation 2.13 defines the variation of specific capacitance (C_{sp}) with regards to the current densities for the ‘as prepared’ ferrite electrodes [22-23].

$$C_{sp} = \frac{I \times t}{V \times m} \quad (2.13)$$

Wherein, 'I' and 't' are respective discharge current and discharge time, 'V' is the applied potential window and 'm' is the mass of the active 'as prepared' ferrite electrodes.

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Chapter 3

*$\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ (x= 0.0-1.0) ferrites: Synthesis,
characterization, solid state properties and their applications*

3.1 Introduction

In the recent decades, the flourishing research on nanomaterials has exhibited intriguing properties; amongst them one propitious nanomaterial class of compounds is the spinel ferrites. The nanosize spinel ferrites can have variations in structural, electric, and dielectric properties as well as magnetic properties which captivate more and more material researchers. The particle size distributions, morphological uniformity and the compositions are the vital parameters that control the performances of the nanoparticles and which make them apt to be used for numerous applications such as in gas sensors, organic catalysis, supercapacitors, etc. Amongst various metal oxides, ferrites have mainly gained attention due to their excellent stability, their non-toxic behavior, attractive surface properties and electric, dielectric and magnetic properties [1-3].

Amongst the magnetic ferrites cobalt ferrite (CoFe_2O_4) nanoparticles are found to show higher saturation magnetization, coercivity, magnetocrystalline anisotropy as well as remarkable chemical stability and hardness, thus making it a suitable candidate to be used for sophisticated technological applications like high density recording media, electronic devices, multiferroic devices, etc. [3]. However, the high crystalline anisotropy and low resistivity makes it unfit to be used for many other applications which require low crystalline anisotropy and high resistivity. Hence many researchers have modified the structural and magnetic properties of cobalt by substituting nickel in CoFe_2O_4 since NiFe_2O_4 has low crystalline anisotropy and high resistivity [3].

The main focus of the present research work as far as this chapter is concerned was synthesizing $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites using combustion method and characterizing them using various techniques as well as studying their applications. In order to find out the proper oxidiser:fuel ratio for combustion synthesis, the middle composition of the $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites series i.e. $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ was initially optimized using ten different oxidizer: fuel ratios. The characterization and study of their magnetic and solid state properties of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites has been done thoroughly in this chapter along with their sintered analogues. The literature reports claim that DL- tartaric acid is a relatively unexplored fuel used in combustion synthesis, hence we employed this fuel for the synthesis of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. Moreover, we have assessed the influence of particle size on various properties when transformed from nano to bulk upon increased sintering temperature. The

‘as prepared’ $Ni_xCo_{1-x}Fe_2O_4$ ($x = 0.0-1.0$) ferrites were further tested for applications in gas sensors and as supercapacitors.

3.2 Optimization of combustion method for synthesizing of $Ni_xCo_{1-x}Fe_2O_4$ ($x = 0.0-1.0$) ferrites using DL- tartaric acid as a fuel

As discussed in the chapter 2, this method of synthesis was optimized using the middle composition of this series viz. $Ni_{0.5}Co_{0.5}Fe_2O_4$ by using 10 different oxidizer to fuel (O: F) ratios. The oxidizers employed in the present study were the respective metal nitrates such as $(Ni(NO_3)_2 \cdot 6H_2O)$, $(Co(NO_3)_2 \cdot 6H_2O)$ and $(Fe(NO_3)_3 \cdot 9H_2O)$ and the fuel utilized was DL-Tartaric acid. The requisite amounts taken for the synthesis of the $Ni_{0.5}Co_{0.5}Fe_2O_4$ compound by varying fuel ratios have been noted in detail in Table 3.1.

Table 3.1 The amount of various metal nitrates (oxidizers) and the fuel taken and the metal nitrate: fuel ratio which was taken for optimization.

Sr. No.	$Ni(NO_3)_2 \cdot 6H_2O$ (g)	$Co(NO_3)_2 \cdot 6H_2O$ (g)	$Fe(NO_3)_3 \cdot 9H_2O$ (g)	DL-Tartaric Acid $C_4H_6O_6$ (g)	Oxidizer: Fuel Ratio
1	1.46863	1.4698	8.2448	1.5160	1:0.25
2	1.46863	1.4698	8.2448	2.2740	1:0.375
3	1.46863	1.4698	8.2448	3.0321	1:0.5
4	1.46863	1.4698	8.2448	3.7901	1:0.625
5	1.46863	1.4698	8.2448	4.5481	1:0.75
6	1.46863	1.4698	8.2448	5.3061	1:0.875
7	1.46863	1.4698	8.2448	6.0624	1:1
8	1.46863	1.4698	8.2448	6.8222	1:1.125
9	1.46863	1.4698	8.2448	7.5803	1:1.25
10	1.46863	1.4698	8.2448	8.2382	1:1.375

3.3 Characterization of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites obtained from different oxidizer:fuel ratios

3.3.1 Thermal analysis of the solidified melt of oxidizer:fuel having optimization ratio of 1: 0.75

The information about the decomposition temperature of the solidified melt of oxidizer:fuel having optimization ratio of 1:0.75 has been obtained from TG-DTA analysis and the decomposition plot of same is depicted in Fig. 3.1. Initially there is a continuous mass loss observed in the TG plot till around 140 °C which is because of loss of water molecules for which two small corresponding DTA endotherms are seen. After this there is a linear mass loss observed from 140-270 °C followed by steep mass loss till 320 °C with an exothermic peak in DTA at 310 °C which is due to combustion of redox mixture of nitrates and fuel that reacts exothermically to form the mixed metal oxide. No substantial weight loss was observed beyond 320 °C. From this study, the calcination temperature which is slightly higher than the decomposition temperature (i.e. 500 °C) was fixed for calcination of all auto-combusted samples in order to remove complete removal of any carbonaceous impurities, if at all present.

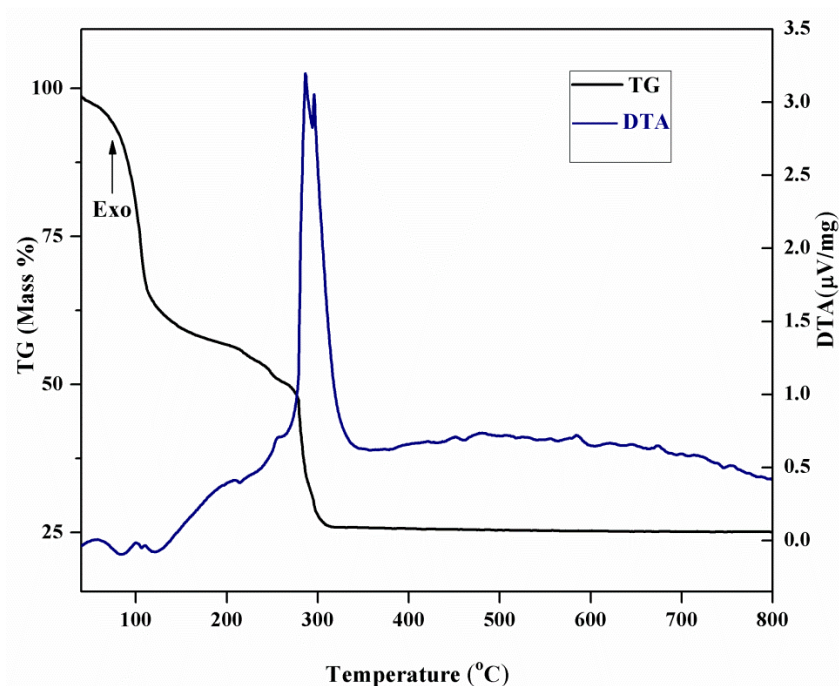


Fig. 3.1 The TG-DTA plot of solidified melt of oxidizer-fuel with optimization ratio 1:0.75 for obtaining $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite.

3.3.2 Powder XRD patterns of $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites obtained from decomposition of optimised oxidizer: fuel ratios

The Fig. 3.2 display the powder XRD patterns of the uncalcined and calcined ferrites of the metal deficit ratios (1:0.25, 1:0.375, 1:0.5, 1:0.625 and 1:0.75) and the metal equal/excess ratios (1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375). Before calcination, the powder XRD patterns show broad peaks indicating smaller particle size and lower crystallinity in all the samples of varying ratios.

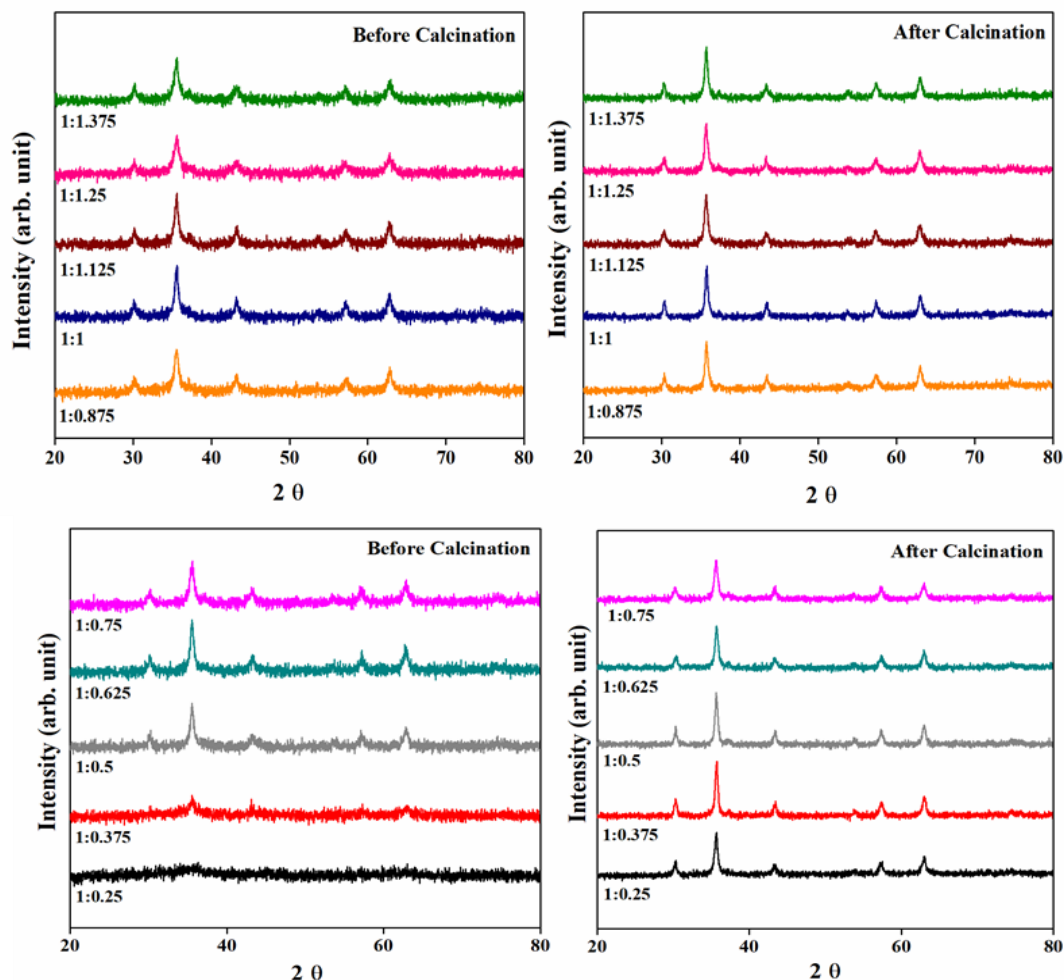


Fig. 3.2 Powder XRD patterns for $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites before and after calcination at 500 °C using fuel deficit ratios 1:0.25, 1:0.375, 1:0.5, 1:0.625, 1:0.75 and fuel equal/excess ratios 1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375.

However, upon calcination at 500 °C the peak broadness is seen to decrease and there is sharpness in the peaks indicating an increase in crystallinity of the samples. The phase purity of all the samples with varying metal nitrate to fuel ratios after calcining was validated by powder XRD which showed single phase cubic spinel structure of all the ferrite samples. The Scherrer's formula was used to find out the average crystallite sizes

(D) and the exact values are tabulated in Table 3.2. The lattice parameter of all the ferrites with various oxidizers to fuel ratios ranges from 8.3302 to 8.3519 Å as can be seen in Table 3.2. It was observed from the data that the oxidizer:fuel ratio of 1:0.75 has the highest lattice parameter and lowest particle size, as the result this ratio was chosen for further synthesis of the ‘as prepared’ and the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites series.

3.3.3 Infrared studies of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites obtained from decomposition of optimised oxidizer: fuel ratios

The room temperature Infrared (IR) studies of all the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite samples synthesized by varying oxidizer; fuel ratios were carried out in the range of 4000-350 cm^{-1} . The Fig. 3.3 (a and b) demonstrate the IR spectra of all the ferrites (with different oxidizer: fuel ratios) in which two notable absorption bands are observed in the spectrum in the range 398-402 cm^{-1} (ν_2) and 593-601 cm^{-1} (ν_1) [Table 3.2] suggesting formation of cubic spinel ferrites [4]. The absorption bands at around $\sim 600 \text{ cm}^{-1}$ (ν_1) is due to the (M_A -O) cation-anion bond stretching vibrations at the tetrahedral sites and the absorption band at $\sim 400 \text{ cm}^{-1}$ attributes to the (M_B -O) cation-anion bond stretching vibrations at the octahedral sites [5].

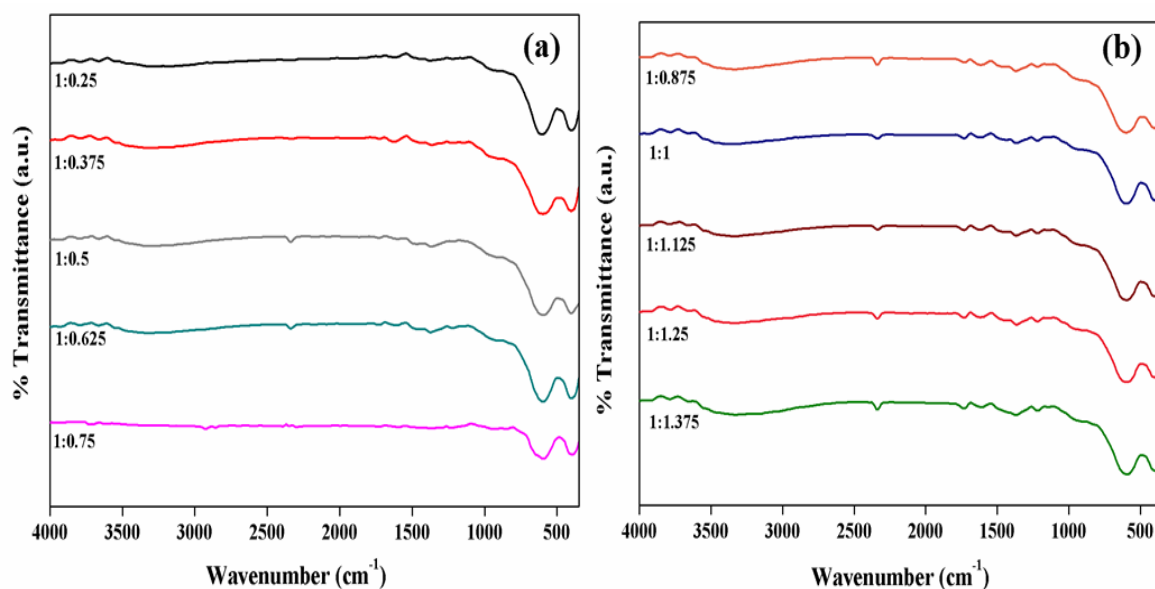


Fig. 3.3 The FTIR spectra for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites synthesized by varying metal nitrates: fuel ratios with a) Fuel deficit ratios 1:0.25, 1:0.375, 1:0.5, 1:0.625 and 1:0.75 b) Fuel equal/excess ratios 1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375.

Table 3.2 The saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c), Curie temperature (T_c), IR frequencies (ν_1 and ν_2), average crystallite size (D) and lattice parameter ($\text{\AA}$) of $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites synthesized by varying metal nitrates: fuel ratios.

Metal nitrate: Fuel ratio	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	T_c (K)	IR frequency		Average crystallite size (nm)	Lattice parameter ($\text{\AA}$)
					M-O _{tet} ν_1 (cm ⁻¹)	M-O _{oct} ν_2 (cm ⁻¹)		
1:0.25	44.80	15.15	680	825	601	399	18	8.3495
1:0.375	51.06	17.51	653	817	597	401	21	8.3402
1:0.5	51.64	16.71	781	826	596	402	21	8.3440
1:0.625	49.26	14.71	715	804	600	400	18	8.3385
1:0.75	48.64	14.25	711	821	601	399	16	8.3519
1:0.875	48.21	13.90	676	822	600	401	19	8.3374
1:1	48.74	15.25	773	813	596	398	18	8.3403
1:1.125	45.2	13.07	617	820	597	399	17	8.3406
1:1.25	49.0	15.73	730	817	593	400	23	8.3305
1:1.375	50.39	16.03	820	814	594	398	21	8.3302

3.3.4 The normalized A.C. susceptibility studies of $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites synthesized by varying metal nitrates: fuel ratios

The normalized alternating current (A.C) susceptibility studies give the information about the Curie temperature (T_c) of the ferrites as well as their domain structure [6]. The Curie temperature is the temperature at which there is transition from ferromagnetic to paramagnetic i.e., a transition from the ordered alignment of the magnetic spins to the random alignment. Usually, A.C. susceptibility technique gives information about three types of magnetization domains viz. the superparamagnetic (SP), single-domain (SD), and multi-domain (MD) [7]. In case of the superparamagnetic materials, the increase in temperature does not allow the magnetic domains to align in one direction thus creating chaos (random alignment) hence contributing negatively to the magnetization. In multi-domain, the magnetization domains perfectly align in one direction and there is no significant increase in magnetisation with increase in temperature. The single domain materials have magnetization values lying between SP and MD materials and their magnetization increases with increase in temperature till Curie temperature is reached after which it decreases.

The normalized A.C. Susceptibility measurements were used to find out the Curie temperatures of all the ferrites obtained with varying oxidizer:fuel ratios and the Curie temperature values are tabulated in Table 3.2. The fuel-deficit ratios exhibited a purely SD nature of the particles (Fig. 3.4a), while the fuel-excess ratios tend towards SD-MD particles (Fig. 3.4b) with majority are SD particles. The ratio chosen for further synthesis of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites series was 1:0.75, possessing a single-domain particle nature.

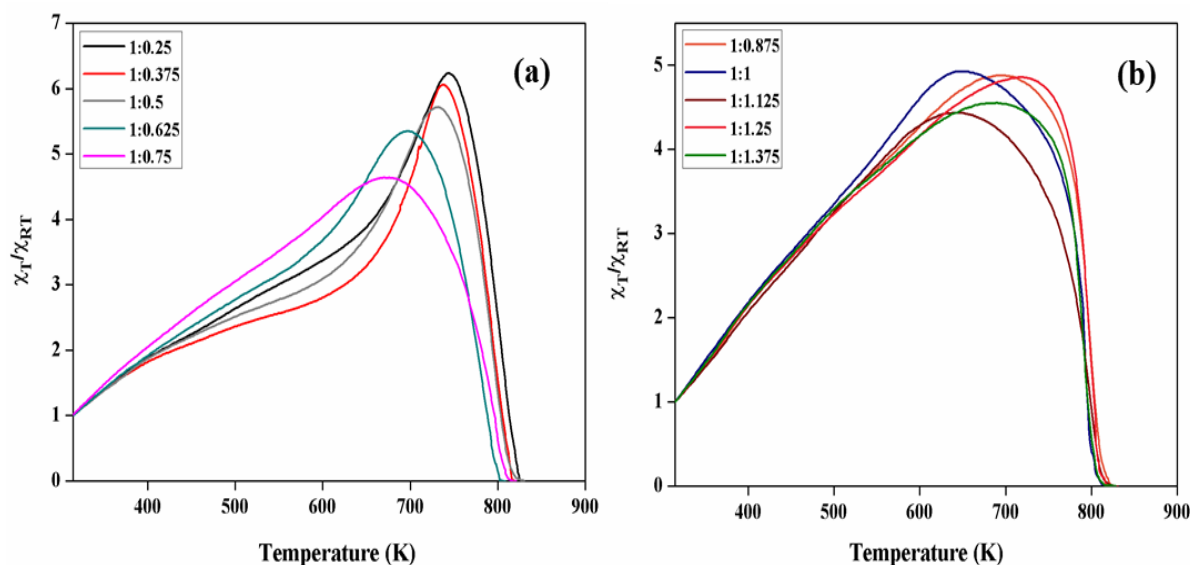


Fig. 3.4 Plots of variation of normalized AC susceptibility as a function of temperature for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites synthesized with a) Fuel deficit ratios 1:0.25, 1:0.375, 1:0.5, 1:0.625, 1:0.75 and b) Fuel equal/excess ratios 1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375.

3.3.5 VSM studies of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites synthesized by optimizing oxidizer:fuel ratios

A vibrating sample magnetometer (VSM) with an applied field of 3 T was employed to study the magnetic properties of all the ferrites obtained by optimizing oxidizer to fuel ratios. The room temperature (300 K) VSM plots of the magnetic moment against magnetic field of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites synthesized by varying oxidizer: fuel ratio, is demonstrated in Fig. 3.5a (fuel deficient ratios) and Fig. 3.5b (fuel equal/excess ratios). The magnetization plots confirm that all the ferrites display ferromagnetic-like behaviour [8] having substantial coercivity (inset pictures). Although the sample with oxidizer:fuel ratio of 1:0.25 has lowest saturation magnetization value, it possesses higher average crystallite size as compared to sample with oxidizer:fuel ratio of 1:0.75 which has lowest average crystallite size. Hence, oxidizer:fuel ratio of 1:0.75 was chosen for the further

synthesis of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites series. The values of the saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) of all the ferrite samples are given in Table 3.2.

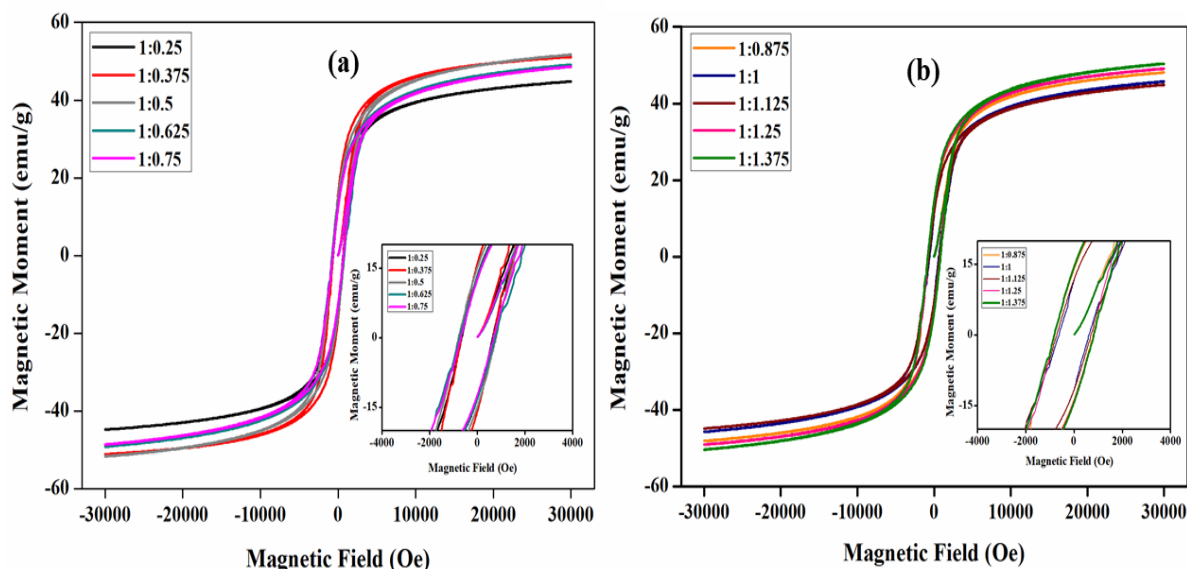


Fig. 3.5 The room temperature VSM plots of magnetic moment v/s magnetic field of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ synthesized using a) Fuel deficit ratios 1:0.25, 1:0.375, 1:0.5, 1:0.625, 1:0.75 and b) Fuel equal/excess ratios 1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375.

3.4 Characterization of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites samples were prepared by using the synthesis method as described in detail in section 2.2.2 of chapter 2.

3.4.1 Chemical analysis of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

To find out the exact stoichiometry of the metals present in the ferrite samples, the chemical analysis of the samples was carried out using ICP-AES. The Table 3.3 presents the experimental percentages of the metal ions in the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites obtained from the ICP-AES along with the theoretically calculated percentage values. The experimental percentages of the metal ions in the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites are found to be in close proximity with the theoretically calculated percentages affirming the stoichiometric formation of the ferrites.

Table 3.3 Theoretical and experimental percentages of nickel, cobalt, and iron present in 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Composition	Ni% (theor.)	Ni% (expt.)	Co% (theor.)	Co% (expt.)	Fe% (theor.)	Fe% (expt.)
x= 0.0	-	-	25.11	25.63	47.61	46.86
x= 0.1	2.49	2.28	22.60	23.12	47.61	47.05
x= 0.2	5.00	4.86	20.09	19.78	47.61	47.20
x= 0.3	7.50	6.90	17.58	17.00	47.60	46.86
x= 0.4	10.00	9.58	15.07	14.86	47.62	47.89
x= 0.5	12.47	13.12	12.56	12.98	47.63	47.60
x= 0.6	15.50	16.35	10.05	9.57	47.63	46.98
x= 0.7	17.52	16.98	7.53	6.89	47.64	47.98
x= 0.8	20.00	19.57	5.02	4.89	47.64	48.23
x= 0.9	22.53	21.95	2.51	2.32	47.65	47.98
x= 1.0	25.03	24.38	-	-	47.65	47.10

3.4.2 Structural characterization of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites by powder XRD studies

The phase identification of all the synthesized 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples was done using powder XRD in the range from 20° - 80° and all the X-ray diffraction patterns are shown in Fig. 3.6. The diffraction peaks in the XRD patterns can be indexed to the (h, k, l) planes of the spinel viz. (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) validating the formation of monophasic cubic spinel structure without any impurities or secondary phases such as the $\alpha\text{-Fe}_2\text{O}_3$ phase [1, 9]. All the peaks matched precisely with the JCPDS card no. 01-088-380 which confirms the monophasic nature of the spinel for $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5$) ferrite.

Table 3.4 tabulates the lattice parameter (a), average crystallite sizes (D), measured density (d_m), theoretical density (d_x) and porosity (P) of the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites obtained from the powder XRD data. The lattice parameter was found to decrease with increase in nickel concentration which can be ascribed to Ni substitution which is having a smaller ionic size ($0.69 \text{ \AA}$) in comparison with Co ($0.74 \text{ \AA}$). The presence of pores in the ferrites is indicated by lower measured density as compared to the theoretical one [10, 11]. The average crystallite sizes in the ferrite samples vary in

the range of 16- 21 nm and it was observed that the average crystallite size decreases with increasing nickel concentration.

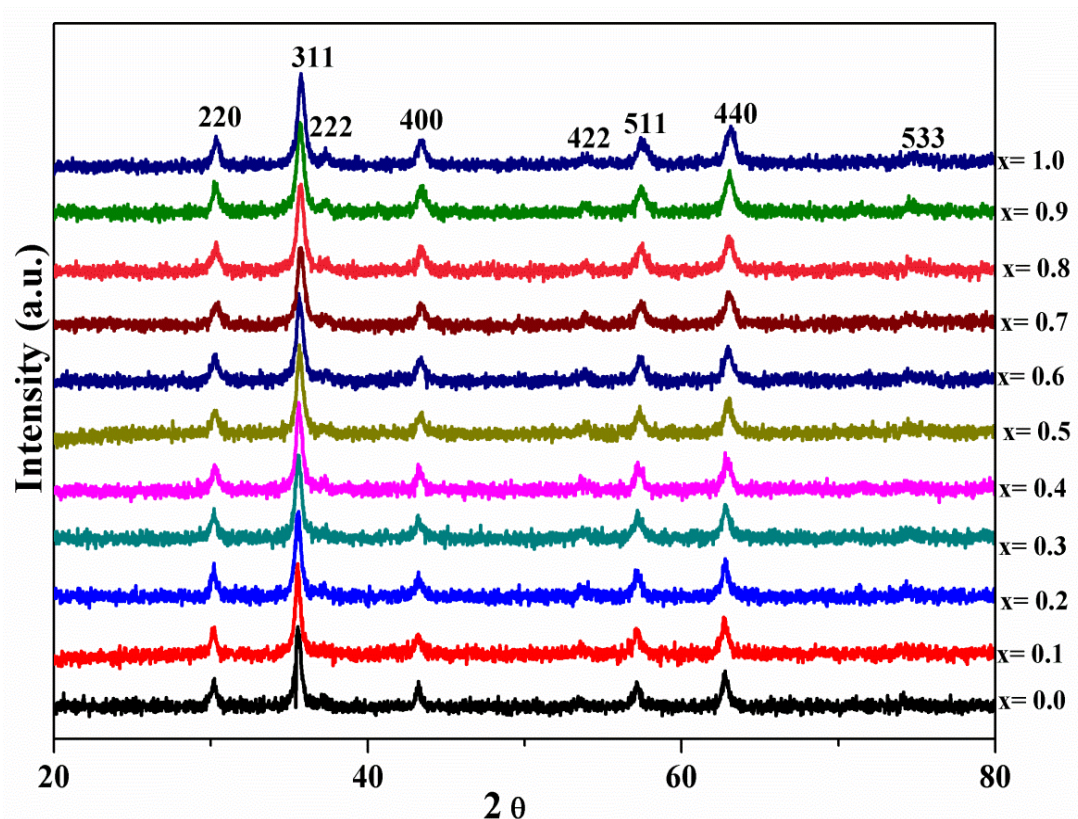


Fig. 3.6 The powder XRD patterns for the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Table 3.4 The lattice parameter (a), measured density (d_m), theoretical density (d_t) porosity (P) and average crystallite size (D) of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Composition (x)	Lattice parameter (a) Å	Measured density (g/cm^3)	Theoretical density (g/cm^3)	Porosity (%)	Average crystallite size (D) nm
0.0	8.3693	2.9047	5.3158	45.35	21
0.1	8.3757	2.8968	5.3031	45.37	20
0.2	8.3722	2.9348	5.3092	44.72	19
0.3	8.3666	2.9376	5.3205	44.78	18
0.4	8.3563	2.9102	5.3385	45.48	18
0.5	8.3488	2.8797	5.3523	46.19	16
0.6	8.3468	2.9196	5.3556.	45.48	16
0.7	8.3344	2.9582	5.3790	45.00	17
0.8	8.3376	2.9112	5.3723	45.81	17
0.9	8.3393	2.9610	5.3684	44.84	17
1.0	8.3282	2.9205	5.3898	45.81	15

3.4.3 Infra-red (IR) spectroscopy of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The room temperature infra-red spectra of all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were recorded in the frequency range between $350-4000\text{ cm}^{-1}$ and the IR plots are depicted in Fig. 3.7. The absorption band at higher frequency side ($\nu_1 \sim 600\text{ cm}^{-1}$) is due to $\text{M}_\text{A}\text{--O}$ stretching vibrations at the tetrahedral sites and the frequency band at a lower absorption value ($\nu_2 \sim 400\text{ cm}^{-1}$) is attributed to the $\text{M}_\text{B}\text{--O}$ stretching vibrations at the octahedral sites [4].

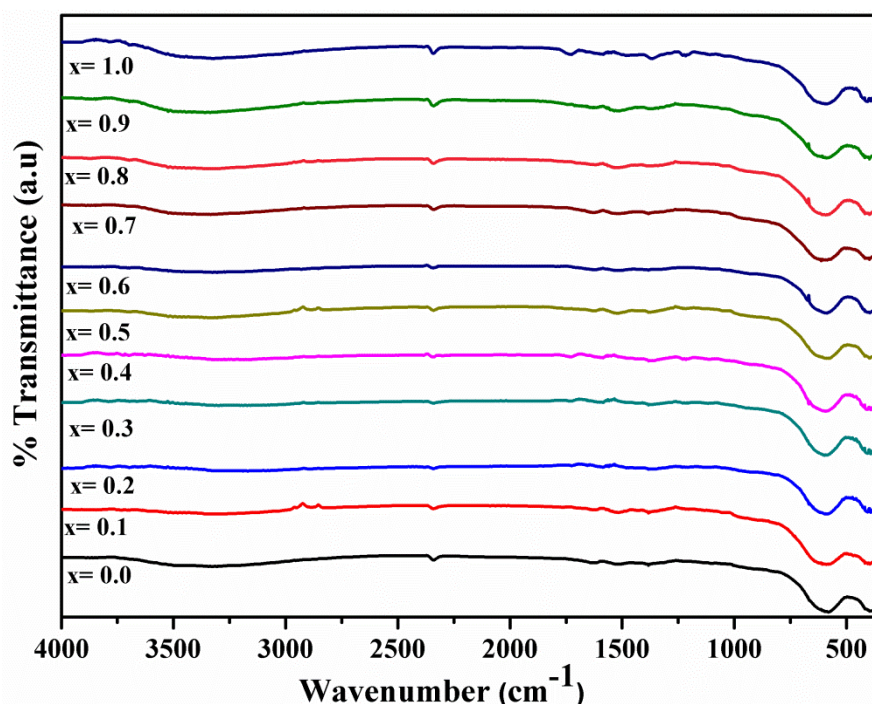


Fig. 3.7 The IR spectra of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Table 3.5 The ν_1 and ν_2 values in the IR spectra of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites.

Composition (x)	IR values of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites in cm^{-1}	
	ν_1	ν_2
0.0	581	396
0.1	583	394
0.2	587	390
0.3	591	401
0.4	593	387
0.5	594	395
0.6	596	397
0.7	597	398
0.8	599	401
0.9	601	396
1.0	603	402

The precise values of ν_1 and ν_2 have been tabulated in Table 3.5. It can be noted from the IR plots that the absorption peaks shift to a higher wavenumber with an increase in nickel content. This might be ascribed to Ni^{+2} ions prefer to occupy octahedral site in the spinel

lattice while Co^{+2} and Fe^{+3} ions have preferences for both tetrahedral and the octahedral sites. Thus, increasing Ni^{+2} content forces Fe^{+3} ions from octahedral site into the tetrahedral sites. Hence increase in the nickel content increases the bond strength at tetrahedral site which results in an increase in the ν_1 [12].

3.4.4 Raman spectroscopy of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Raman spectroscopy is used for the characterization of ferrites, since it is sensitive towards cation distribution and can reveal the extrinsic iron oxide phases like haematite and magnetite, thus assisting in differentiating the impurities, if present in the sample.

The Raman spectroscopic measurements of all the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites was recorded at room temperature from $100-800\text{ cm}^{-1}$ and the Raman plots are demonstrated in Fig. 3.8 (a and b). From the figures, it is observed that all the samples show five main peaks in the Raman spectra. The approximate values of all the peaks are depicted in Table 3.6. The substituted Ni–Co ferrite has a cubic mixed inverse ferrite structure with O_h^7 (Fd3m) symmetry space group and has 42 normal vibrational modes predicted from group theory, out of which five are Raman active modes (A_{1g} , E_g , $3T_{2g}$). The vibrational modes above 600 cm^{-1} can be assigned to the symmetrical stretching of metal–oxygen bonding at the tetrahedral (A) sites, and the vibrational modes below 600 cm^{-1} represent the symmetrical and asymmetrical bending of metal–oxygen in the octahedral (B) sites [13]. There is an absence of the impurity phase like $\alpha\text{-Fe}_2\text{O}_3$ which would show sharp spikes at around 240 and 300 cm^{-1} in the spectra, thus confirming the formation of the single phase ferrite compounds [14].

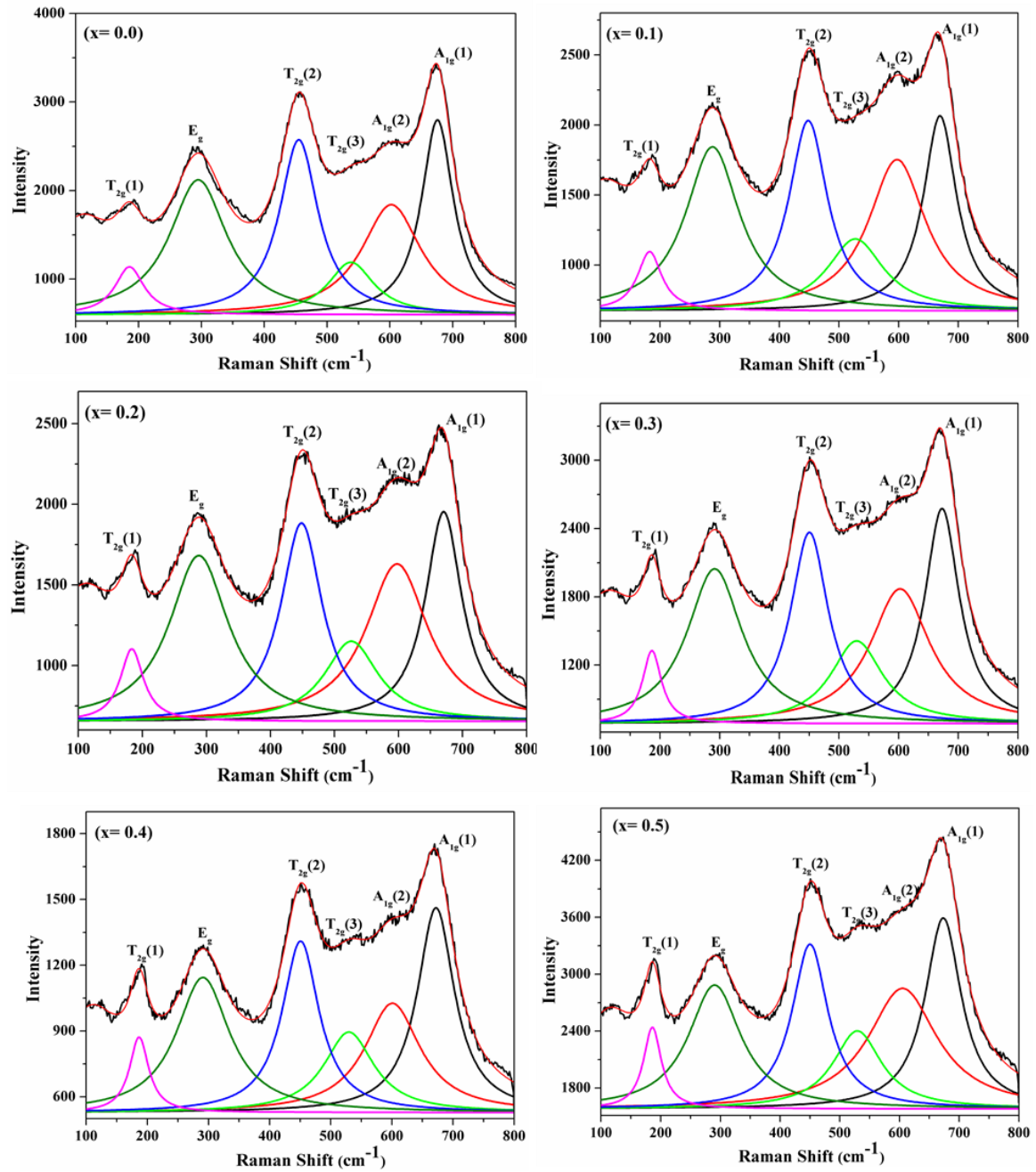


Fig. 3.8a The Raman spectra of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

The prominent band observed in the frequency range of 666-686 cm^{-1} is of A_{1g} symmetry and it is due to the symmetric stretching of the oxygen atom along the metal oxygen bond at the tetrahedral sites. The A_{1g} band has a shoulder to its left in the range from 603-623 cm^{-1} due to the mixed spinel nature of the ferrite samples. The E_g and T_{2g} (3) modes which arise at approximately 300 cm^{-1} and at around 535 cm^{-1} respectively are attributed to the symmetric and asymmetric metal-oxygen bond bending at the octahedral site [15].

T_{2g} (2) mode occurs due to the asymmetric metal-oxygen stretch at octahedral site and T_{2g} (1) band is due to translational motion of the cations and oxygen tetrahedral unit.

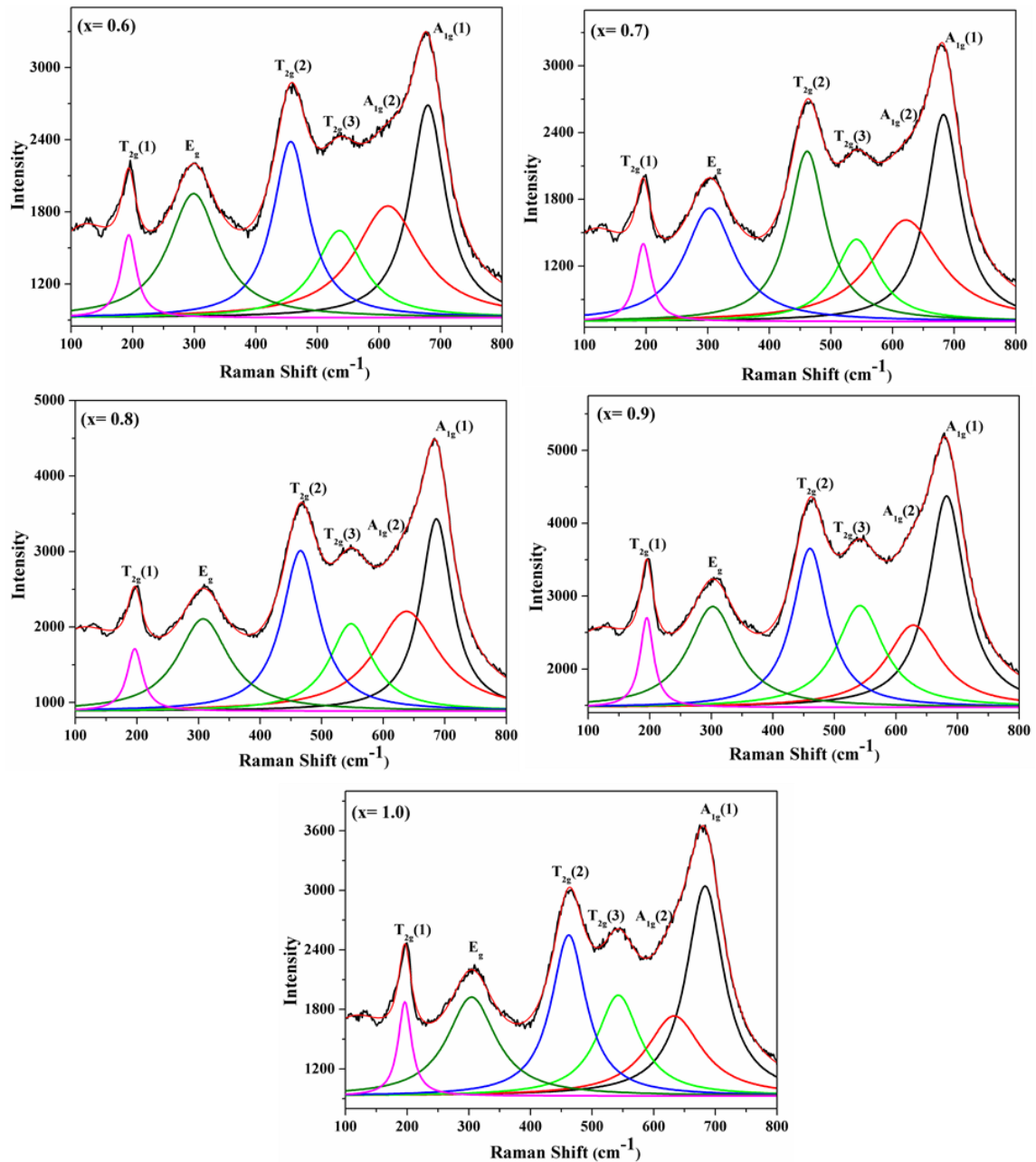


Fig. 3.8b The Raman spectra of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) ferrites

The presence of the crystalline disorder and the grain boundaries is represented by the Raman shift in the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites. The line broadening in Raman shift reported to be observed in polycrystalline materials which are due to restriction of optical phonons in small crystalline particles [16]. With the Ni^{2+} ion substitution there is a shift in Raman mode towards higher wavelength [14]. In a Raman spectrum the force constant of the bond is the major factor in determining the positions of

the bands [17]. Hence more is the force constant; the peaks will appear at a higher wavenumbers. With increase in the nickel substitution, the Ni^{2+} ions are introduced into the octahedral sites causing a Fe^{3+} ions shift in the tetrahedral sites in similar number thus replacing Co^{2+} ions in the tetrahedral sites. There is an increase in $\text{Fe}^{3+}-\text{O}^{2-}$ bond strength at the tetrahedral sites due to smaller sizes of the Fe^{3+} ions. This leads to increasing force constant of bond (at the tetrahedral site) thus showing a shift in the peak positions to higher wavenumbers.

Table 3.6 The Raman values of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites.

Composition (x)	$A_{1g}(1) \text{ cm}^{-1}$	$A_{1g}(2) \text{ cm}^{-1}$	$T_{2g}(3) \text{ cm}^{-1}$	$T_{2g}(2) \text{ cm}^{-1}$	$E_g \text{ cm}^{-1}$	$T_{2g}(1) \text{ cm}^{-1}$
0.0	667	603	529	450	288	185
0.1	666	605	531	451	290	187
0.2	666	607	533	451	292	188
0.3	670	609	534	452	293	190
0.4	674	609	535	453	293	193
0.5	676	611	536	454	295	194
0.6	679	614	538	457	299	195
0.7	681	615	540	463	303	198
0.8	682	618	542	465	305	199
0.9	683	622	543	466	308	200
1.0	686	623	546	467	310	202

3.4.5 X-ray photoelectron spectroscopy (XPS) of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

XPS is a surface characterization method by the virtue of which oxidation states of the elements can be found out along with their chemical compositions after determining the binding energies of the samples. XPS studies confirmed the oxidation states of all elements of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. The full survey scan range was calibrated (charge corrected) as designated for the carbon 1s peak possessing at a fixed value of 284.8 eV and later deconvolution of the spectra was done. The deconvoluted core level XPS spectra for all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ samples, were plotted using the XPS PEAK 41 software of the elements Ni 2p, Co 2p, Fe 2p, and O 1s and are illustrated in Fig. 3.9 ($x = 0.0$), Fig 3.10 ($x = 0.3$), Fig. 3.11 ($x = 0.6$), Fig. 3.12 ($x = 0.8$) and Fig.3.13 ($x = 1.0$). The binding energies of all the elements are tabulated in Table 3.7.

From the deconvoluted spectra of Ni 2p, the two major peaks at the binding energies of ~ 855 eV and ~ 872 eV are for Ni $2p_{3/2}$ and Ni $2p_{1/2}$ respectively in the ferrite samples [18, 19]. The satellite peaks at ~ 861 eV and at ~ 879 eV analogous to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ respectively verify that nickel is in 2+ oxidation state [20]. Moreover, the possibility of formation of NiO is eliminated since there is no satellite peak (1.2 eV) with the main peak which is a feature of NiO [21]. The deconvoluted spectra of Co 2p show two peaks at the binding energies of ~ 795 eV and ~ 780 eV, for Co $2p_{1/2}$ and Co $2p_{3/2}$ respectively thus confirm that cobalt is present in its divalent state [22, 23]. Additionally, the intense satellite peaks at ~ 786 eV and ~ 803 eV are in agreement with cobalt appearing in 2+ oxidation states [24]. All the ferrites under study have a satellite at ~ 6 eV that indicates presence of high spin Co^{2+} . Generally, in case of low spin $\text{Co}^{2+}/\text{Co}^{3+}$ compounds there is no satellite peak around ~ 6 eV while the high spin samples have a very strong satellite peak [25].

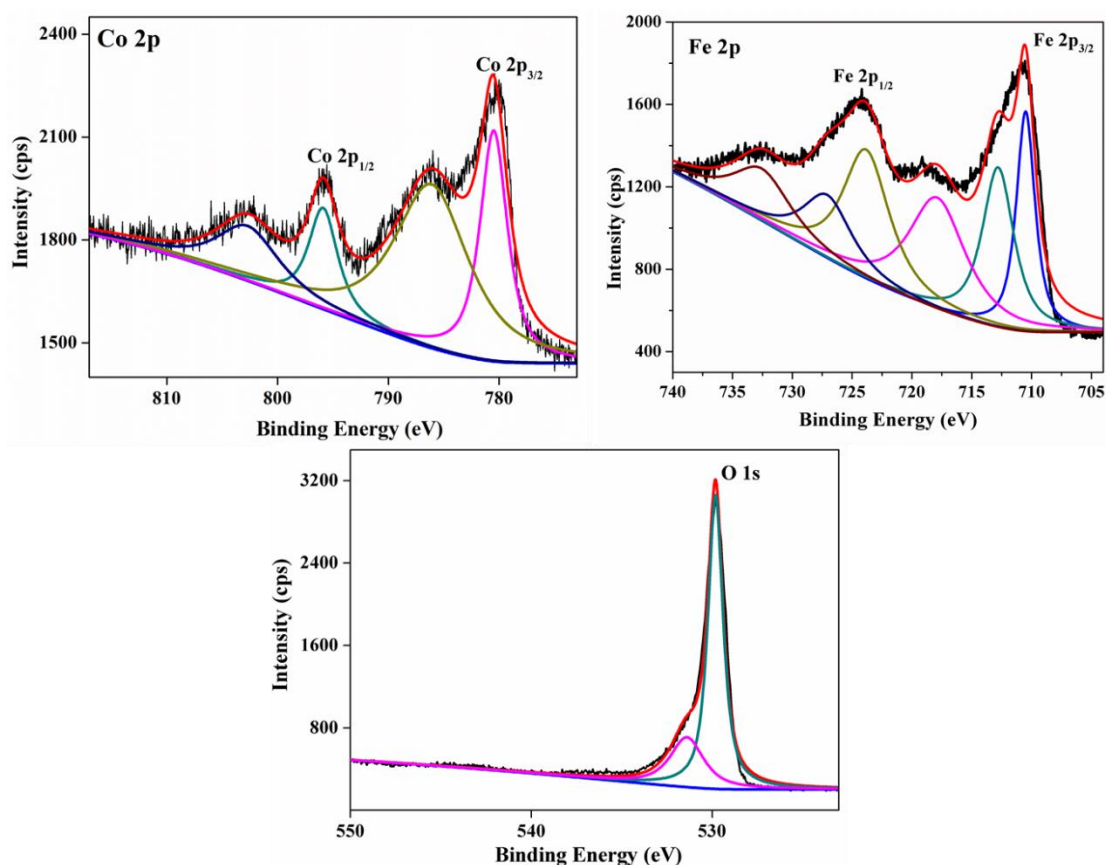


Fig. 3.9 High resolution deconvoluted XPS spectra corresponding to Co 2p, Fe 2p and O 1s of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0$) ferrite.

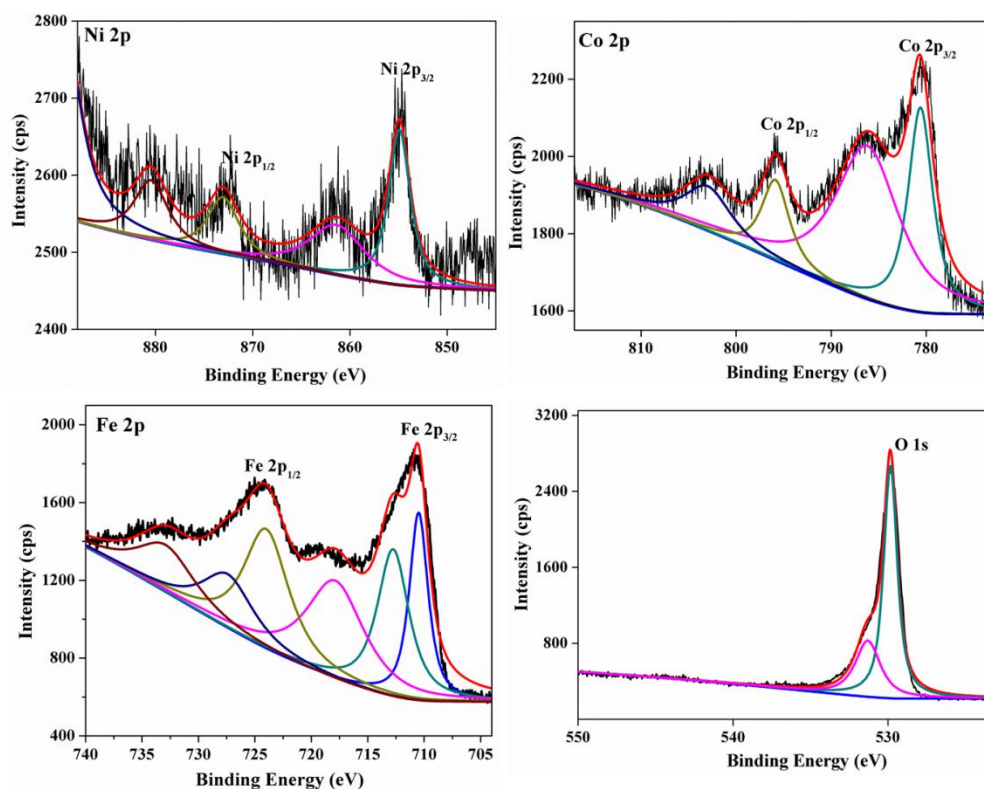


Fig. 3.10 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p and O 1s of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.3$) ferrite.

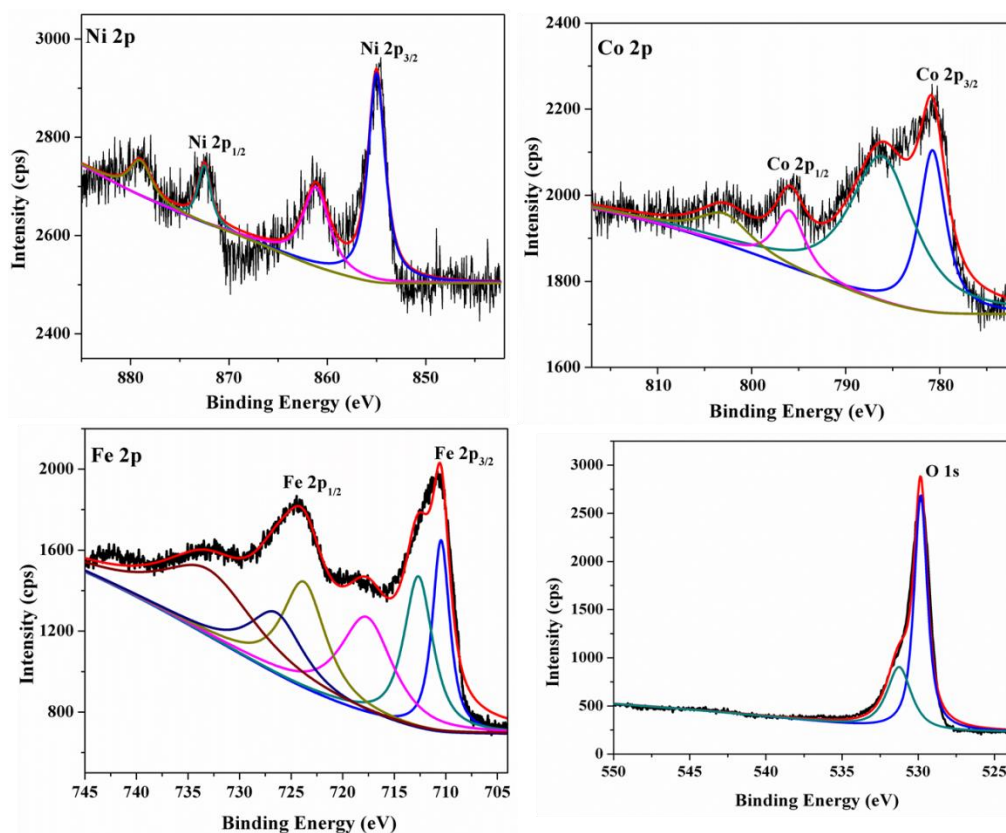


Fig. 3.11 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p and O 1s of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6$) ferrite.

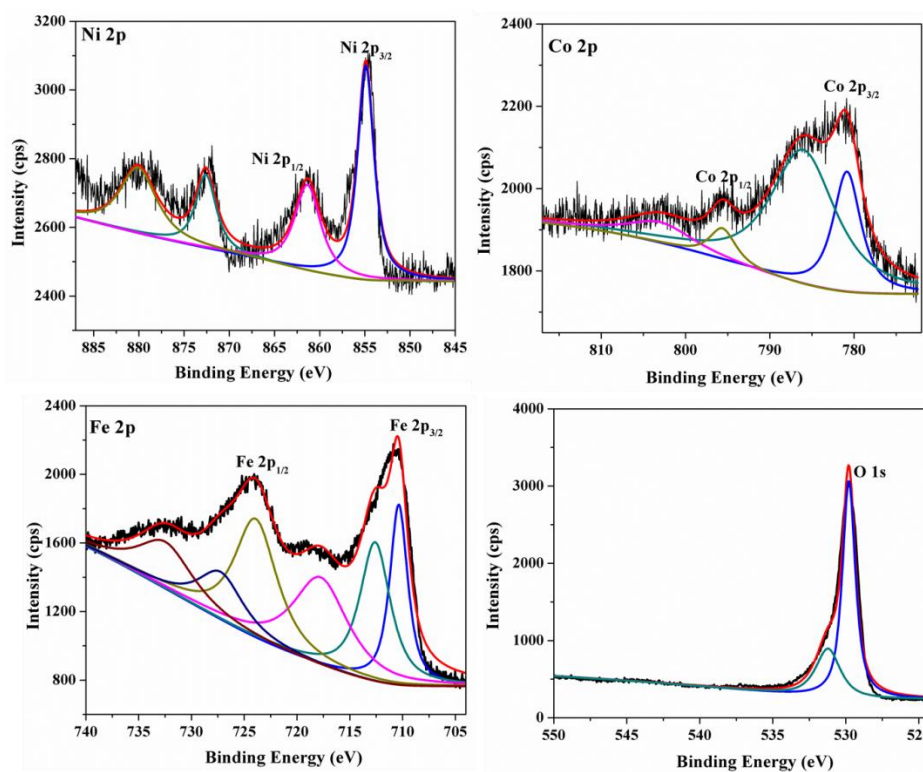


Fig. 3.12 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p and O 1s of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.8$) ferrite.

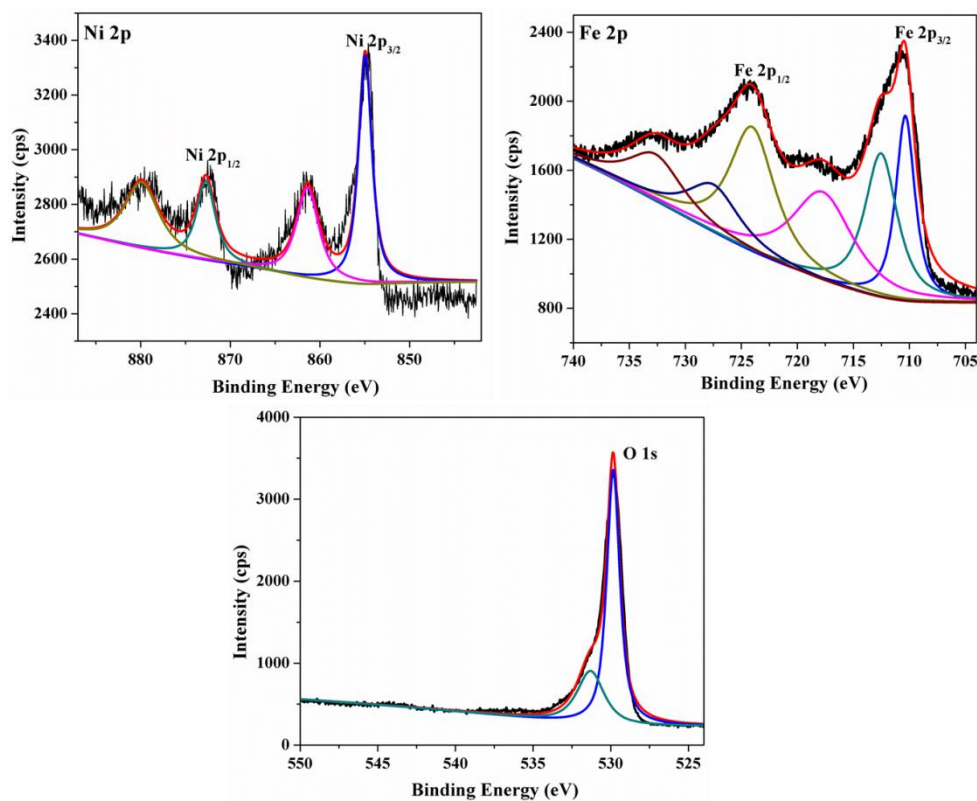


Fig. 3.13 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Fe 2p and O 1s of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 1.0$) ferrite.

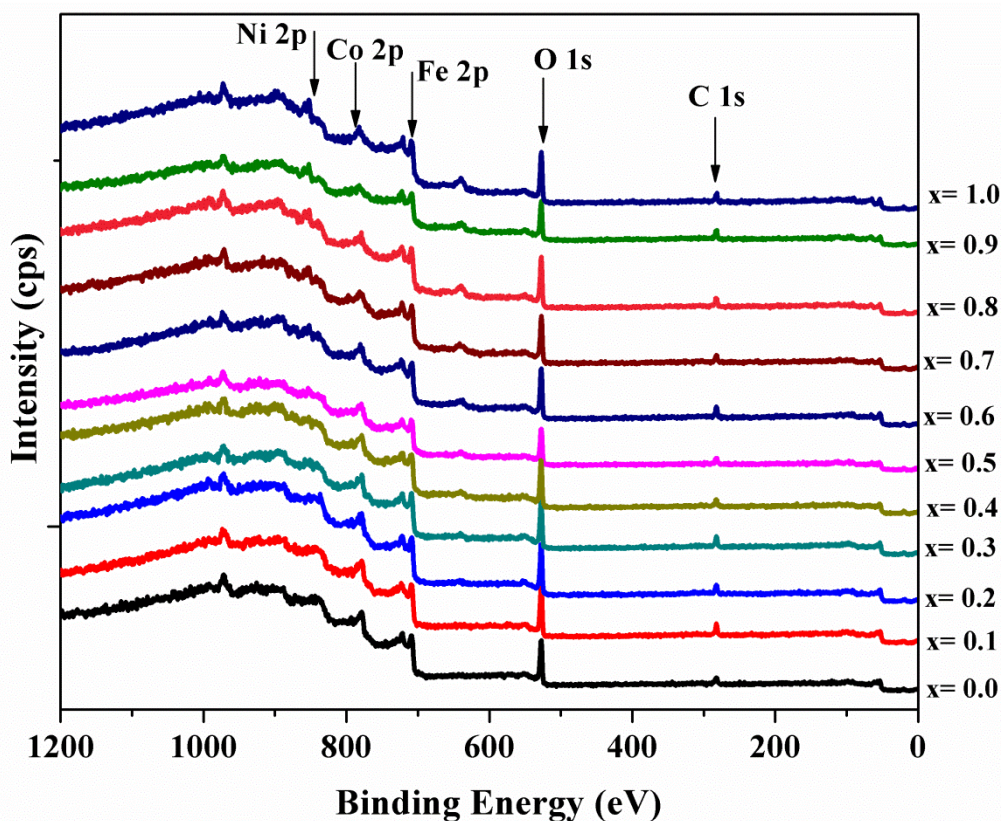


Fig. 3.14 The full scan XPS spectra of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

The Fe 2p XPS spectra of all the ferrite samples show two peaks with binding energies approximately 724 and at ~ 710 eV which accredits respectively to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ [21, 26]. A satellite peak is seen at ~ 718 eV which appears at a binding energy 8 eV higher than Fe $2p_{3/2}$, thus confirming Fe in $3+$ oxidation state [27]. The peaks nearly at 710 eV and at 724 eV validate Fe^{3+} distribution in the octahedral sites while the peaks approximately at 712 and 726 eV are due to tetrahedral occupancy of iron [28, 29]. Similarly, the Fe $2p_{1/2}$ peak is ascribed to the ionic state of Fe^{3+} ions which exhibits a satellite peak at the binding energy of ~ 732 eV [30]. The XPS core level spectra for O 1s shows a peak at ~ 529 eV (main peak) which is assigned to lattice oxygen contribution whereas the shoulder peak at ~ 531 eV is due to low coordination of the lattice oxygen which implies defects in the structure or due to surface adsorbed oxygen [28, 30].

The full scan XPS spectra of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites are given in Fig. 3.14.

Table 3.7 The binding energies of all the elements got from deconvolution of XPS peaks of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Compositions (x)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Ni 2p _{3/2}	-	854.8	854.7	855.0	854.8	855.2	855.6	855.1	855.4	855.7	855.6
Satellite	-	861.4	860.6	861.6	861.3	860.8	861.1	860.6	861.3	861.4	860.9
Ni 2p _{1/2}	-	871.9	872.4	872.8	872.8	871.8	872.4	872.8	872.8	872.0	872.5
Satellite	-	879.8	880.1	880.6	879.0	879.8	880.0	880.3	879.0	879.9	880.2
Co 2p _{3/2}	780.5	780.7	780.5	780.7	780.7	780.8	780.7	780.2	780.4	780.5	-
Satellite	786.2	786.3	785.7	786.3	786.2	786.5	786.1	785.9	786.5	786.6	-
Co 2p _{1/2}	795.9	796.0	795.8	795.9	795.8	795.9	796.1	795.7	795.8	795.5	-
Satellite	802.8	802.9	802.8	803.2	802.9	802.7	803.0	802.7	803.1	802.6	-
Fe 2p _{3/2} (oct)	710.5	710.6	710.4	710.4	710.5	710.6	710.4	710.3	710.2	710.6	710.7
Fe 2p _{3/2} (tetra)	712.6	712.8	712.5	713.0	712.6	712.5	712.6	712.7	713.1	712.5	712.6
Satellite	717.9	717.9	718.4	718.1	718.0	718.0	718.2	718.4	718.3	718.0	718.1
Fe 2p _{1/2} (oct)	724.6	724.8	724.3	724.8	724.6	724.5	724.7	724.2	724.6	724.7	724.5
Fe 2p _{1/2} (tetra)	726.4	727.0	726.8	726.5	726.9	726.4	727.1	726.7	726.6	726.5	726.3
Satellite	732.3	732.7	732.4	732.6	732.5	732.6	732.8	732.2	732.8	732.4	732.2
O 1s (lattice)	529.8	529.8	529.7	529.8	529.7	529.9	530.0	530.0	529.7	529.6	529.9
O 1s (surface)	531.4	531.3	531.2	531.3	531.3	531.3	531.2	531.1	531.4	531.2	531.3

3.4.6 Surface area characteristics of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.4.6.1 Brunauer-Emmett-Teller (BET) surface area measurements of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The surface area measurements of all the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite nanoparticles were performed using the multipoint (20 points) Brunauer-Emmett-Teller (BET) surface area measurements. Principally the surface of the nanoparticles reacts with its surrounding and large surface area adsorbs more gaseous molecules improving many catalytic performances [31]. Larger the surface area of the nanoparticles more is the adsorption area for the oxygen molecules and the reacting target gas. The surface area, total pore volume and average pore sizes of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples were measured by recording their nitrogen adsorption-desorption isotherms. The N_2 adsorption-desorption isotherms of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites are depicted in Fig. 3.15 and isotherms of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) are shown in the Fig. 3.16 and the exact values of the surface area, total pore volume and average pore sizes are tabulated in Table 3.8.

Usually, any porous material is categorized on the basis of its pore structure. If the pore diameter is less than 2 nm it is microporous, if the pore diameter is in between 2-50 nm, it is said to be mesoporous and if it is more than 50 nm then it is macroporous. All the isotherms above are categorized as type IV isotherms as per the IUPAC classifications which possess a distinct H3 type broad hysteresis loop which implies mesoporous nature of the nanoparticles having a narrow slit shaped pores [31, 32]. The initial hysteresis part comprises of monolayer-multilayer adsorption at low relative pressures followed by the pore filling mechanism (capillary condensation) and later reaching saturation at higher relative pressures [32]. The surface area of the ferrite samples was found to be in the range of $24-32 \pm 1 \text{ m}^2/\text{g}$. The surface area for the samples was found to increase with nickel substitution and the average pore size and the total pore volume was found to decrease.

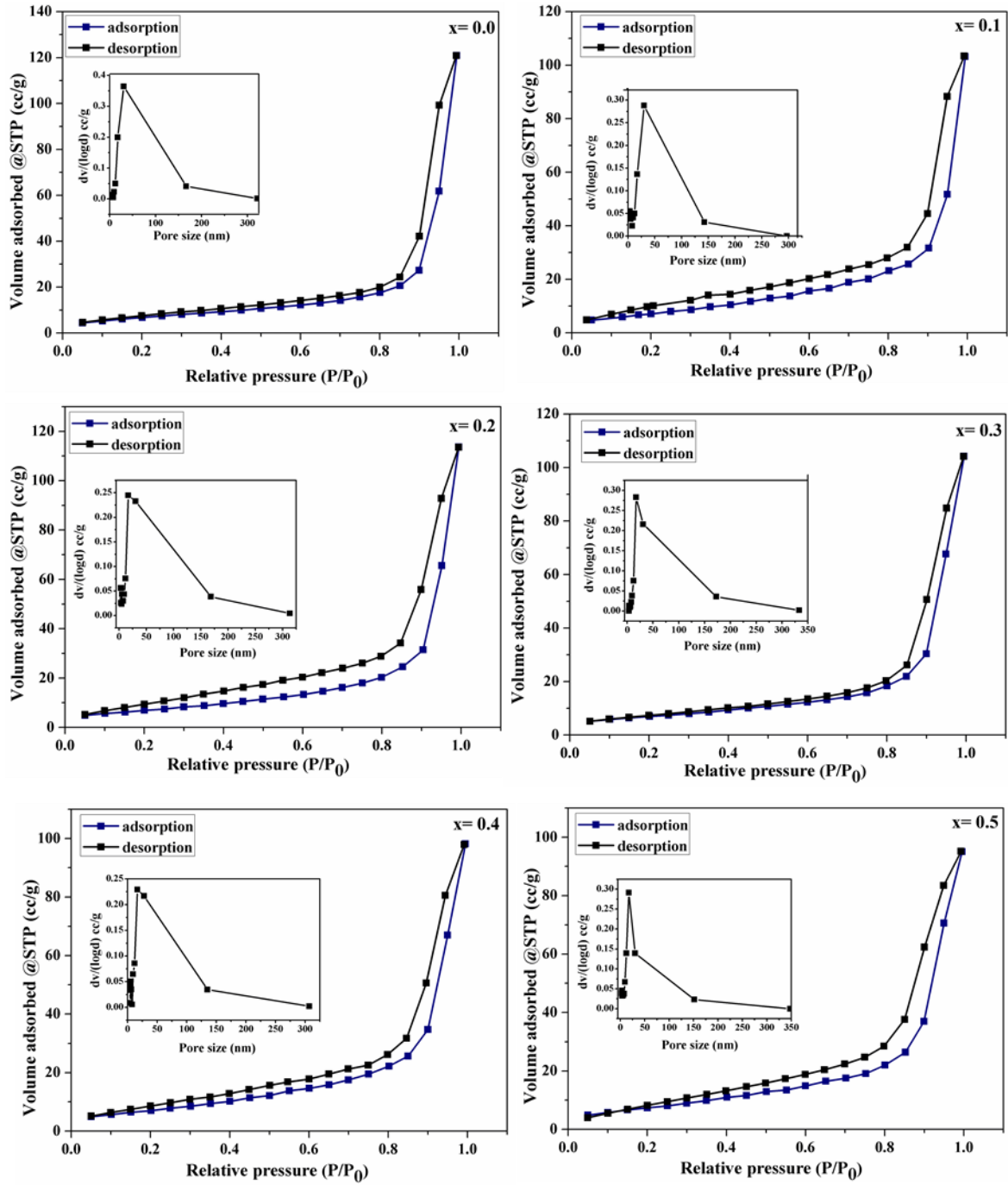


Fig. 3.15 The N₂ adsorption-desorption isotherms of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites [Inset figure: plot of $[dv/d(\log d)]$ cc/g against pore size (nm)].

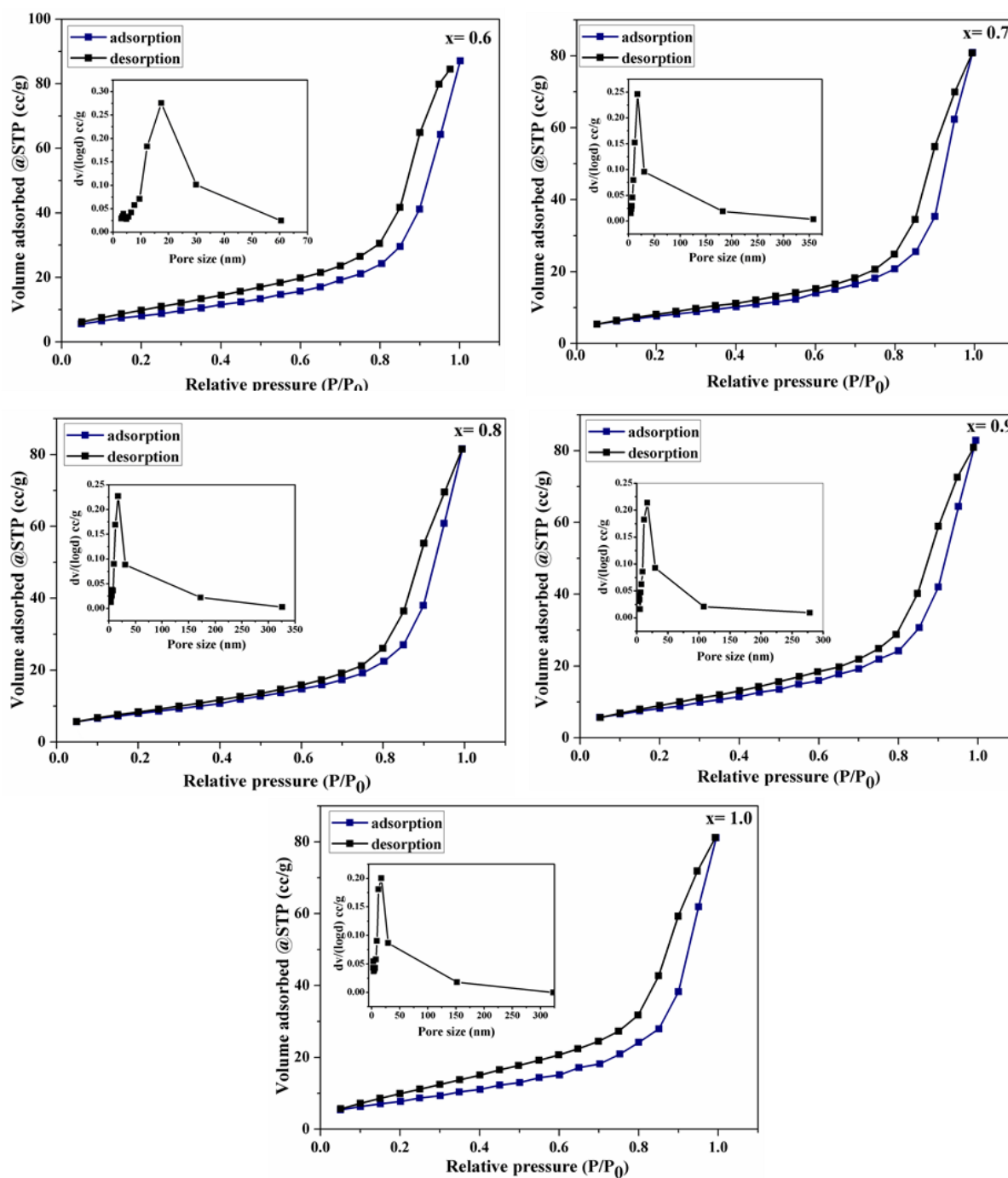


Fig. 3.16 The N₂ adsorption-desorption isotherms of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) ferrites [Inset figure: plot of $[dV/d(\log d)]$ cc/g against pore size (nm)].

Table 3.8 BET surface area, average pore sizes and the pore volumes of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Composition (x)	BET surface area (m^2/g) $\pm 1 \text{ m}^2/\text{g}$	Average pore size (nm)	Total pore volume (cc/g)
0.0	26.10	31.00	0.187
0.1	27.85	29.00	0.159
0.2	26.06	24.00	0.175
0.3	24.85	18.00	0.161
0.4	27.00	18.00	0.152
0.5	26.80	18.00	0.147
0.6	29.50	17.00	0.134
0.7	30.00	17.00	0.125
0.8	31.50	18.00	0.126
0.9	31.00	16.00	0.128
1.0	30.00	15.00	0.125

3.4.6.2 Acid base properties by temperature programmed desorption (NH_3 -TPD) and (CO_2 -TPD)

The surface acidity of all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples was ascertained by the NH_3 -temperature programmed desorption studies and the plots are shown in Fig. 3.17. Four peaks are observed in the NH_3 desorption profile which shows NH_3 evolution in four distinct regions. The first small peak is observed at $\sim 97-150^\circ\text{C}$ for all the ‘as prepared’ ferrite samples. The second peak (prominent) is at around $340-440^\circ\text{C}$ for all samples, followed by a third peak which is a small hump at $\sim 480-500^\circ\text{C}$. The final prominent peak is roughly in the range from $574-620^\circ\text{C}$. The peak $\sim 97-150^\circ\text{C}$ can be assigned to the weakly adsorbed ammonia which requires lesser energy to desorb from the ferrite surface. The two peaks at $\sim 480-500^\circ\text{C}$ and a small hump from $574-620^\circ\text{C}$ can be attributed to existence of medium acidic sites in the ferrite samples. However the last peak at a higher temperature reveal strongly adsorbed NH_3 molecules which require more energy to desorb from the surface [33, 34]. NH_3 desorption at lower temperatures is considered as Bronsted (weak acidic) sites and that at a higher temperature are the Lewis (strong acidic) sites [35].

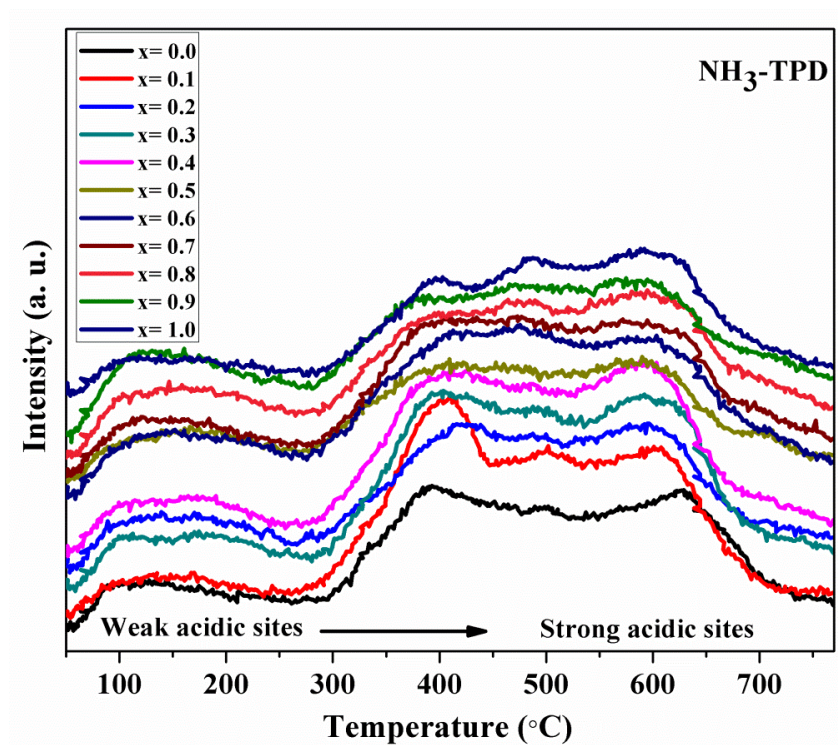


Fig. 3.17 NH_3 -temperature programmed desorption profiles of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

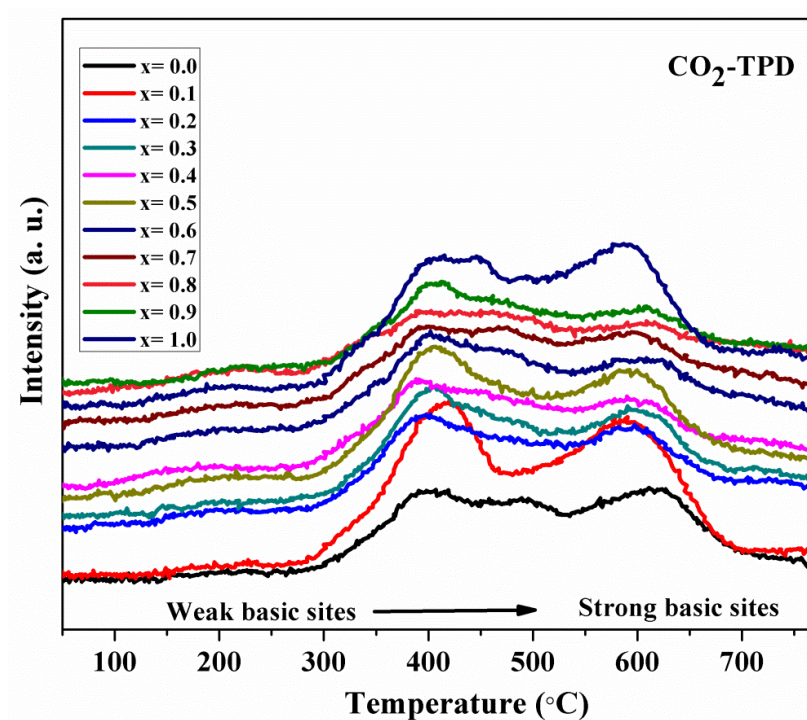


Fig. 3.18 CO_2 -temperature programmed desorption profiles of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

The strength of the basic sites (related to CO_2 desorbed) on all the magnetic ferrites was found out by CO_2 temperature programmed desorption studies. The typical CO_2 desorption profiles are depicted in Fig. 3.18. Three peaks are observed for all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) in the present case referring to presence of medium basic active sites and strong basic sites. The first peak identified at $\sim 380-410^\circ\text{C}$ is due to the presence of medium basic sites which is followed by a small hump at $\sim 440-470^\circ\text{C}$. The prominent peak at $\sim 560-620^\circ\text{C}$ accredits to desorption of CO_2 gas from strong basic site [35, 36].

From NH_3/CO_2 –TPD it was concluded that all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite nanoparticles have strong, medium, weak acidic sites and medium and strong basic sites that are advantageous for any application [37].

3.4.7 Morphological studies of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.4.7.1 Scanning Electron microscopy (SEM) studies of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The SEM micrographs of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites are represented in the Fig. 3.19, Fig. 3.20 and Fig. 3.21. The SEM images revealed that the particles are nanosized in nature, nearly spherical in shape and they occur as agglomerated lumps. The large amount of gases generated during the combustion reduced considerable agglomeration leading to the nanosized nature of the particles which resulted in porous materials [38]. The agglomeration of the particles can also be ascribed to high surface area and strong magnetism of the nanoparticles [39].

The presence of the corresponding metal ions on the surface of the ferrites is also confirmed from the EDX spectra without any impurity element peak. From the EDAX spectra a decrease in intensity of cobalt peak and an increase in the intensity of nickel peak is clearly observed with increasing nickel concentration. The remaining unmarked peaks in the EDAX spectra are basically due to the sputtering of the noble metals Au during sample preparation.

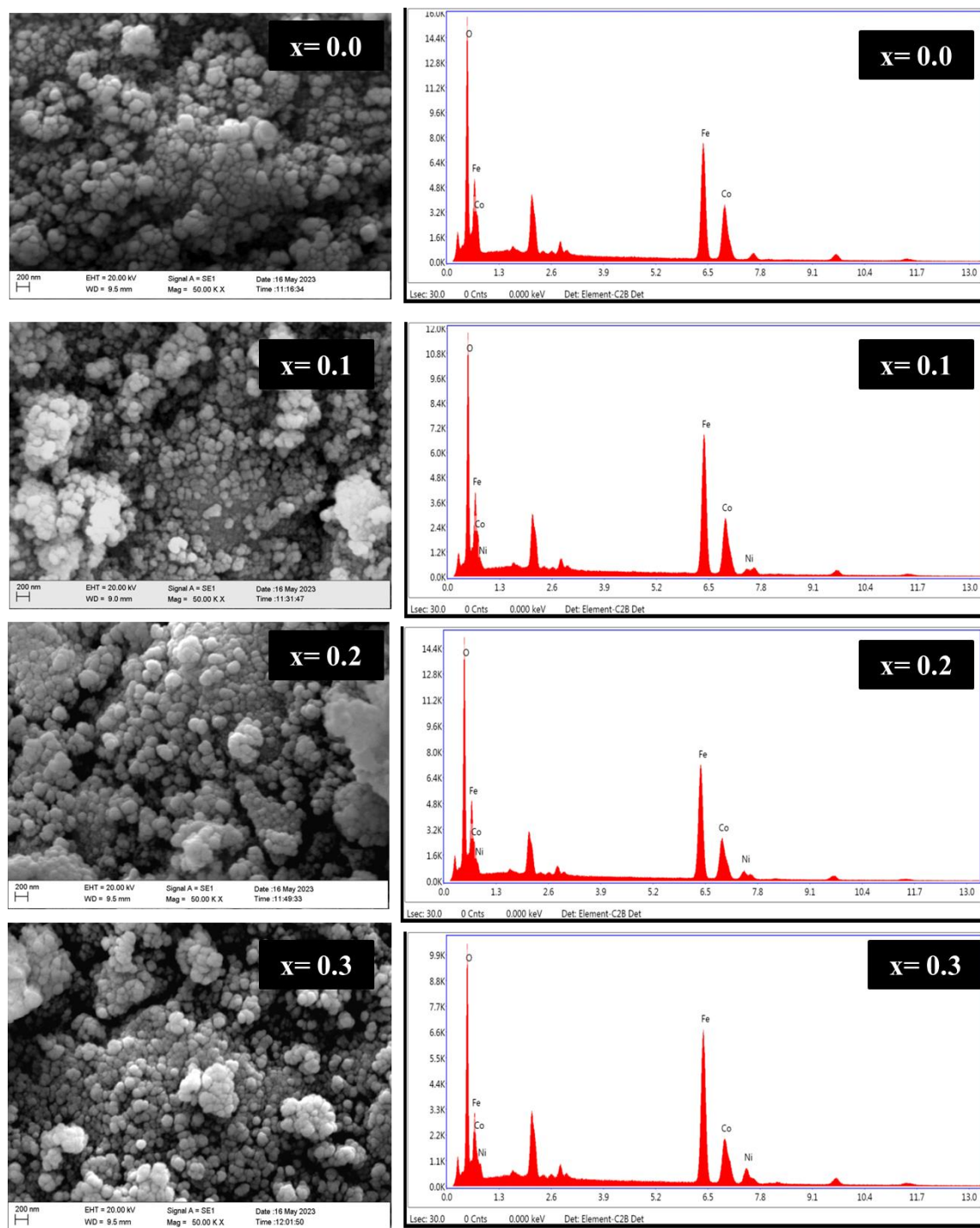


Fig. 3.19 The SEM micrograph and EDAX spectra of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.3$) ferrites.

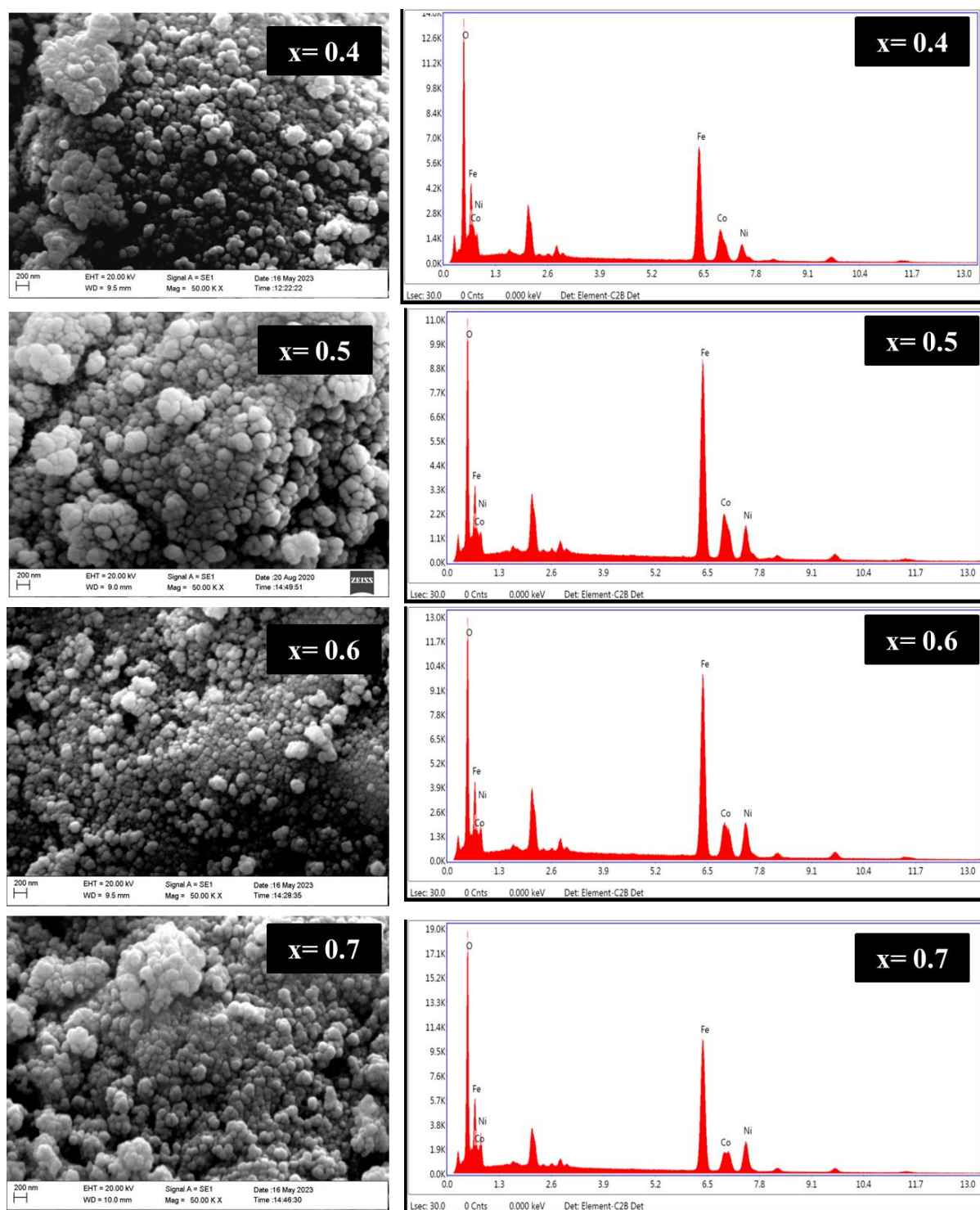


Fig. 3.20 The SEM micrograph and EDAX spectra of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.4-0.7$) ferrites.

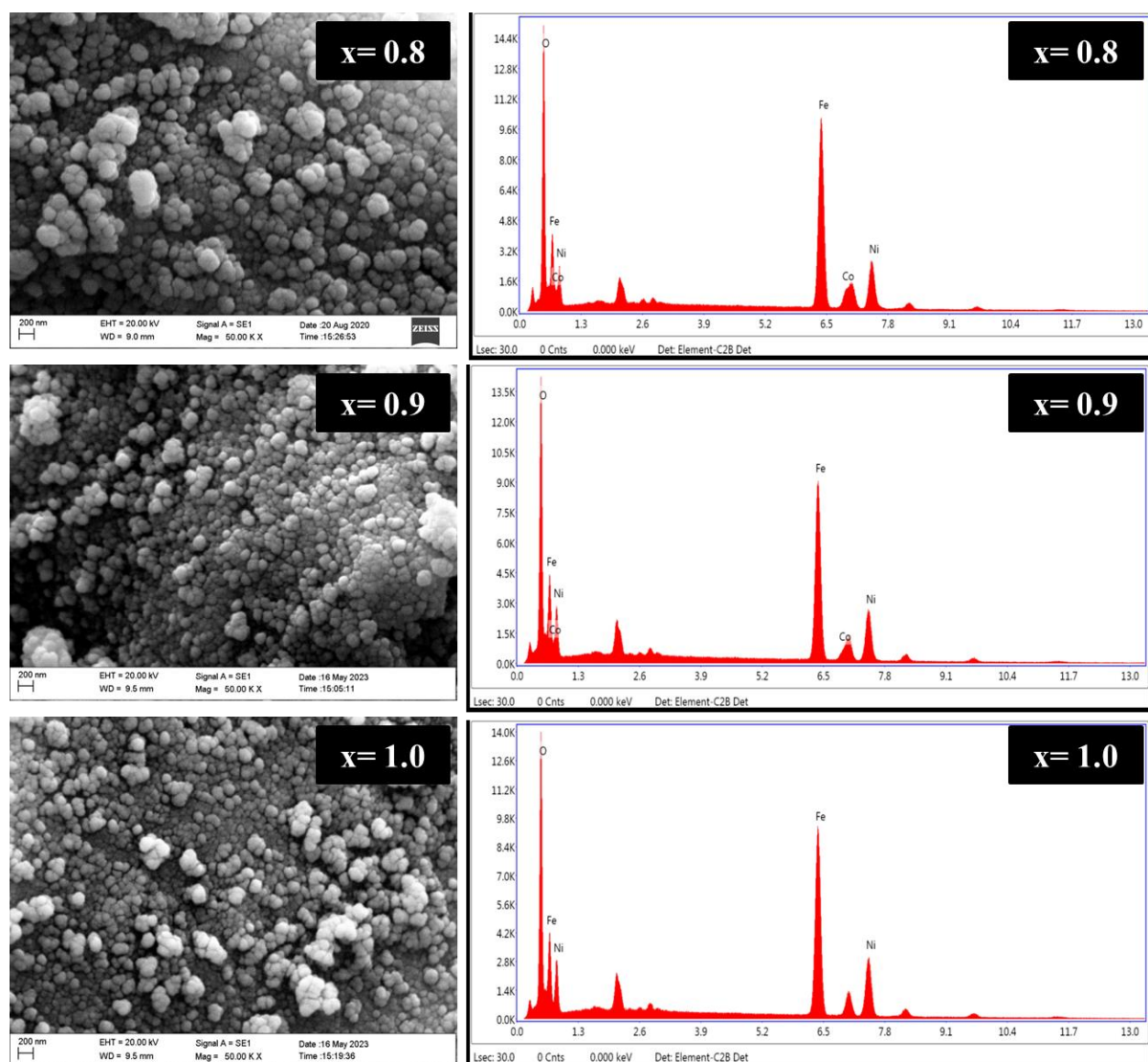


Fig. 3.21 The SEM micrograph and EDAX spectra of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.8-1.0$) ferrites.

3.3.7.2 High Resolution Transmission Electron microscopy (HR-TEM) studies of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The HR-TEM images of all the as prepared $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples along with their SAED patterns are displayed in the Fig. 3.22 and Fig. 3.23. From the figures it is concluded that the particles are nearly cuboidal to distorted hexagonal in shape which are bound together or exists as agglomerates [40].

The SAED patterns having obvious concentric rings for all compositions are indexed with bright spot in the diffraction pattern thus confirming the nanocrystalline behaviour of the nanoparticles [41, 42]. The brightest spot is for the highest intensity peak (3 1 1).

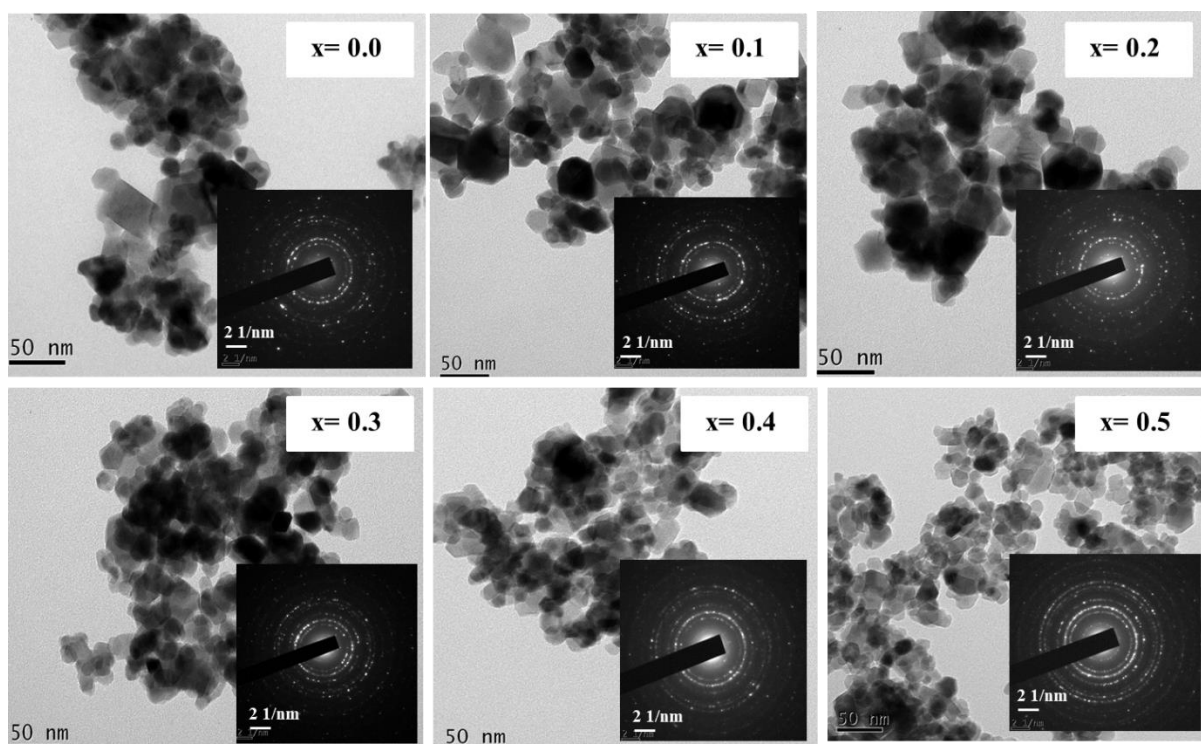


Fig. 3.22 The HR-TEM micrographs and SAED patterns of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

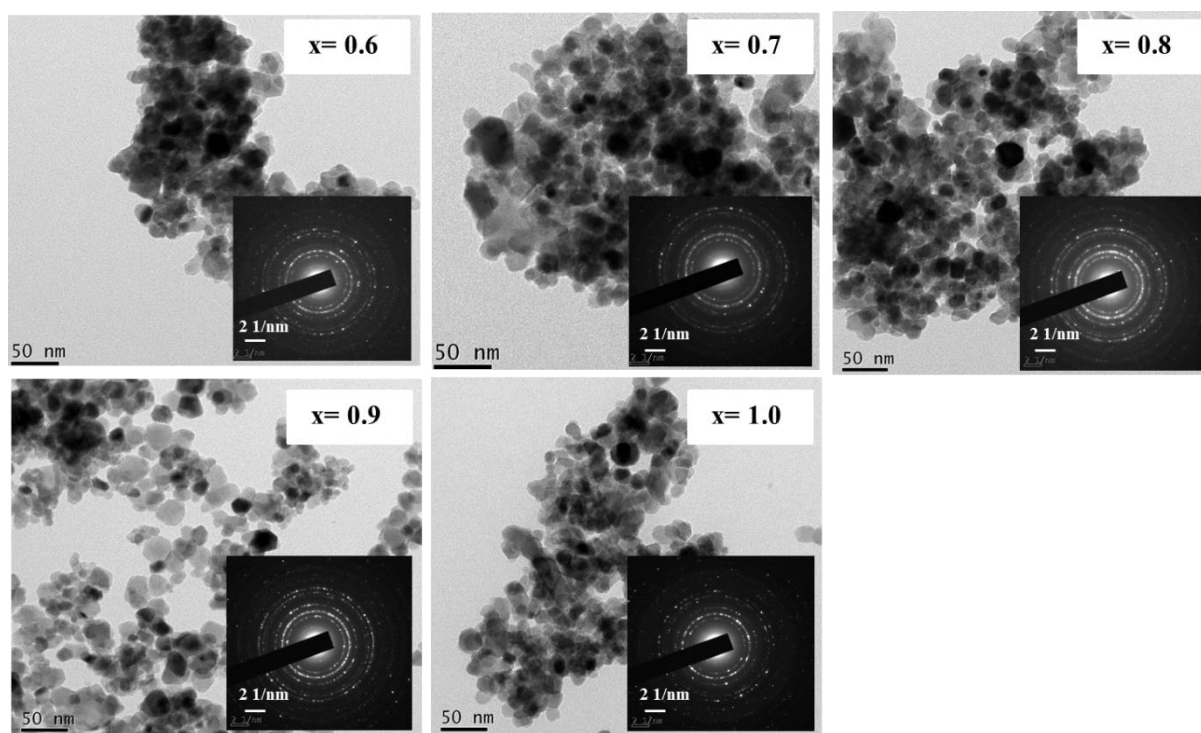


Fig. 3.23 The HR-TEM micrographs and SAED patterns of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) ferrites.

3.5 Solid state studies of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.5.1 DC resistivity studies of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The electrical resistivity of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites samples was examined by the two probe resistivity setup at from room temperature to 500 °C and the plots for heating and cooling are shown in Fig. 3.24. The electrical property of ferrites depends on various factors like the grain sizes, chemical compositions, porosity of the samples, density etc. which directly or indirectly affect this property [43, 44]. From the plots, the resistivity was found to decrease with increase in the temperature which indicates the semiconducting nature of the ferrite samples. All the samples show variation in resistivity with temperature for three zones; the first being at lower temperature is mainly due to any impurities, voids and adsorbed species, the second zone is due to ferrimagnetic region and the third region is the random paramagnetic region [45-47].

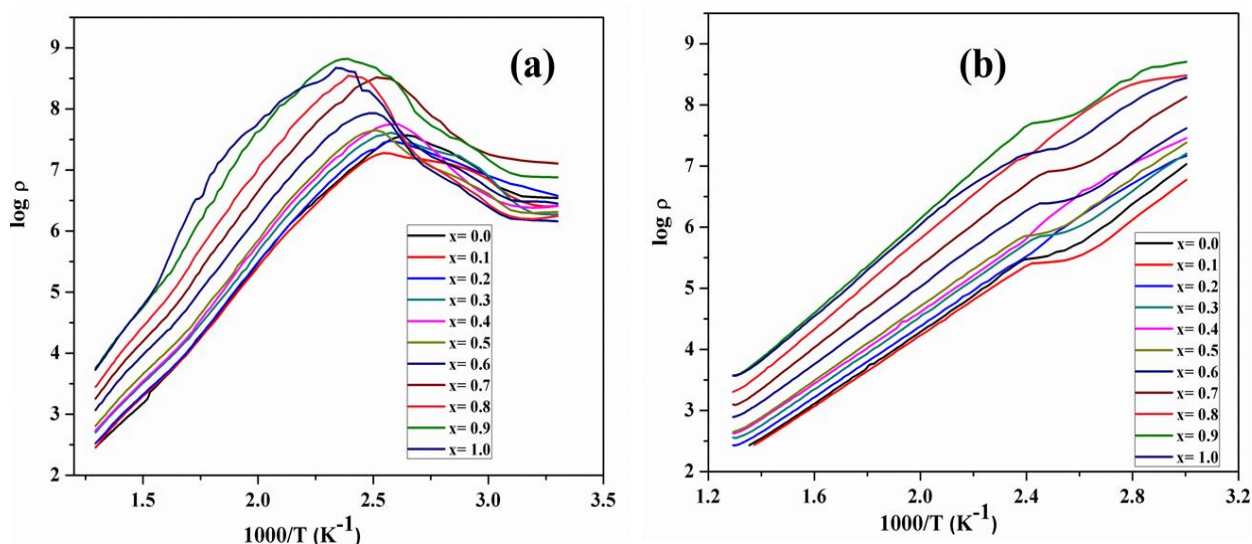


Fig. 3.24 The dc resistivity against $1000/T$ (K^{-1}) plots of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites during (a) Heating and (b) Cooling.

The DC resistivity measurements are done to find out the conduction mechanism which is shown by ferrites. As per the Verwey model, the conduction mechanism is as a result of electron hopping between ions of same element in different oxidation states. In case of the second region, the ordered alignment allows easy electron hopping hence needing lesser activation energy. For the paramagnetic region the irregular spin orientation requires large energy to move electrons from one ion to another, thus requiring larger activation energy [48]. From the plots it was observed that the resistivity decreases with an increase in the Cobalt content. This decrease in resistivity with increase in the cobalt content is attributed to difference in ionic size of the cations. The addition of Co^{+2} ions distorts the ferrite lattice as

they have higher ionic sizes than Ni^{+2} and Fe^{+3} ions. The distortion causes the changes in the resistivity as Co^{+2} content increases [11].

3.5.2 Dielectric properties of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.5.2.1 Dielectric measurements as a function of frequency for the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The dielectric properties for all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were performed at room temperature at frequency from 20 Hz to 10 MHz. Fig. 3.25a and Fig. 3.25b depict the dielectric constant (ϵ') and the dielectric loss tangent ($\tan \delta$) for the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites respectively.

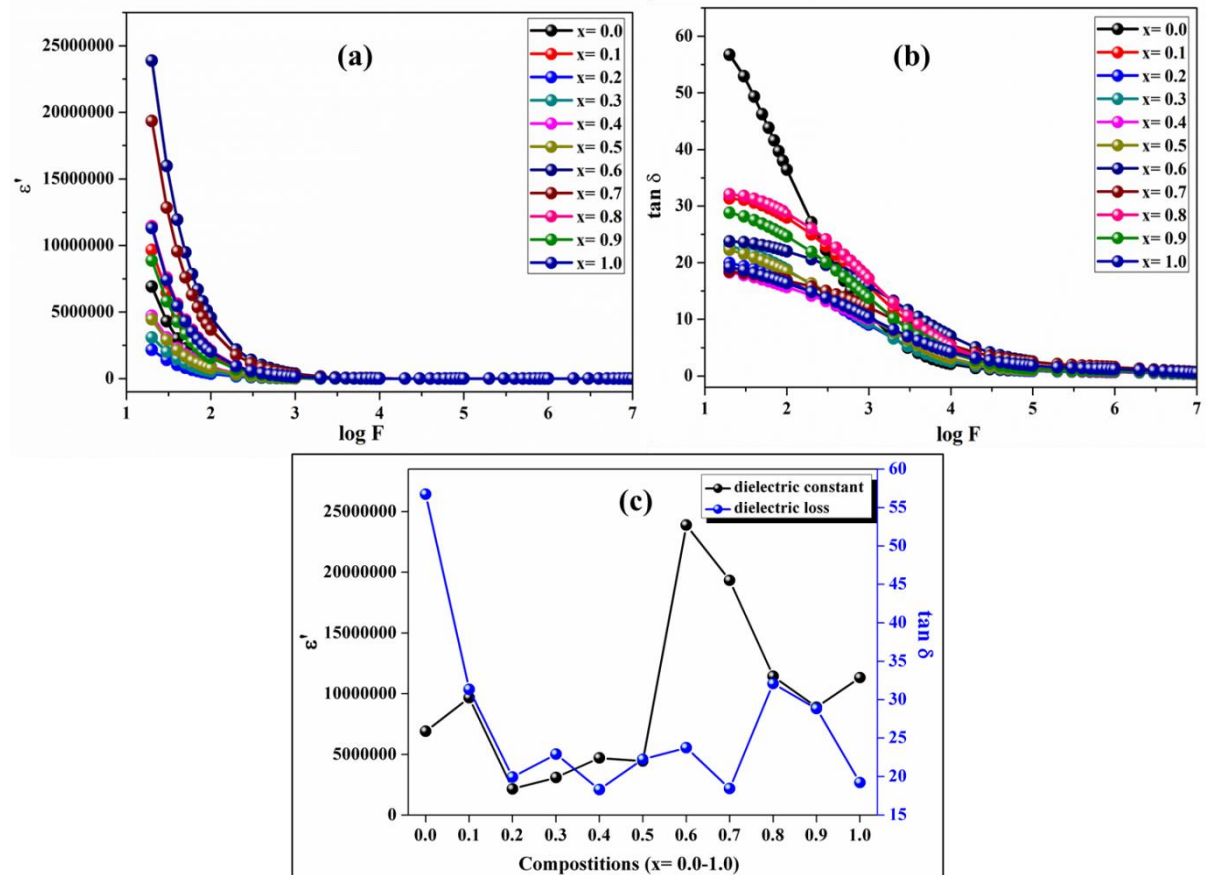


Fig. 3.25 The plots of (a) Dielectric constant against log frequency (b) dielectric loss tangent ($\tan \delta$) against log frequency (c) Plot of dielectric constant and loss tangent as a function of composition at 20 Hz of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites.

All the ‘as prepared’ samples show a decrease in the dielectric constant with increase in frequency which is a normal behaviour observed in case of ferrite samples. It is observed that

the dielectric constant continuously decreases at low frequencies and later almost becomes constant at higher frequencies after around 1 KHz; this decrease in the dielectric constant is prompt at lower frequencies. After 1 KHz the dielectric constant is independent of frequency. The dielectric constant (ϵ') is the amount of energy stored in a dielectric material as polarization. The dielectric constant in spinel ferrites is because of four types of polarization effects viz. electronic, ionic, dipolar and space charge polarizations. The decreasing trend of the dielectric constant can be due to two factors viz. the space charge polarization and hopping between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ electrons. This decreasing trend of the dielectric constant with increasing frequency can be also explained by virtue of Maxwell and Wagner's two-layer theory which is in agreement with the Koop's phenomenological theory [49, 50]. This theory states that any dielectric material comprises of two layers, one large layer of highly conducting grains boundaries segregated by a thin layer of poorly conducting grain boundaries. These highly conducting grains inside the grain boundaries produce the space charge polarization. On application of the external electric field, due to hopping, the electrons reach the grain boundary by hopping and if resistance at the grain boundary is quite high then these electrons accumulate at the grain boundaries which produce polarization (space charge polarization). With further increase in the applied field at certain frequency the space charge carriers cannot continue to sustain the field and variation of their dielectric lags behind the field [51]. Hence the dielectric constant decreases with increasing frequencies [52, 53]. The dielectric constant did not have any as such trend with increase in the nickel concentration and the sample $x = 0.6$ shows the highest value of dielectric constant.

The dielectric loss tangent ($\tan \delta$) measures the amount of energy lost in the ferrite sample. The angle δ is the difference in phase between the applied electric field and the induced current. The variations of loss tangent with respect to frequency of the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) samples at room temperature are shown in the Fig. 3.25b. The dielectric loss is initially high and with further increasing frequency, the dielectric loss tangent decreases. This decrease can be justified using the Koop's theory wherein the resistivity is high at low frequencies and hence the main effect is of the grain boundaries. Due to which the energy needed for the electron-hopping for Fe^{2+} and Fe^{3+} is large at grain boundary and the energy losses are higher [52]. Rezlescu [51] and Iwauchi [54] have established a correlation between conduction mechanism and the dielectric behaviour of ferrites. Their conclusion is that the electronic exchange between $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ results in the local charge displacement, responsible for polarization in ferrites. The magnitude of exchange depends

upon the concentration of Fe^{2+} and Fe^{3+} ions on octahedral sites [55]. When the hopping frequency is nearly equal to that of external applied electric field a maximum of loss tangent may be observed. As for the dielectric constant, dielectric loss tangent also do not have any specific trend with increasing nickel substitution and the composition $x = 0.0$ shows the highest dielectric loss.

3.5.2.2 Dielectric measurements as a function of temperature for the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The dielectric properties of the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were also conducted as a function of temperature at constant frequencies of 10 KHz, 100 KHz, 500 KHz and 1 MHz from room temperature to 500 °C and the plots are presented in Fig. 3.26. The dielectric constant against the temperature plots indicate that upon increasing the temperature, the dielectric constant is nearly constant at lower temperatures however it eventually increases with an increase in the temperature. The lower temperature region where the dielectric constant remains constant is said to be independent of temperature and the higher temperature area is temperature dependent since the dielectric constant increases exponentially at this temperature. The reason for this increasing dielectric constant with temperature can be due to the excess thermal energy of charge carriers at higher temperature that leads to an increase in their mobility thus causing them to align in the easy direction of the applied field and hence increasing the space charge polarization contribution [56]. At lower frequency (10 KHz), the dielectric constant is very large however; as the frequency is increased (1 MHz) the dielectric constant is comparatively lower.

The dielectric material undergoes four types of polarization effects such as electronic, ionic, dipolar and space charge polarizations. The dipolar and space charge polarizations are important at lower frequency and these are highly temperature dependent. As the temperature rises, the space charge polarization increases due to crystal defects whereas the dipolar polarization decreases as the temperature is increased. Moreover at higher frequencies, ionic and electronic polarizations contribute which are not temperature-dependent and hence causing lower values of dielectric constant at high frequencies [44, 52, 56-58] although there is no particular trend in the dielectric constant with increasing nickel concentration, but $x = 0.1$ and $x = 0.4$ show highest values of dielectric constant.

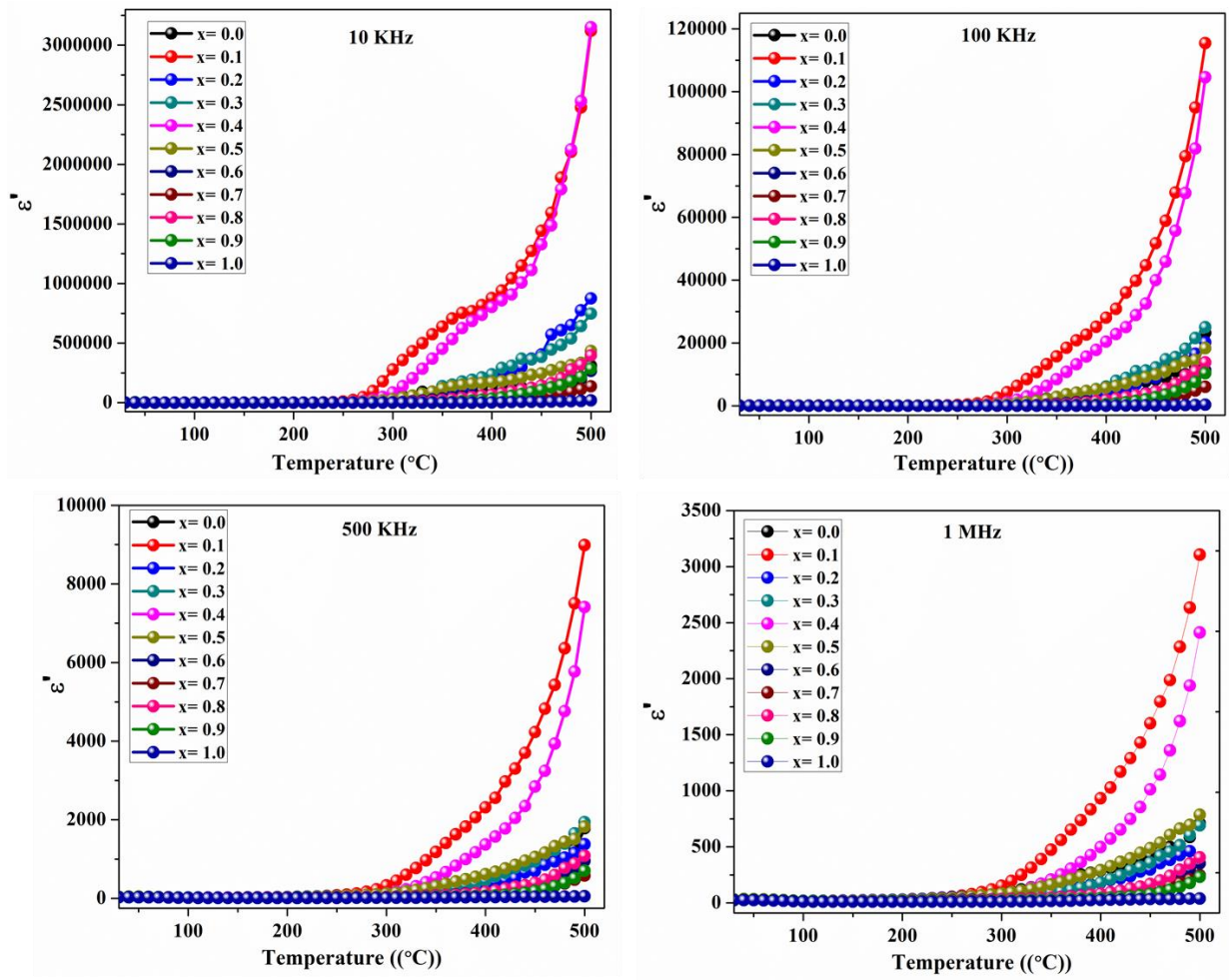


Fig. 3.26 The plots representing variation of dielectric constant as a function of temperature for the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at four different frequencies (10 KHz, 100 KHz, 500 KHz and 1 MHz).

A similar trend has been observed in case of the dielectric loss tangent with increase in temperature. Fig 3.27 presents the dielectric loss tangent ($\tan \delta$) against temperature plots for the all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. All the ferrite samples showed a higher dielectric loss tangent at lower frequency (1 KHz) as compared to that at the higher frequencies (1 MHz). At lower frequencies, the grain boundaries play a key dominant role and the grain boundaries possessing higher resistivity imply that the electrons need higher energy for movement and thus the dielectric loss is higher [59]. Due to the conducting nature of the grains at higher frequency, the dielectric loss is very less. As can be seen from the figures, at lower frequency the samples show peaks in the samples which are called as the relaxation peaks. These peaks occur when the relaxation frequency equals the time period of

applied electric field. Again it was observed that $x = 0.1$ and $x = 0.4$ compositions were found to show high dielectric loss.

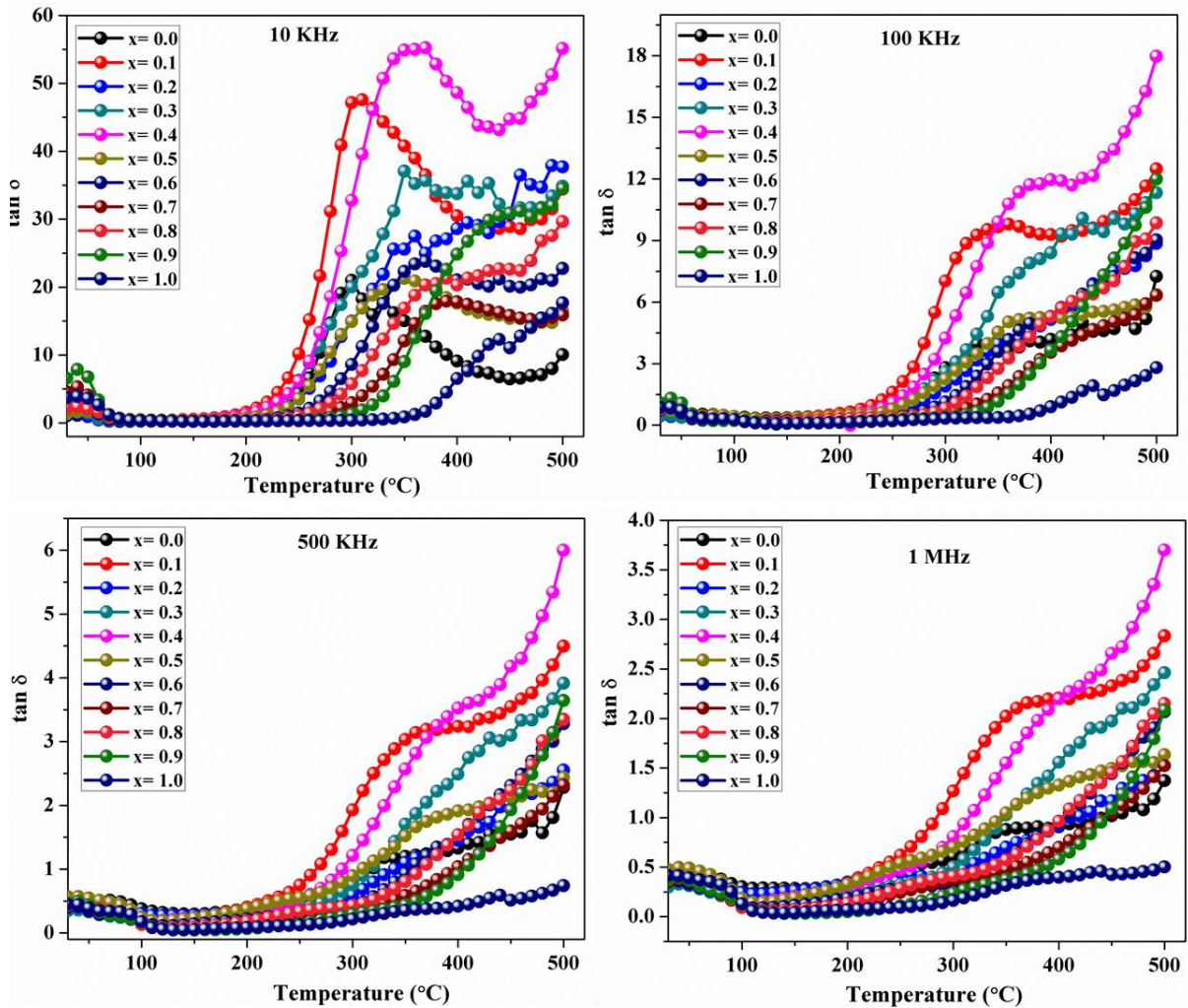


Fig. 3.27 The plots representing variation of dielectric loss tangent ($\tan \delta$) as a function of temperature for the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at four different frequencies (10 KHz, 100 KHz, 500 KHz and 1 MHz).

3.5.3 The magnetization studies of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.5.3.1 The normalized A.C. susceptibility studies of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

As discussed in the Section 3.3.4 of this chapter A.C. susceptibility gives information about the Curie temperature of the material. Besides, this technique gives information about the three types of magnetizations i.e. superparamagnetic (SP), single-domain (SD), and multi-domain (MD) [7]. The temperature at which a transition from ferro/ferrimagnetic material happens to the paramagnetic material is said to be the Curie temperature of the material;

which means the transition from the proper arrangement of magnetic spins to the random arrangement. The exact values of the Curie temperatures have been given in Table 3.9.

Table 3.9 The Curie temperature of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites determined using AC susceptibility studies.

Composition (x)	Curie Temperature (K)
0.0	773
0.1	783
0.2	789
0.3	792
0.4	797
0.5	821
0.6	824
0.7	830
0.8	839
0.9	846
1.0	863

The AC susceptibility of all the ferrite samples was found to increase with temperature, reaches the maximum value and later it was found to tend to zero just before the Curie temperature, indicating presence of single domain particles. This steady fall also rules out the possibility of impurities as affirmed from powder XRD and Raman analysis. Fig. 3.28a and Fig. 3.28b show the normalized AC Susceptibility plots of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) samples. The ferrites with compositions, $x = 1.0, 0.9, 0.8, 0.7$ and 0.6 show single domain particle nature while the compositions with $x = 0.5, 0.4, 0.3, 0.2, 0.1$ and 0.0 show single domain nature of particles with Hopkinson’s peak.

The Curie temperatures of the synthesized ‘as prepared’ ferrites are shown in the Table 3.9. As per the Neel’s two lattice model, three types of interactions are present (A-A, A-B and B-B) out of which A-B interactions are of highest intensity. It can be seen that as the nickel content increases, the Curie temperature also increases. This is due to decrease in lattice parameter [Table 3.4] with increase in the nickel content since, as the nickel content increases, it causes an increase in superexchange interactions between magnetic ions between A and B sublattices which basically leads to an increase in the Curie temperature [10].

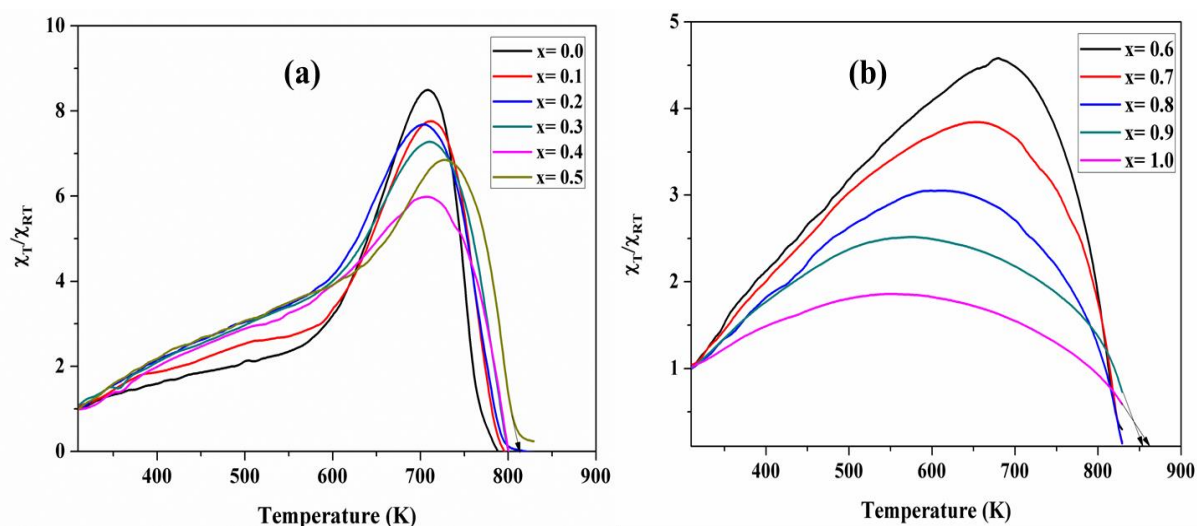


Fig. 3.28 Plots of normalized AC susceptibility against temperature of **a)** the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) and **b)** the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) samples.

3.5.3.2 Vibrating sample magnetometry (VSM) of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The magnetic properties of the all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were evaluated using the vibrating sample magnetometer (VSM) as a function of magnetic field (M-H) and as a function of temperature (M-T) in maximum external field strength from -3 Tesla to 3 Tesla. The M-H measurements were carried out at two different temperatures i.e. at room temperature (300 K) and at a lower temperature (60 K) to study if any magnetic changes occur at lower temperatures. Besides, the temperature dependent studies were performed at two different fields at 5000 Oe and at 10000 Oe. All the related parameters such as saturation magnetization (M_s), remanant magnetization (M_r), coercivity (H_c), and blocking temperatures are given in Table 3.10.

Fig. 3.29 and Fig. 3.30 demonstrates the room temperature (300 K) and 60 K VSM plots of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites respectively). The room temperature (300 K) studies as well as the low temperature (60 K) studies depict a notable decrease in the saturation magnetization (M_s) with increase in nickel substitution. The exact values of M_s for both the cases are shown in (Table 3.10). This decrease in magnetization with increasing nickel content is due to smaller Ni^{2+} substitution ($2 \mu_B$) with higher Co^{2+} ($3 \mu_B$) in the octahedral sites [60]. It is also assumed that Fe^{3+} ions are equally shared in tetrahedral and octahedral sites thus giving the net magnetic moment of $3 \mu_B$ for cobalt and $2 \mu_B$ for nickel, hence decreasing the saturation magnetization with increasing nickel concentration [10]. The remnant magnetization (M_r) is also found to decrease with increasing nickel content. A

similar trend is been observed by Ali et al. [61] where the M_r values decrease with increasing nickel substitution. (Table 3.10)

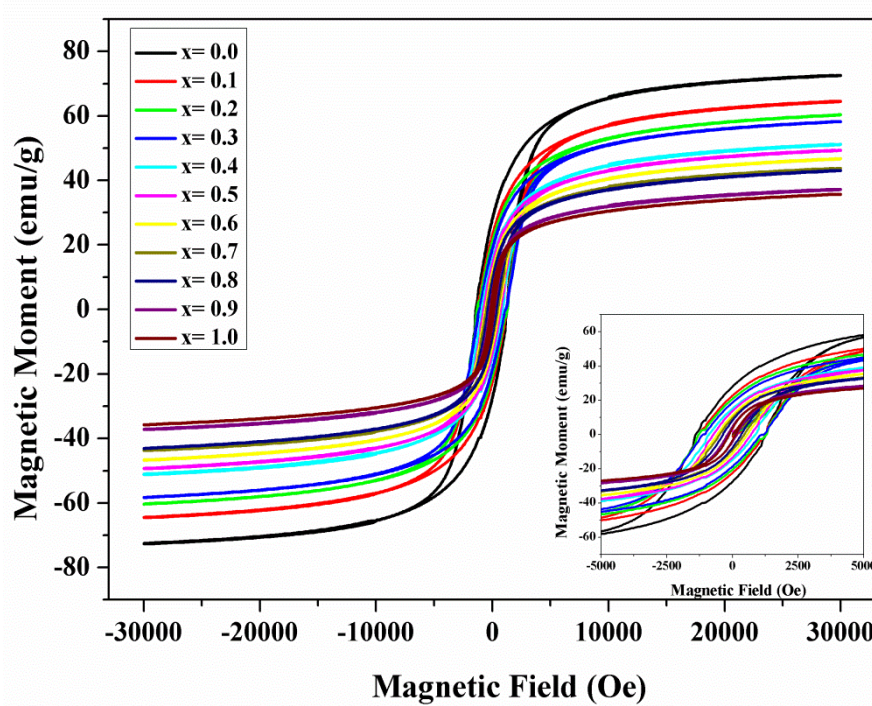


Fig. 3.29 The plot of magnetic moment against magnetic field at 300 K from field for -3T to 3T of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites [Inset: Magnified region (-0.5 T to +0.5 T) showing coercivity].

It was observed that the coercivity (H_c) decreased with increased nickel content which is attributed to presence of the anisotropic effect thus indicating a magnetically distorted state for both the VSM measurements i.e. at 300 K and 60 K. However, the increased values of coercivity in case of CoFe_2O_4 are due to the large magnetocrystalline anisotropic effect of the cobalt ions. These increased coercivity values for increased cobalt ions can be also originated from spin canting effect (spin disorder) at the particle surface [61, 62]. The decreasing H_c values with increasing nickel content are associated with decreased crystallite sizes (powder XRD) implies high surface defects which affect the surface properties thus even affecting gas sensing performances [32, 63].

The magnetization values (hysteresis loop) obtained at 60 K (Fig. 3.30) indicates improved saturation magnetization and coercivity values as compared to the values obtained at 300 K. These increased magnetization values are due to cubic anisotropy showing multi axial anisotropy [64]. In case of room temperature the magnetic moments have various disordered states whereas with decreased thermal energy (60 K) the alignment of the spin is in the same

direction as that of the externally applied magnetic field [62]. At low temperatures the disordered spins are in the surface layer and they freeze into spin glass like phase.

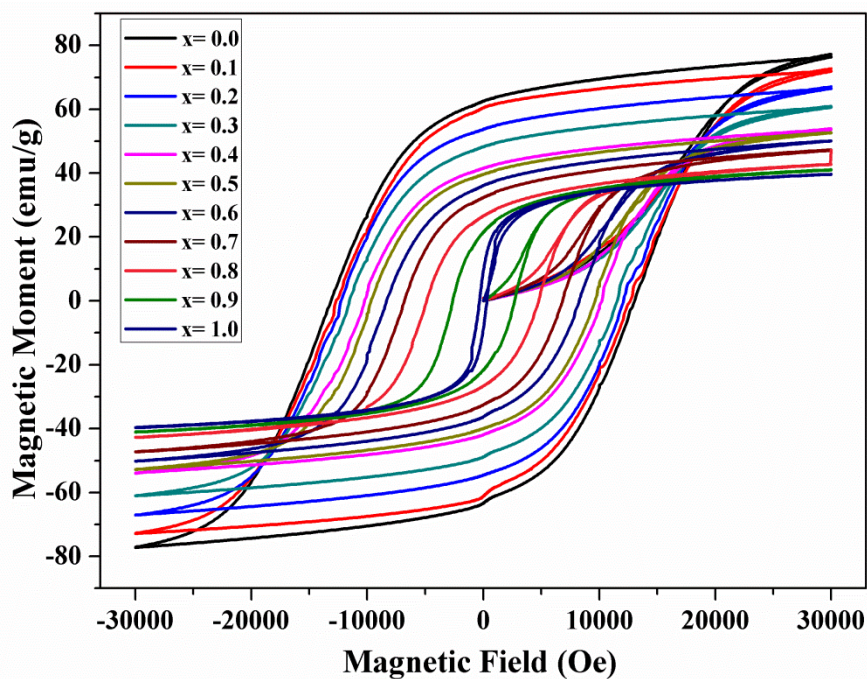


Fig. 3.30 The plot of magnetic moment against magnetic field at 60 K from field for -3T to 3T of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Thus the higher saturation magnetization values at lower temperature are ascribed to the thermal fluctuation effects on the magnetic ions [65]. While, the increased coercivity values at 60 K can be associated with the exchange anisotropy in which there is spin obstruction hence causing an increase in the exchange anisotropy. This increases the coercivity values [66] in the nanoparticles with decrease in the temperatures.

Table 3.10 Saturation magnetization (M_s), remnant magnetization (M_r), coercivity (H_c), blocking temperature (T_B) at 5000 Oe and 10000 Oe, magnetocrystalline anisotropy (K_{eff}) and squareness ratio of 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Composition (x)	Temperature	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
M_s (emu/g)	60 K	77.16	72.22	66.58	60.80	53.68	52.97	50.20	47.25	43.09	41.18	40.14
	300 K	72.57	64.58	60.35	58.19	51.44	49.07	46.64	44.47	42.83	37.10	35.46
M_r (emu/g)	60 K	62.86	61.04	53.48	48.24	41.67	36.50	32.68	26.18	22.02	20.15	14.63
	300 K	29.73	24.43	21.24	20.16	16.41	12.00	9.86	7.92	6.28	5.88	4.26
η_B	60 K	3.24	3.03	2.79	2.55	2.25	2.22	2.10	1.98	1.80	1.72	1.68
	300 K	3.04	2.71	2.53	2.44	2.16	2.06	1.95	1.86	1.79	1.55	1.48
H_c (Oe)	60 K	13051	12703	12106	11608	10339	9631	8223	6747	4751	2545	376
	300 K	1381	1306	1281	1107	933	711	650	400	299	198	112
$K_{\text{eff}} * 10^5$ erg ⁻¹	60 K	10.2	9.3	8.06	7.1	5.6	5.1	4.1	3.2	2.0	1.0	0.9
	300 K	10.1	8.5	7.7	6.5	4.8	3.5	3.0	1.8	1.3	0.7	0.4
M_r/M_s	60 K	0.81	0.84	0.80	0.79	0.77	0.68	0.65	0.55	0.51	0.48	0.36
	300 K	0.40	0.37	0.35	0.34	0.31	0.22	0.21	0.17	0.15	0.14	0.12
T_B (K)	5000 Oe	298	294	288	285	283	278	271	262	231	177	143
	10000 Oe	251	247	240	233	229	223	216	184	165	130	96

The temperature dependent zero field cooled (ZFC) and field cooled (FC) magnetization studies were performed on all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites in the temperature range from 60 K-350 K in externally applied magnetic fields of 5000 Oe and 10000 Oe. Fig. 3.31 and Fig. 3.32 depict the ZFC-FC plots at 5000 Oe and 10000 Oe, respectively for all the ‘as prepared’ samples. In case of ZFC studies, the ferrite nanoparticles are initially cooled from 350 K to 60 K in absence of the applied magnetic field. Later, the samples were heated to 350 K by concomitantly measuring the magnetization by applying the magnetic field (5000 Oe and 10000 Oe). Moreover while in the case of FC studies ferrite nanoparticles were first cooled to 60 K in the presence of applied magnetic field by simultaneously measuring the magnetization as the temperature rise from 60 K to 350 K.

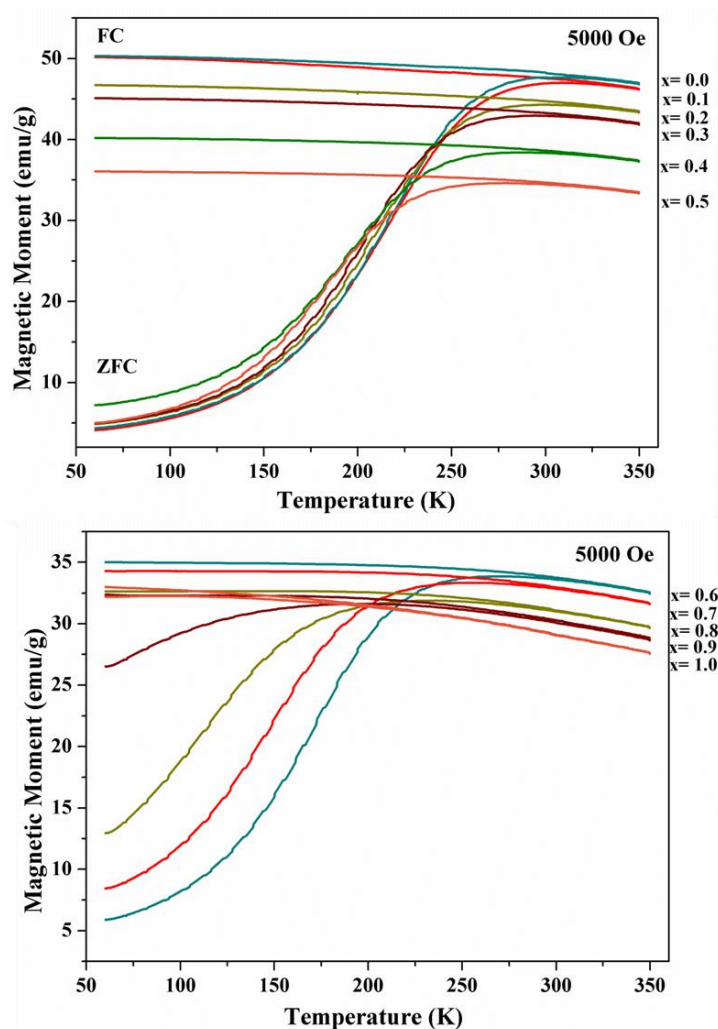


Fig. 3.31 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 5000 Oe and for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

As the temperature increases in ZFC, the ferrite nanoparticles have the peak at maximum magnetization values which is called as the blocking temperature (T_B) which later decreases with further increase in temperature. However in the case of the FC study the magnetization decreases continuously with increase in temperature. This difference in the magnetization behaviour can be explained on the basis of wide particle size distribution (confirmed from HR-TEM and SEM), corresponding domain states and magnetic anisotropic energy with regards to the temperature [67].

With an increase in temperature, there is a reduction in thermal fluctuations due to orientation of spins to align the structure to ferrimagnetic nature [1, 68]. The magnetic anisotropy energy prevents the orientation of the magnetic domains along the axis of magnetization. Thus, at lower temperature (60 K) a wide distribution of particle sizes results in the nanoparticles to orient randomly along the axis while results in a low magnetization value. With an increase in temperature, the particles possessing magnetic anisotropy is overcome by thermal energy and the magnetization direction of these nanoparticles get aligned in direction of the field thus increasing the magnetization value [67].

The blocking temperature values for all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites are found to decrease from 298 to 143 K for 5000 Oe and from 251 to 96 K in case of 10000 Oe at the both the fields with an increase in nickel concentration and with increased field. This can potentially be explained on the basis of Néel’s theory that shows that blocking temperature is dependent on the magnetocrystalline anisotropy [62]. The nanoparticles of all the ferrites are classified as ferrimagnetic since cobalt has high magnetic anisotropy as compared to nickel [70]. Hence in cobalt ferrite higher temperature is required to align all the magnetic spins in the direction of magnetic field for attaining highest magnetization at its blocking temperature [67]. Besides, the narrowed ZFC curve with increasing nickel substitution can be also attributed to its decreasing crystallite size (confirmed from powder XRD).

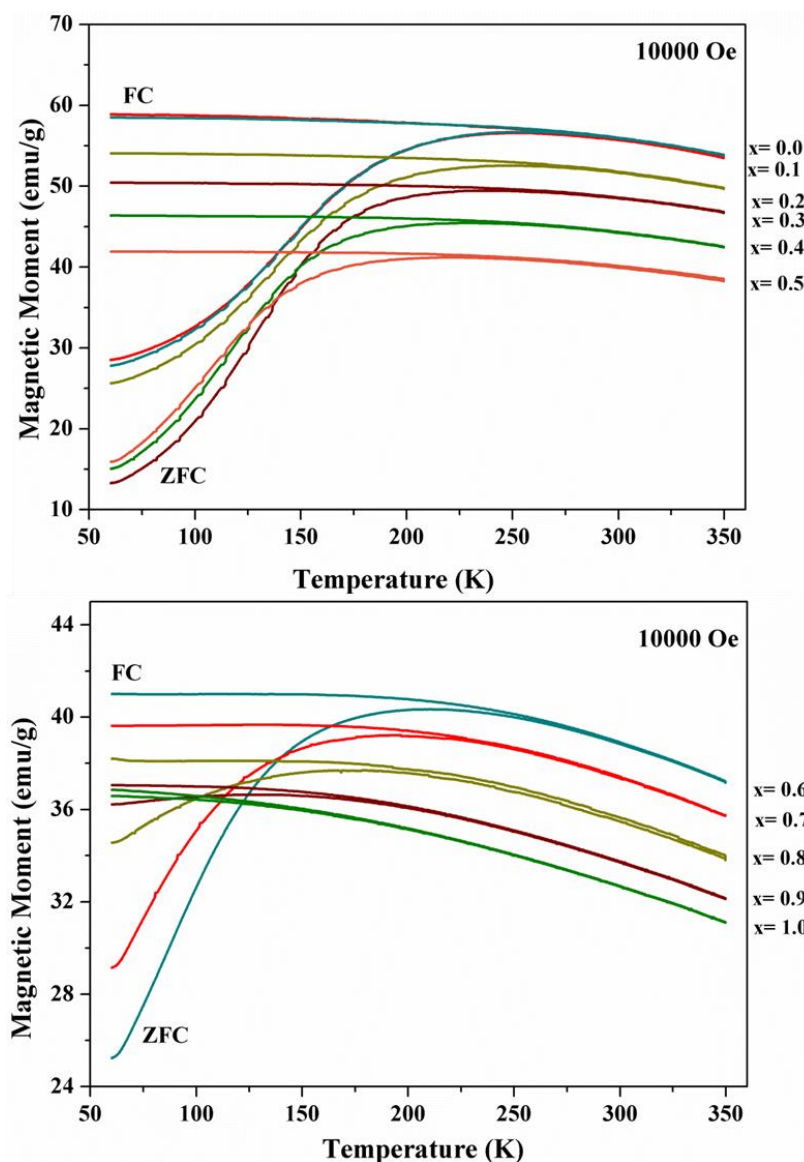


Fig. 3.32 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 10000 and for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

The temperature at which the FC and ZFC curves meet is called as the Irreversible temperature (T_{irr}). From the ZFC-FC curves it can be observed that increasing applied magnetic field leads to an increase in T_{irr} . Ahead of T_{B} the magnetization values decrease and the ZFC plot bifurcates with the FC curve at T_{irr} . At lower field however the applied magnetic field shows an obvious bifurcation of the FC and the ZFC curves and thermomagnetic irreversibility which implies magnetically non-homogenous system even when the material is chemically homogenous [1].

3.6 Characterisation of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.6.1 Structural characterization of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites by powder XRD studies

The $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples sintered as per schedule described in chapter 2 section 2.2.2 were checked for their phase purity using powder XRD and the diffraction patterns are given in Fig. 3.33. The Table 3.11 tabulates the various parameters such as the lattice parameter (a), crystallite sizes (D), measured density (d_m), theoretical density (d_x), porosity (P) for all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples. The lattice parameter values for ‘sintered’ ferrites are found to be higher as compared to the ‘as prepared’ ferrites. The surface tension of the nanomaterial is decreased with increase in the particle size and hence the lattice parameter increases [70]. Besides this smaller ionic size of nickel as compared to cobalt also contribute to increase in lattice parameter.

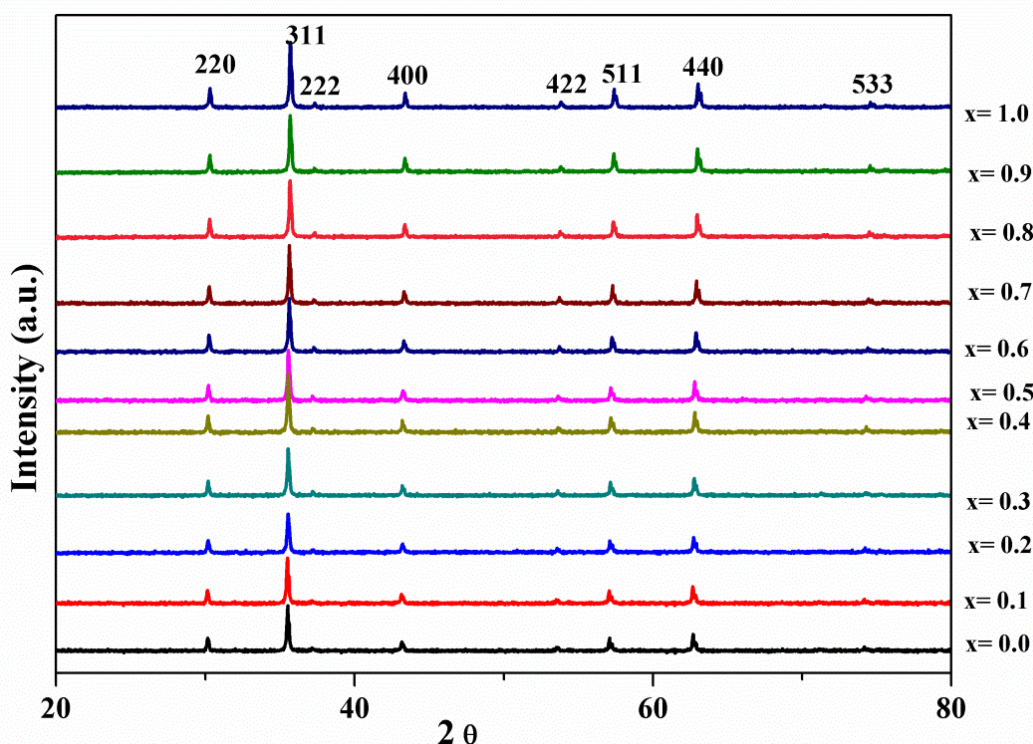


Fig. 3.33 The powder XRD patterns for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

The increase in the particle size upon sintering is confirmed using the SEM technique. Besides, if the particle size is in nanosize, it causes reduction in the lattice parameter mainly due to the change in oxygen coordination number with cations and participation of excess volume of grain boundaries [71]. The average crystallite size (D) was found to be

more in ‘sintered’ as compared to that in their ‘as prepared’ analogues. Numerous factors, for instance, surface pressure, surface strain, the finite size effect and various defects contribute to the increase or decrease in the crystallite sizes in nanoparticles [68].

Table 3.11 The lattice parameter (a), measured density (d_m), theoretical density (d_x) porosity (P) and crystallite sizes (D) of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Composition (x)	Lattice parameter (a) in Å	Measured density (g/cm^3)	Theoretical density (g/cm^3)	Porosity (%)	Crystallite size (D) in nm
0.0	8.3886	3.3670	5.2794	36.22	50
0.1	8.3837	3.1325	5.2880	40.76	52
0.2	8.3738	3.1847	5.3064	39.98	49
0.3	8.3724	3.2386	5.3083	38.98	52
0.4	8.3679	3.119	5.3165	41.33	50
0.5	8.3621	3.0573	5.3271	42.60	46
0.6	8.3598	3.119	5.330	41.48	56
0.7	8.3581	2.9740	5.3338	44.24	47
0.8	8.3542	2.9740	5.3408	44.31	47
0.9	8.3510	2.928	5.3461	45.23	46
1.0	8.3482	3.1070	5.3510	41.93	45

3.6.2 Infra-red (IR) spectroscopy of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The room temperature IR spectra of all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) recorded between $350-4000\text{ cm}^{-1}$ are shown in the Fig. 3.34. All the ferrite samples have the characteristic two peaks; one at $\sim 600\text{ cm}^{-1}$ which is due to the M–O stretch at the tetrahedral site and the other peak at $\sim 400\text{ cm}^{-1}$ is as the result of the M–O stretching vibrations at the octahedral sites. The bond lengths of Fe^{3+} and O^{2-} are uneven for the tetrahedral and octahedral sites, i.e. the Fe–O bond length is shorter on the A-site than at the B-site. [5,67]. With increase in the nickel substitution, ν_1 shifts to higher wavenumber since Ni^{2+} ions prefer the octahedral sites. Thus, with increasing nickel, Fe^{3+} pushes itself to tetrahedral sites thus resulting in the increased bond strength at the tetrahedral sites, leading to an increase in ν_1 .

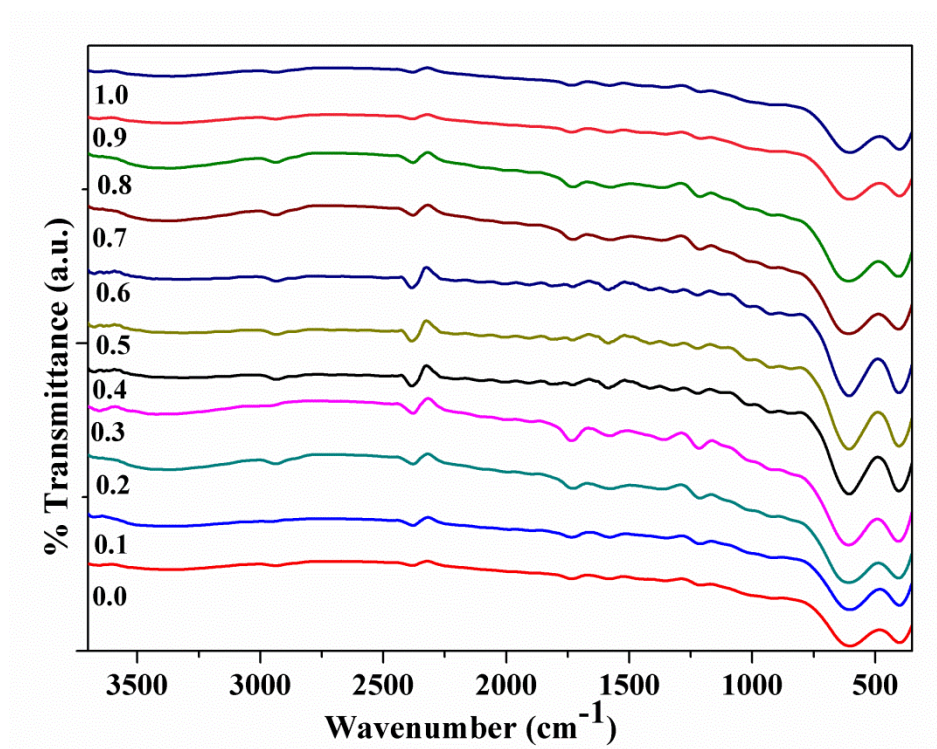


Fig. 3.34 The IR spectra of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Table 3.12 The ν_1 and ν_2 values in the IR spectra of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Composition (x)	IR values of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites in cm^{-1}	
	ν_1	ν_2
0.0	618	430
0.1	620	428
0.2	624	426
0.3	627	423
0.4	631	421
0.5	634	417
0.6	629	415
0.7	638	415
0.8	640	414
0.9	645	413
1.0	648	413

3.6.3 Raman spectroscopy of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The room temperature Raman spectra for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites are shown in the Fig 3.35. The five Raman active vibrational modes present are namely, A_{1g} , E_g and 3 T_{2g} modes [72]. The exact locations of all the peaks are given in Table 3.13. The peak at $\sim 700 \text{ cm}^{-1}$ is due to A_{1g} (1) mode in all ferrite samples. This prominent band occurs because of symmetric stretch of the oxygen atoms for M–O band at tetrahedral site [73]. A small shoulder peak appearing at around 640 cm^{-1} is due to the mixed spinel nature of all the ‘sintered’ samples. The T_{2g} (1) band observed at around 200 cm^{-1} is due to the translational motion of the oxygen tetrahedral unit. The E_g mode ($\sim 300 \text{ cm}^{-1}$) was observed at a lower wave number is due to the symmetric M–O bond bending at the octahedral sites in ferrites. The ionic radii of Ni^{2+} is more than of the Fe^{3+} ions; hence there is a shrinkage of MO_6 octahedra when Fe^{3+} is replaced by Ni^{2+} . Hence decrease in the sizes leads to shift in the E_g peak to high wavenumber with increasing nickel content. An absence of peak ($\alpha\text{-Fe}_2\text{O}_3$) at 240 cm^{-1} confirms the single phase nature of all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples.

Table 3.13 The Raman values of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Composition (x)	A_{1g} (1) cm^{-1}	A_{1g} (2) cm^{-1}	T_{2g} (3) cm^{-1}	T_{2g} (2) cm^{-1}	E_g cm^{-1}	T_{2g} (1) cm^{-1}
0.0	686	626	555	468	296	201
0.1	688	627	558	469	298	202
0.2	690	628	559	470	300	203
0.3	693	629	559	471	302	203
0.4	695	631	560	472	304	204
0.5	696	632	562	472	308	205
0.6	697	634	563	473	310	206
0.7	700	636	564	475	315	208
0.8	702	638	564	476	318	208
0.9	703	638	565	476	322	209
1.0	704	639	566	477	327	210

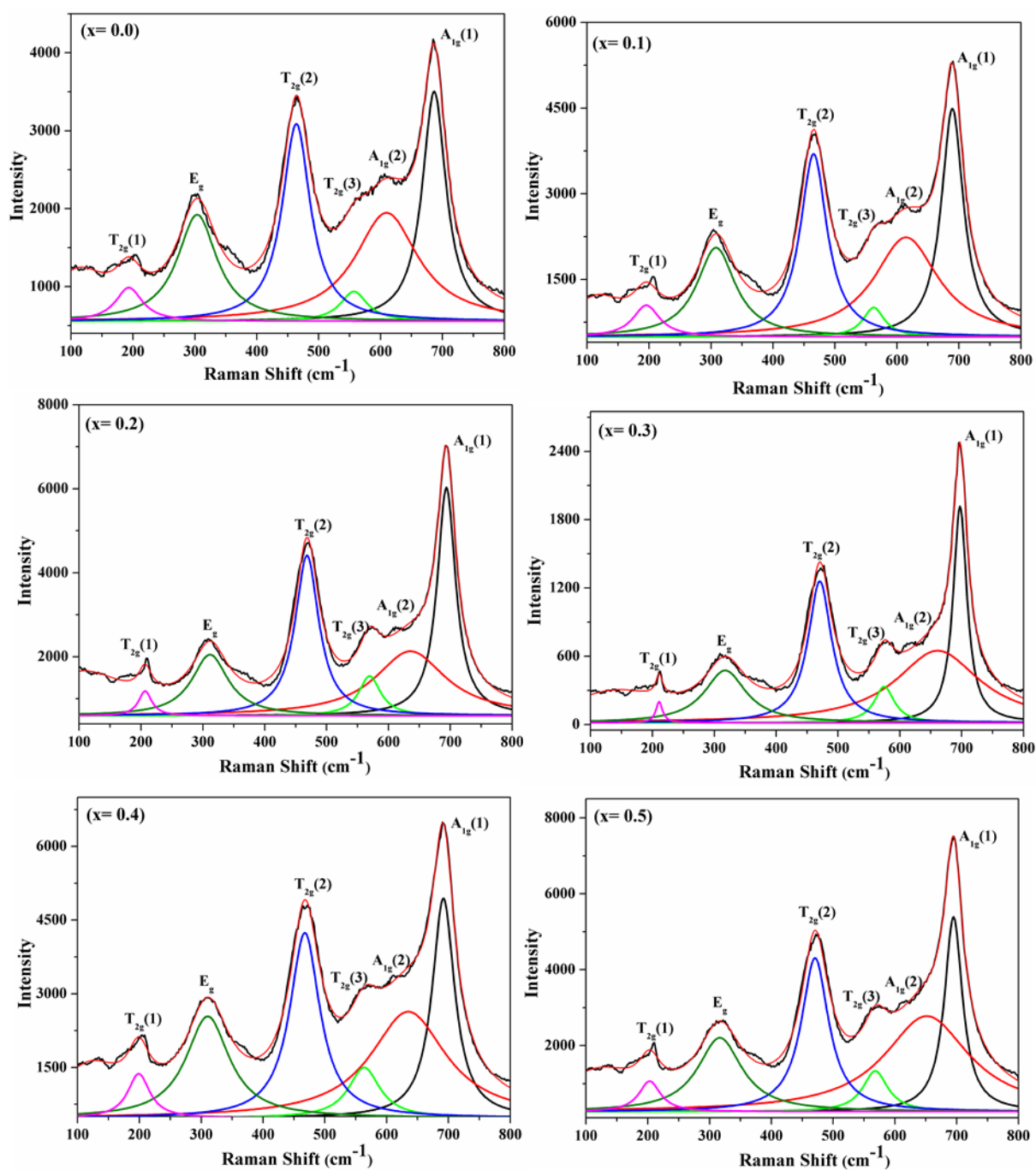


Fig. 3.35a The Raman spectra of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

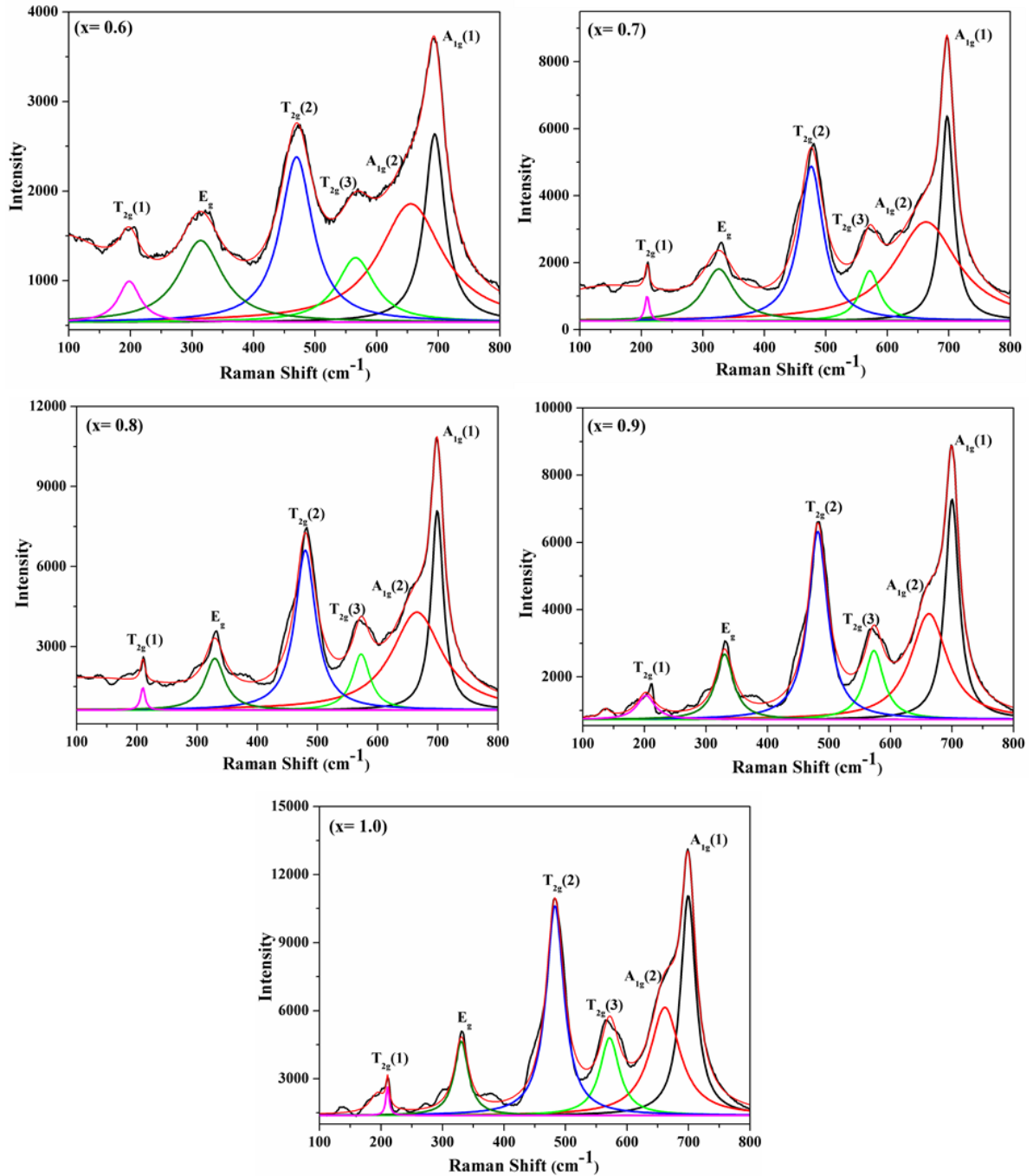


Fig. 3.35b The Raman spectra of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) ferrites.

3.6.4 Morphological studies of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.6.4.1 Scanning Electron microscopy (SEM) studies of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The SEM micrographs of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites are depicted in Fig. 3.36, Fig. 3.37 and Fig. 3.38. Upon sintering there is an increase in the particle sizes of the ferrite samples and the particles merge together to form larger agglomerates. The

average particle sizes of the particle increase and it is found to be roughly 80-150 nm. The EDAX spectra verify the presence of corresponding metal ions, i.e. nickel, cobalt, iron and oxygen in the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples.

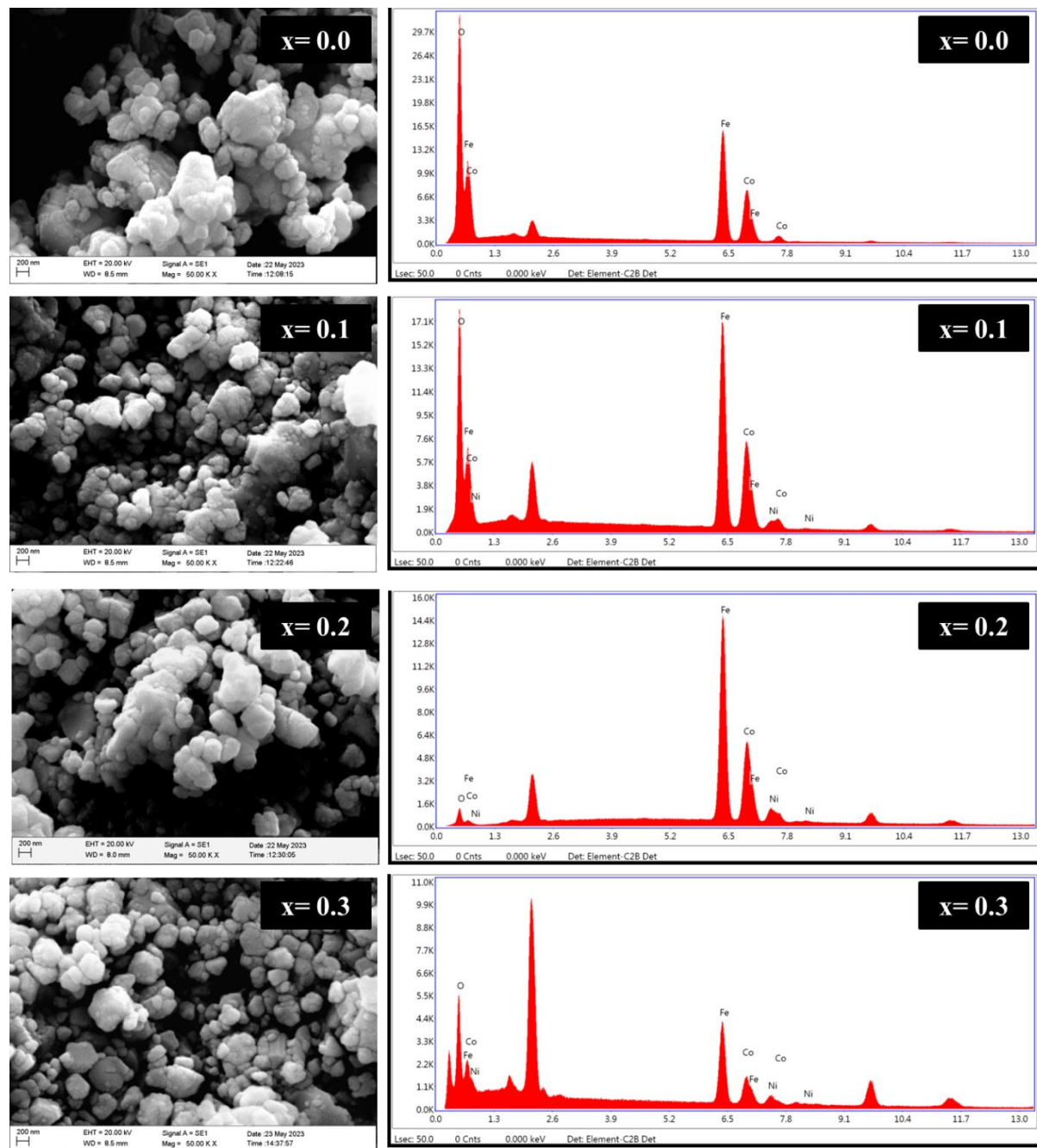


Fig. 3.36 The SEM micrograph and EDAX spectra of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.3$) ferrites.

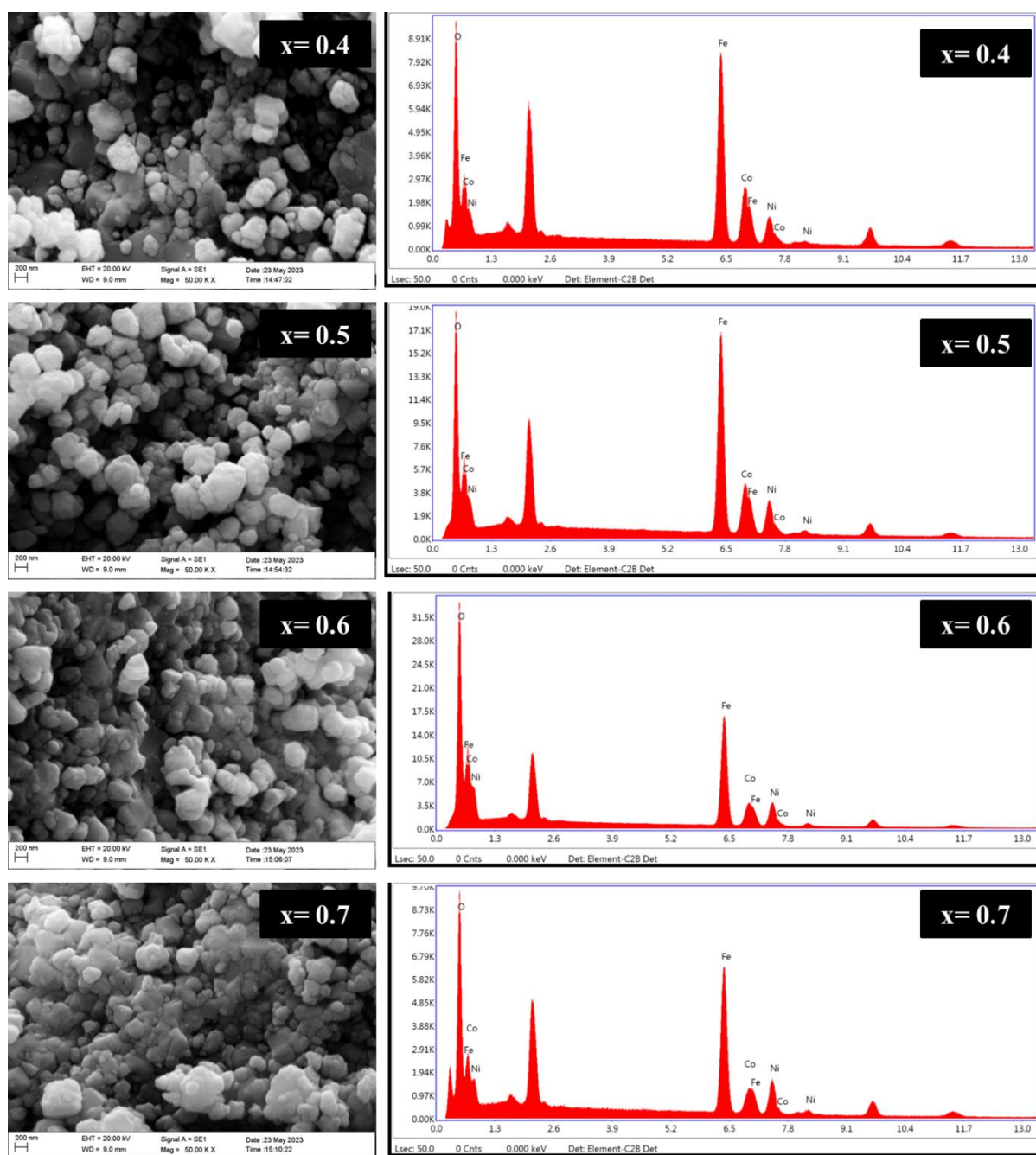


Fig. 3.37 The SEM micrograph and EDAX spectra of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.4-0.7$) ferrites.

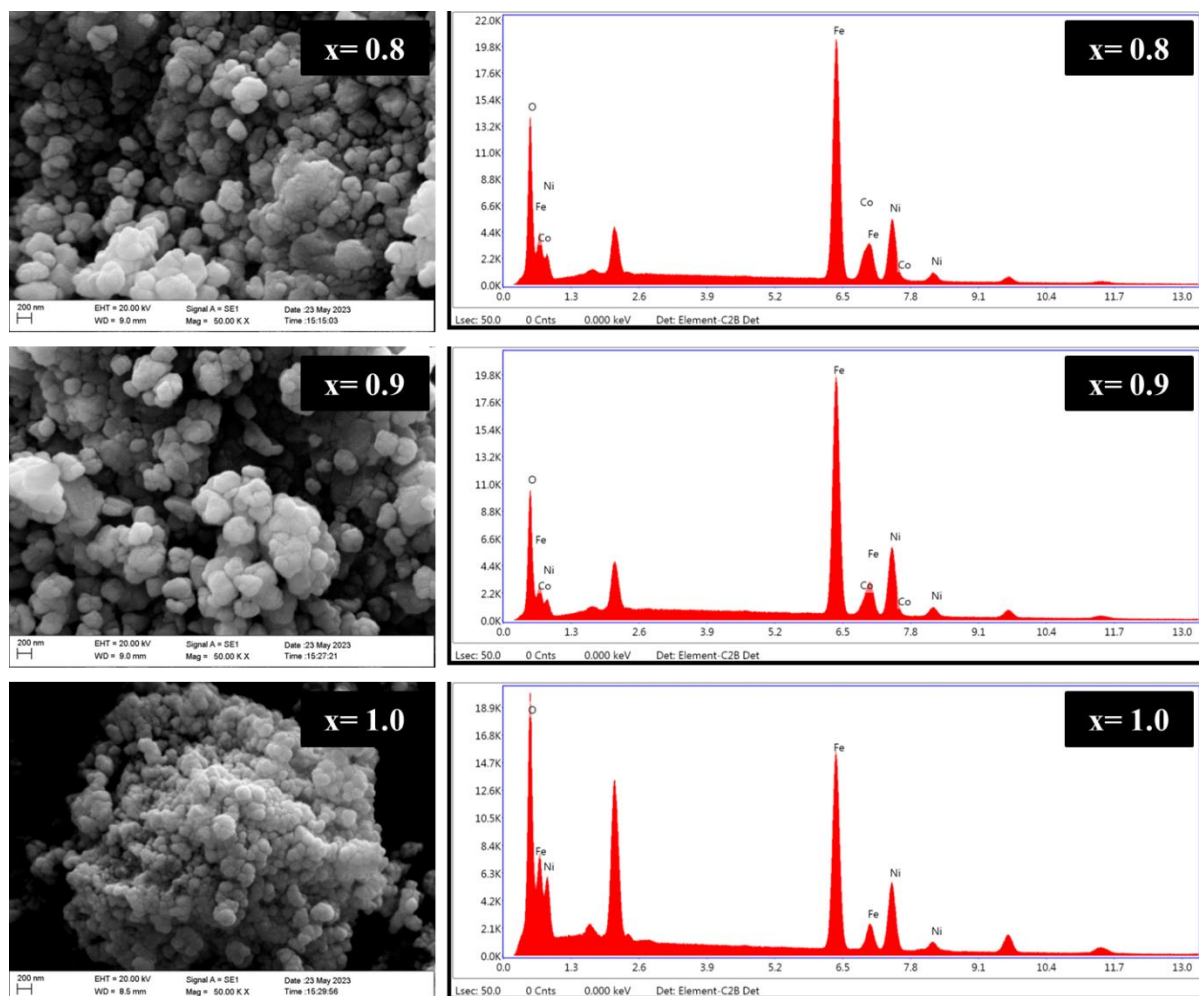


Fig. 3.38 The SEM micrograph and EDAX spectra of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.8-1.0$) ferrites.

3.7 Solid state studies of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.7.1 DC resistivity studies of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Fig. 3.39 indicates the DC resistivity plots of all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. All the samples show a decrease in resistivity with an increase in temperature which depicts the semiconducting behaviour of the nanoparticles [74]. With increase in temperature, the resistivity decreases due to the increase in drift mobility of charge carriers. Also, at high temperatures hopping of electrons from Fe^{+3} to Fe^{+2} leads to conduction of ferrites. The charge carriers are mainly the electrons or the holes which appear from $\text{Ni}^{3+}/\text{Ni}^{2+}$, $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ pairs of ions which are accountable for conduction in ferrites [75].

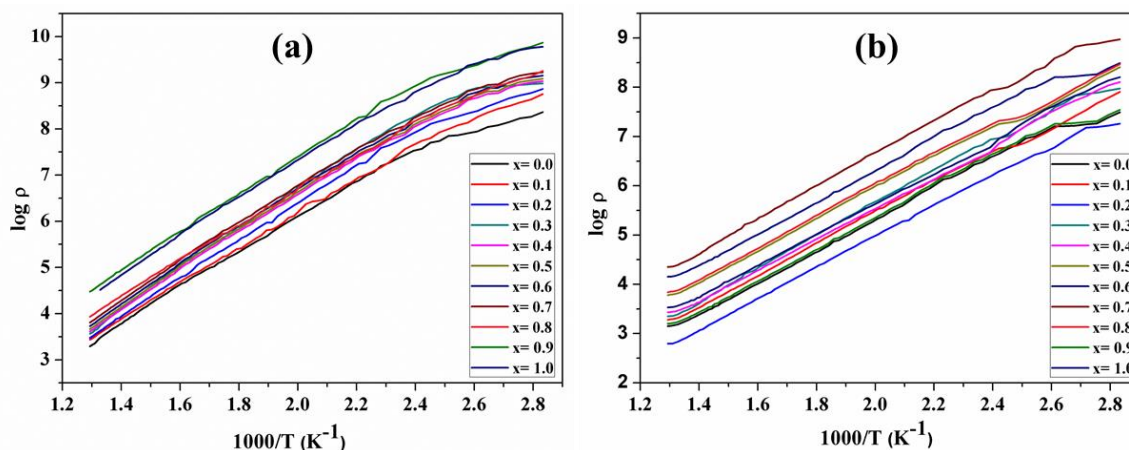


Fig. 3.39 The dc resistivity against $1000/T$ (K^{-1}) plots of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites during (a) Heating and (b) Cooling.

3.7.2 Dielectric properties of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.7.2.1 Dielectric measurements as a function of frequency for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Since, the dielectric properties largely depend on frequency and temperature, all the ‘sintered’ ferrites were studied for their dielectric properties with frequency and temperature in order to observe the difference on their properties upon sintering. Fig. 3.40a depicts the dielectric constant ν/s frequency for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. These measurements were performed at room temperature in the frequency range from 20 Hz to 10 MHz. The dielectric constant decreased drastically with increase in frequency for all the ferrite samples as also observed in case of the ‘as prepared’ samples. The decrease in the dielectric constant is sharp at lower frequency up to almost 1 KHz and as there is increase in the frequency the dielectric constant decreases and later shows a frequency independent behaviour by remaining constant by further increasing frequency. This phenomenon is in accordance with the Koop’s theory as discussed in section 3.5.2.1 of this chapter along with the Maxwell-Wagner theory [50, 76]. According to this theory the dielectric structure comprises of grains which are highly conducting and are segregated by the weakly conducting grain boundaries. The grain boundaries are responsible for polarization at lower frequencies however at higher frequencies grains play a key role [77]. The hopping of same ions in different valence states occurs when the charge carriers (electrons or holes) move inside the grain internally

in the octahedral sites. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ hopping causes the n-type charge carriers while $\text{Co}^{2+}/^{3+}$ and $\text{Ni}^{2+}/^{3+}$ hopping results in p-type charge carriers.

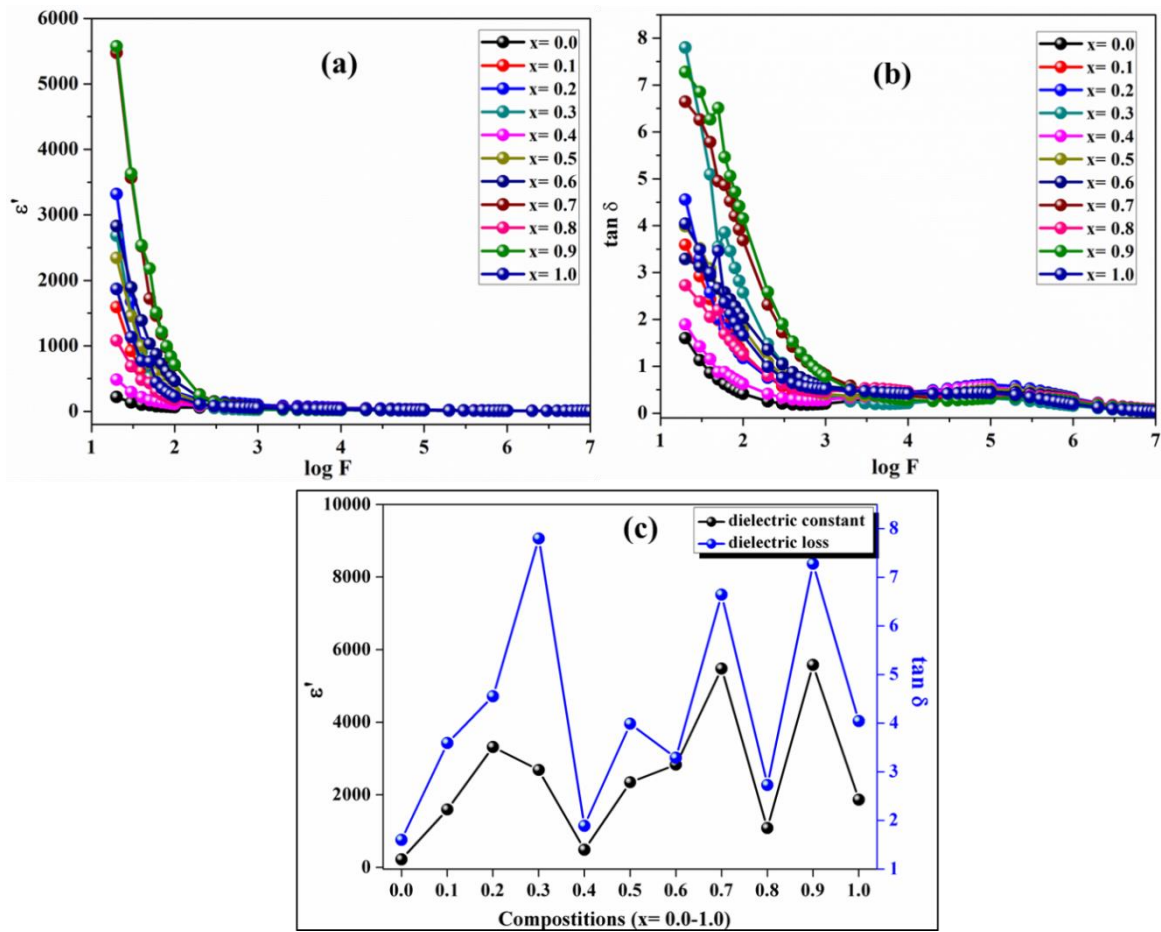


Fig. 3.40 The plots of (a) Dielectric constant against log frequency (b) dielectric loss tangent ($\tan \delta$) against log frequency (c) Plot of dielectric constant and loss tangent as a function of composition at 20 Hz for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The movement of these charge carriers within the grain by hopping drive them to the grain boundaries but they cannot permeate due to the resistive behaviour of the grain boundaries. This leads to charge accumulation at the grain boundaries thus resulting in space charge (interfacial) polarization [78]. The values of dielectric constant were found to be lower for the ‘sintered’ ferrites as compared to that for the ‘as prepared’ samples. With increasing nickel content, there is no trend in the dielectric constant in particular for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites but the highest values for the dielectric constant was found to be for the composition $x = 0.7$ and $x = 0.9$.

Fig. 3.40b demonstrates the dielectric loss tangent against frequency plots for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. All the plots show a similar behaviour for

ferrites wherein the loss tangent values ($\tan \delta$) values decreases with increasing frequency. This decrease is prominent till the frequency up to almost 1 KHz and further it remains constant implying higher dielectric loss at lower frequencies. The dielectric loss tangent also did not have any specific trend with increasing nickel content. The highest dielectric loss was observed for the compositions $x = 0.7$ and $x = 0.9$. The dielectric loss tangent values are found to be higher for the ‘as prepared’ samples and the values were found to decrease upon sintering.

3.7.2.2 Dielectric measurements as a function of temperature for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

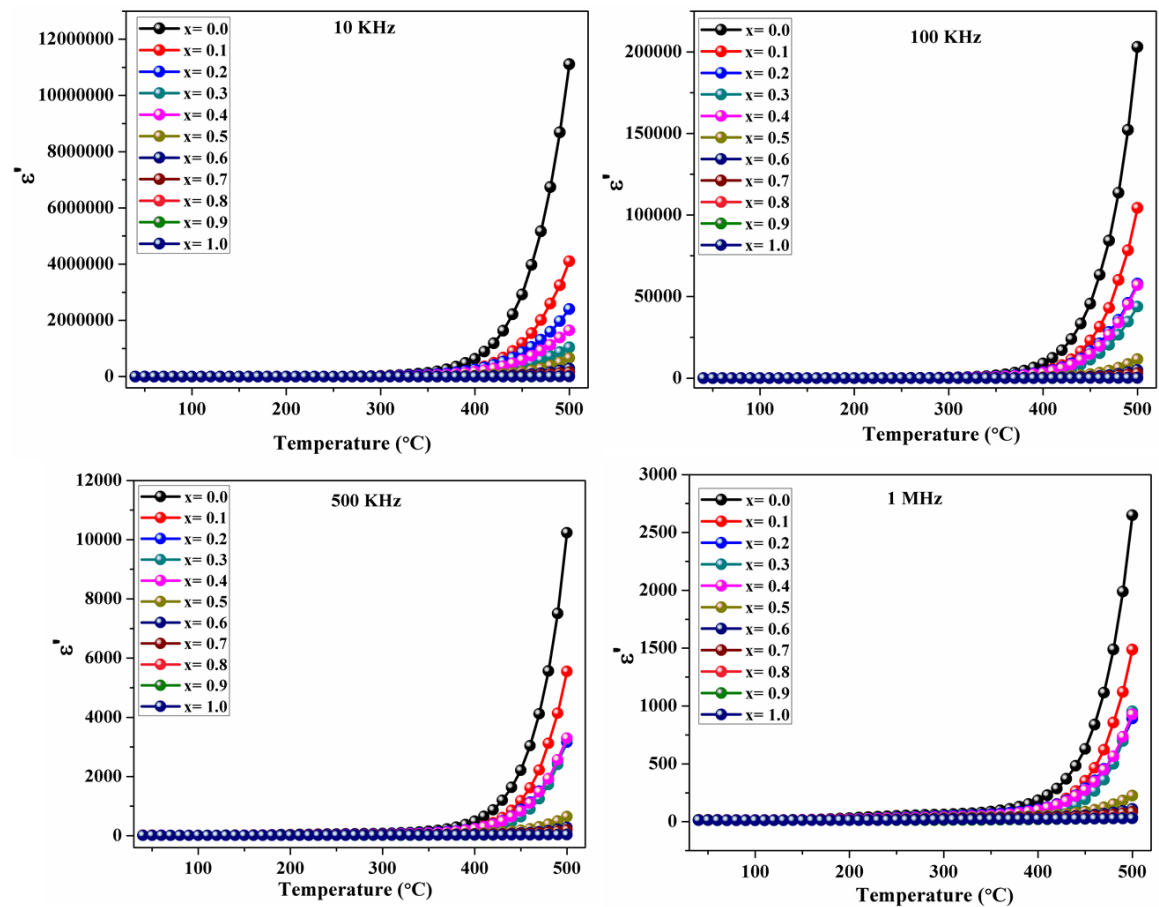


Fig. 3.41 The plots representing variation of dielectric constant as a function of temperature for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at four different frequencies (10 KHz, 100 KHz, 500 KHz and 1 MHz).

Fig 3.41 presents the plots of the variation of dielectric constant as a function of temperature for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at four different frequencies of 10 KHz, 100 KHz, 500 KHz and 1 MHz from room temperature to 500 °C.

The dielectric constant initially was found to remain constant at lower temperature, however after further increasing the temperature the dielectric constant drastically increases.

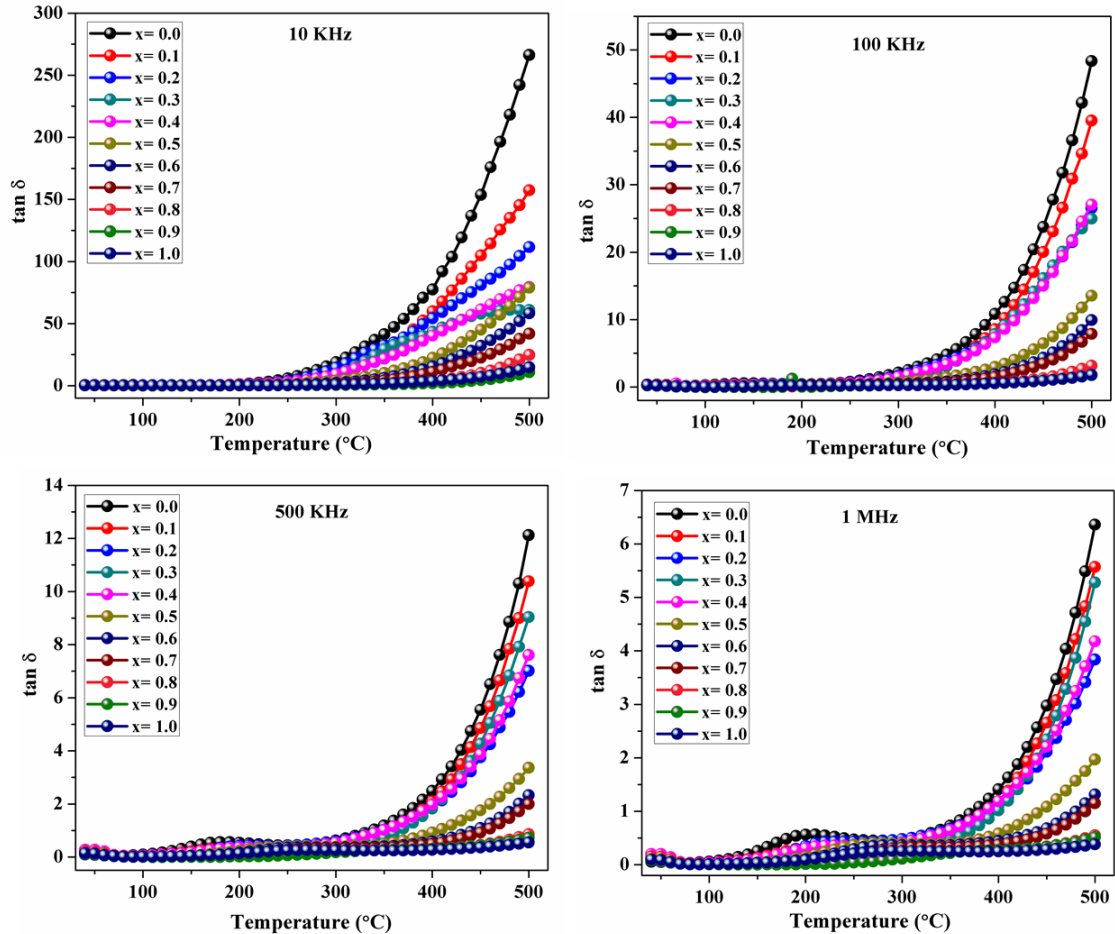


Fig. 3.42 The plots representing variation of dielectric loss tangent ($\tan \delta$) as a function of temperature for the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at four different frequencies (10 KHz, 100 KHz, 500 KHz and 1 MHz).

As it is already discussed in 3.5.2.1 of this chapter for the ‘as prepared’ samples, the four types of polarizations namely, electric, ionic, dipolar and space charge polarizations accounts for the variation in the dielectric constant of any material [79]. The dipolar and space charge polarizations are strongly temperature dependent and thus these polarizations are responsible for the high dielectric constant values at lower frequency since they are active at lower frequency (10 KHz). However at higher frequency the ionic and electronic polarizations dominate which are temperature-independent. Hence, there is minimum impact on the dielectric values thus resulting in lower values at higher frequencies (1 MHz) [79]. From the dielectric constant plots it was observed that the

highest dielectric constant value for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites was found for $x = 0.0$ composition. The values were found to decrease with an increase in nickel concentration. This might be due to the high temperature which leads to the diminishing contribution of the positive charge carriers. Hence only the negative charge carriers (electrons) contribute to polarization and since their concentration decreases due to increasing Fe^{3+} at the octahedral sites, thus the dielectric constant decreases with increasing nickel.

The dielectric loss tangent follows the similar trend for all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites for all the four frequencies (10 KHz, 100 KHz, 500 KHz and 1 MHz) wherein the dielectric loss was found to remain constant at lower temperatures and as the temperature increased the values were found to increase (Fig 3.42). It can be clearly seen that there is high dielectric loss in case of the composition $x = 0.0$ and with increasing nickel content, the dielectric loss was found to decrease, the same trend observed for dielectric constant.

3.7.3 The magnetization studies of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.7.3.1 The normalized A.C. susceptibility studies of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Fig. 3.43 a and 3.43 b demonstrate the normalized AC Susceptibility plots of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples. In all the ‘sintered’ samples initially there is a gradual increase in the magnetization which is succeeded by the steep increase at a higher temperature forming a sharp peak (Hopkinson peak) exactly before the Curie temperature (T_c) and later accompanied by a sharp fall at the Curie temperature which suggests multidomain type of behavior. The increasing Hopkinson peak is due to the competition between thermo-magnetic randomization and the magnetic ordering by boundary as there is an increase in thermal energy [80]. The exact values of the Curie temperatures for the ‘sintered’ samples are shown in Table 3.14.

The modifications in the cation distribution of the lattice of octahedral and the tetrahedral sites is a prime factor in accounting for the decrease in the Curie temperature with increasing particle sizes (seen in SEM images) which is perhaps due to the strength of the exchange interactions [81].

Since nickel is more magnetic than cobalt, it results in an increased magnetic interaction amongst the ions at the tetrahedral and octahedral sites thus leading to an increase in the Curie temperature with increase in nickel content.

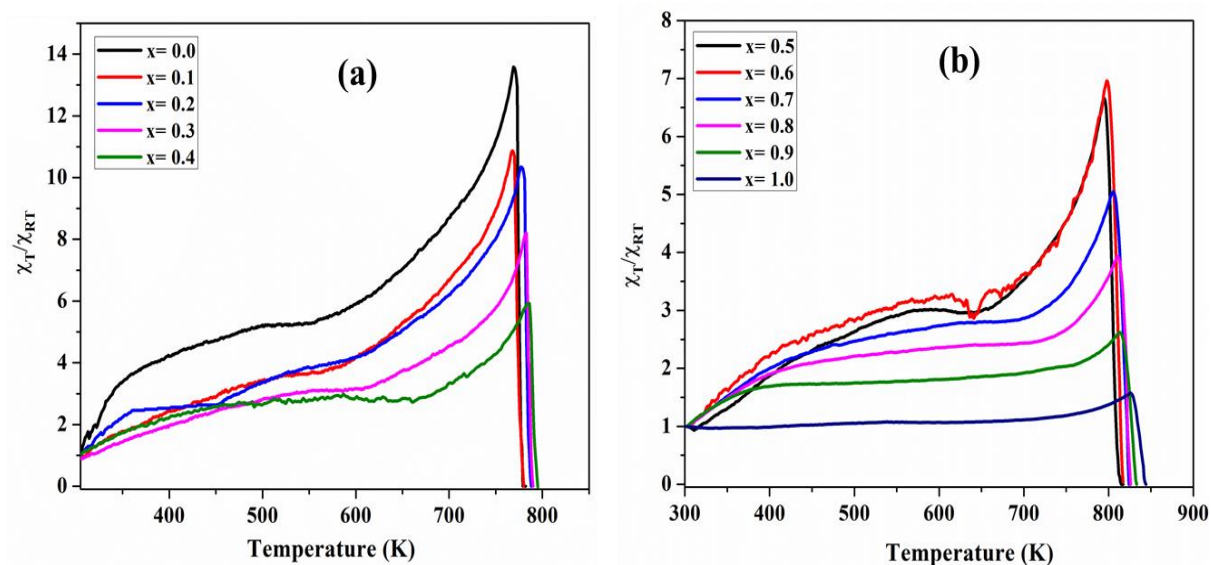


Fig. 3.43 Plots of normalized AC susceptibility against temperature of **a)** the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.4$) and **b)** the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5-1.0$) samples.

Table 3.14 The Curie temperature of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites determined using AC susceptibility studies.

Composition (x)	Curie Temperature (K)
x= 0.0	770
x= 0.1	780
x= 0.2	786
x= 0.3	790
x= 0.4	793
x= 0.5	817
x= 0.6	820
x= 0.7	825
x= 0.8	830
x= 0.9	835
x= 1.0	850

3.7.3.2 Vibrating sample magnetometry (VSM) of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The magnetic properties of all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples were carried out using the VSM equipment at external applied magnetic field from -3 Tesla to +3 Tesla. The magnetic studies were performed on all samples as a function of magnetic field (M-H) at two different temperatures i.e. at room temperature (300 K) and at 60 K. Also, the magnetization was found out as a function of temperature at two

different fields viz. 50000 Oe and at 10000 Oe. The saturation magnetization (M_s), remanant magnetization (M_r), coercivity (H_c), and blocking temperature values are shown in Table 3.15. The Fig. 3.44 and Fig. 3.45 demonstrate the hysteresis loops for the magnetic properties of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at room temperature (300 K) and at 60 K, respectively.

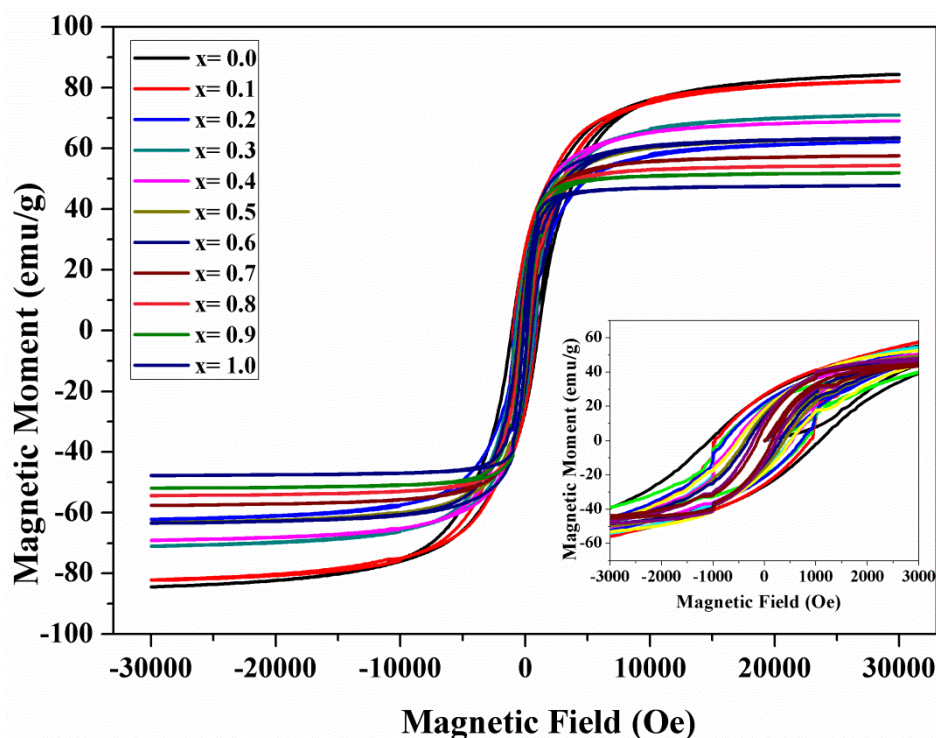


Fig. 3.44 The plot of magnetic moment against magnetic field at 300 K from field for -3T to 3T of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites [Inset: Magnified region (-0.3 T to +0.3 T) showing coercivity].

For both, the room temperature (300 K) study and the low temperature (60 K) study, it was observed that there is an obvious decrease in the saturation magnetization value seen with increase in the nickel content. This is because of the substitution of Ni^{+2} with Co^{+2} in the octahedral sites. The magnetic moment value for Ni^{+2} ($2 \mu_B$) ions is smaller as compared to that of Co^{+2} ($3 \mu_B$) ions. Thus replacing Co^{+2} by Ni^{+2} decreases the magnetization. It has been reported that if the concentration of the Co^{+2} in octahedral sites is increase, there is an improvement in the saturation magnetization values [Table 3.15] [11]. The same trend is observed for the saturation magnetization for the ‘as prepared’ analogues as discussed in section 3.5.3.2 where the M_s values were found to decrease with increasing nickel concentration. However it was observed that the M_s in the

‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites is higher as compared to that of their ‘as prepared’ analogues. A similar trend has been reported in the literature [3, 82] where the M_s was found to be more for the ‘annealed’ ferrites. The increase in particle sizes increases the overall net magnetic moment upon sintering. Due to the spin canting effect the particles do not have any saturation even at higher fields thus causing lowered M_s in the smaller particles [83]. Additionally, due to minimum thermal variations at lower temperature (60 K) than at 300 K, the M_s values increase [65].

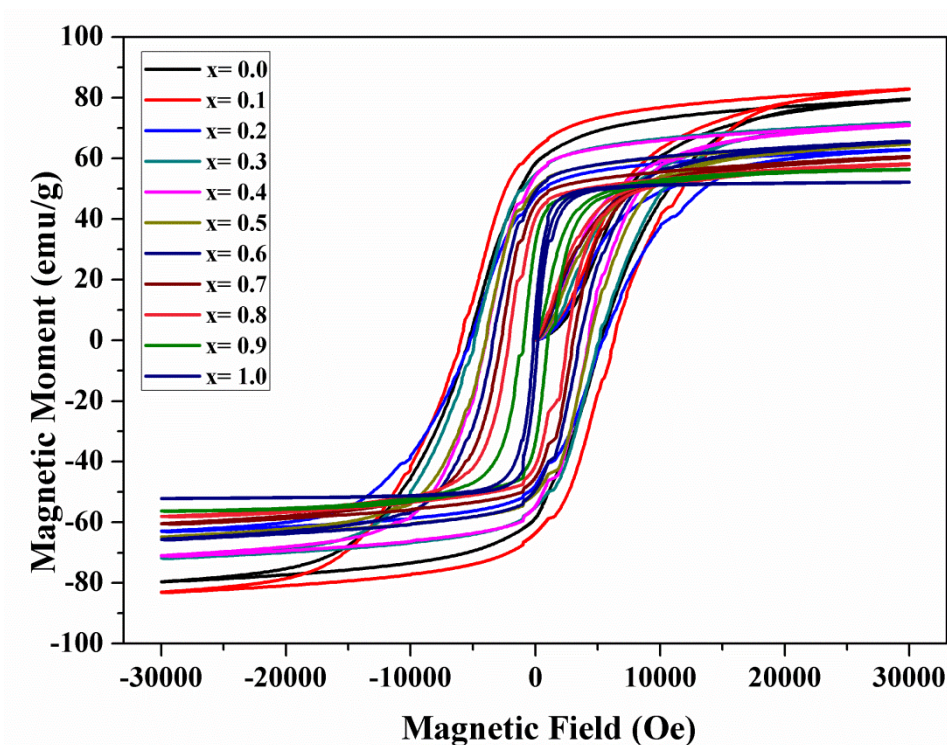


Fig. 3.45 The plot of magnetic moment against magnetic field at 60 K from field for -3T to 3T of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Furthermore, the coercivity values decreased with increasing nickel substitution in case of all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 300 K and 60 K. The M-H plots for both 300 K and at 60 K have a lower coercivity for ‘sintered’ ferrites in comparison with their ‘as prepared’ analogues. This is principally due to the dependence of coercivity on the grain size and smaller the grain size, more is the coercivity. In other words, coercivity is inversely proportional to the particle sizes. The change in the particle nature from single domain to the single domain-multi domain nature (as confirmed by A.C. susceptibility studies) is responsible for the decreasing trend of coercivity upon sintering. This decrease is mainly because of the magnetocrystalline anisotropy, shape anisotropy

and macrostrain in the structure [1,19]. The coercivity and remnant magnetization were found to decrease with an increase in the Ni^{2+} concentration which is since the magnetocrystalline anisotropy is more for Co^{2+} ions as compared to that in the Ni^{2+} ions.

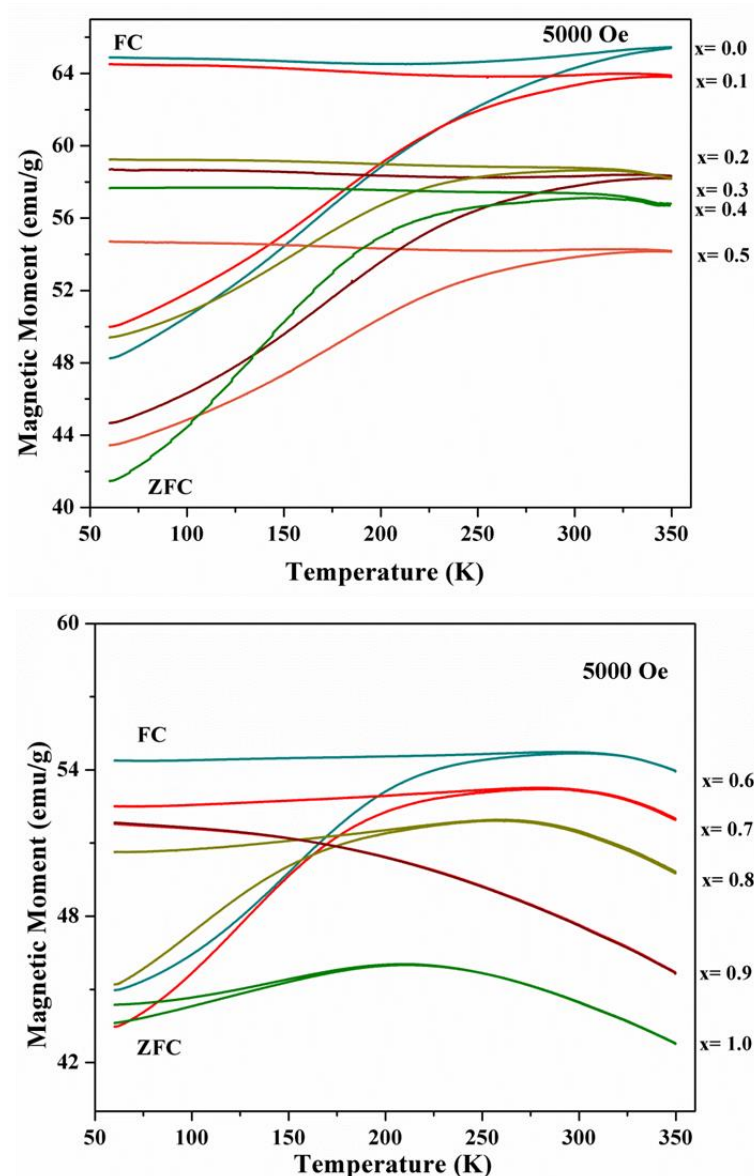


Fig. 3.46 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 5000 Oe and for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

As observed in the ‘as prepared’ ferrites, the magnetization values for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites samples also shows higher M_s and H_c at lower temperature (60 K) as compared to 300 K [Table 3.15]. It is observed that the M_s values are higher for the ‘sintered’ ferrites than their ‘as prepared’ analogues. These higher values for ‘sintered’ samples can be ascribed to larger particle sizes of the samples and change in the

magnetic domains from single domain to multidomain particles upon sintering (as confirmed by A.C susceptibility measurements). Besides, in case of ‘sintered’ samples there is a decrease in the canted spins which is notable in the ‘as prepared’ samples due to their high surface to volume ratio [85].

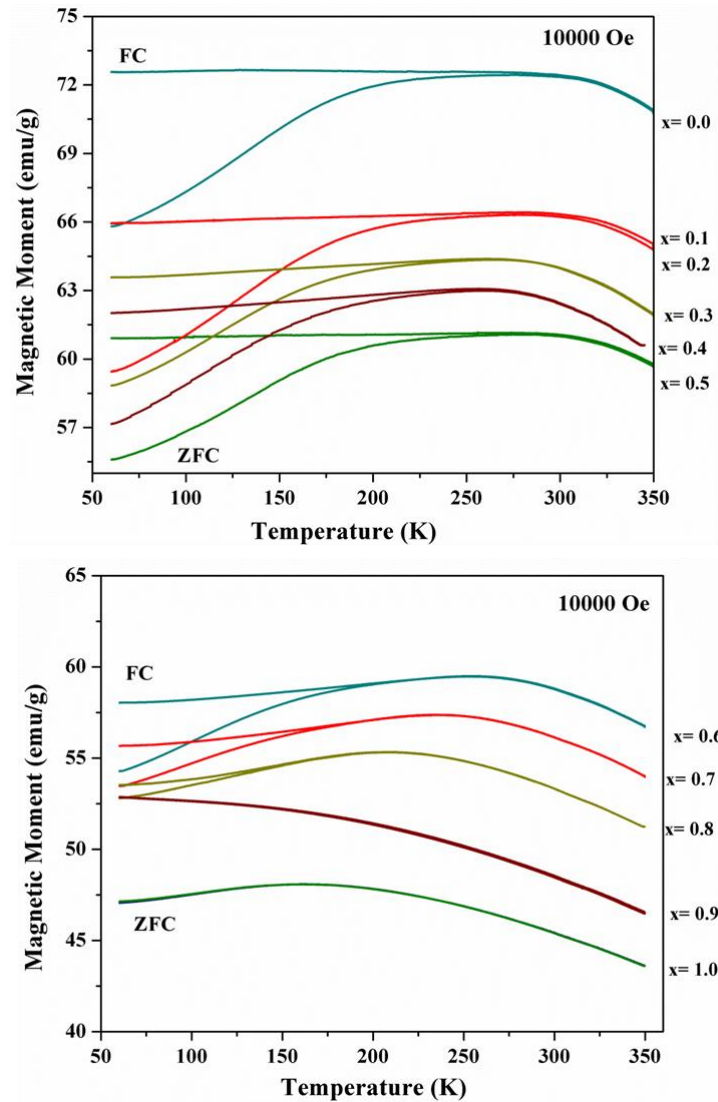


Fig. 3.47 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 10000 Oe and for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

Furthermore, the magnetization of ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were conducted as a function of temperature in the temperature range from 60 K to 350 K. The zero field cooled and the field cooled curve at the applied fields of 5000 Oe and 10000 Oe for all the ‘sintered’ samples are demonstrated in Fig. 3.46 and Fig. 3.47. At lower temperature, the FC curve is indicating almost a temperature-independent behaviour

implying presence of the magnetic interparticle correlations with long-range, causing high anisotropy having magnetically ordered state [86]. The magnetization at the ZFC curve however shows a decrease with decreasing temperature [1]. This decrease indicates that at ambient temperature, the spins of transition metal ions in octahedral and the tetrahedral sites diverge from the antiparallel alignment and hence lattice has partially disorganised spin structure [1, 87].

Both the magnetization at zero field and at field cooled curves show bifurcation over the whole range of temperature thus implying magnetically non-homogenous system. The Table 3.15 demonstrates the blocking temperature values for all the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites and the values were found to decrease from 344 K to 235 K at 5000 Oe and from 295 K to 142 K for 10000 Oe with increase in nickel content. This decrease can be explained by the virtue of Néel’s theory which indicates that T_B is highly dependent on the magnetocrystalline anisotropy [62]. With increasing grain volume the T_B increases which can be due to large agglomerations of the nanoparticles upon sintering [88] (as confirmed by the SEM analysis). Hence, the blocking temperature was found to be more for ‘sintered’ ferrites as compared to their ‘as prepared’ analogues.

Table 3.15 Saturation magnetization (M_s), remnant magnetization (M_r), coercivity (H_c), blocking temperature (T_B) at 5000 Oe and 10000 Oe, magnetocrystalline anisotropy (K_{eff}), magnetic moment (η_B) and squareness ratio of 'sintered' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

Composition (x)	Temperature	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
M_s (emu/g)	60 K	80.36	79.38	72.15	70.80	65.99	67.78	63.39	62.62	58.57	56.45	52.31
	300 K	79.52	78.66	71.69	69.02	63.58	66.25	62.33	57.70	54.43	52.02	47.88
M_r (emu/g)	60 K	63.10	59.05	55.39	53.85	52.61	51.67	47.44	45.76	40.75	33.81	23.50
	300 K	31.25	30.64	29.86	26.81	25.22	24.64	23.85	22.85	20.92	18.65	16.52
H_c (Oe)	60 K	6393	5595	5361	4070	3718	3623	3155	2569	1091	504	293
	300 K	1066	844	804	719	789	606	554	321	253	178	98
η_B	60 K	3.37	3.33	3.03	2.97	2.77	2.84	2.66	2.62	2.45	2.36	2.19
	300 K	3.34	3.30	3.01	2.89	2.66	2.64	2.61	2.42	2.28	2.18	2.00
$K_{\text{eff}} * 10^5$ erg^{-1}	60 K	5.2	4.5	3.9	2.9	2.4	2.49	2.0	1.6	0.65	0.62	0.55
	300 K	0.86	0.67	0.58	0.50	0.48	0.40	0.35	0.18	0.13	0.09	0.047
M_r/M_s	60 K	0.78	0.74	0.76	0.76	0.79	0.76	0.74	0.73	0.69	0.59	0.44
	300 K	0.39	0.38	0.41	0.38	0.39	0.37	0.38	0.39	0.38	0.35	0.34
T_B (K)	5000 Oe	344	338	330	328	324	320	311	292	282	256	235
	10000 Oe	295	290	284	283	279	277	229	217	211	206	142

3.8 Applications of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

3.8.1 Electrochemical Properties of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The electrochemical properties of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The fabrication of the working electrodes has been discussed in detail in chapter 2. The cyclic voltammetry (CV) studies were performed on all the ‘as prepared’ ferrite samples using the three electrode system along with an electrolytic solution of 3 M KOH at different scan rates from 10 – 200 mV/s. The studies were carried out between the potential window from 0 to 0.6 V and the respective voltammograms are depicted in Fig. 3.48 and Fig. 3.49. Two distinct peaks are seen approximately at 0.4 V (upper peak) and at 0.2 V (lower peak) in all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites for oxidation and reduction processes, respectively. These peaks in the voltammograms are due to the faradaic type of capacitive behaviour which signifies the pseudocapacitive character of the ferrites [89-91]. The exact values of the specific capacitance (C_{sp}) at different scan rates are shown in the Table 3.16. The C_{sp} obtained by CV measurements is dependent on the scan rate where there is an increase in the current density of the sample with increasing scan rates. Thus, the lowest scan rate (10 mV/s) has the highest C_{sp} values as compared to that at a higher scan rate (200 mV/s) (as obtained from Table 3.16).

The presence of large ohmic resistance at higher scan rates is one of the reasons for this behaviour. Besides, decreasing C_{sp} with increasing scan rates can also be attributed to certain parts of the electrode surface which are inaccessible at higher charging-discharging rates. Although at lower scan rates C_{sp} is almost due to the complete use of the electrode surface of the material [92]. Similarly for faradaic reactions occurring at higher potential rates, the electrolyte ions do not have sufficient time for complete diffusion through the electrode nanopores [93]. This results in the unavailability of some of the active parts of the surface area for charge storage at higher scan rates [94].

After calculating the specific capacitance values for all the ‘as prepared’ samples, it was found that although the C_{sp} for all the samples have good values ranging from 50 to 85.9 F/g but the sample $x = 0.3$ shows the highest C_{sp} values of 84.95 F/g at a scan rate of 10 mV/s thus showing a better pseudocapacitive behaviour. Better C_{sp} can also be related to better surface area of the nanomaterials as observed from the BET measurements.

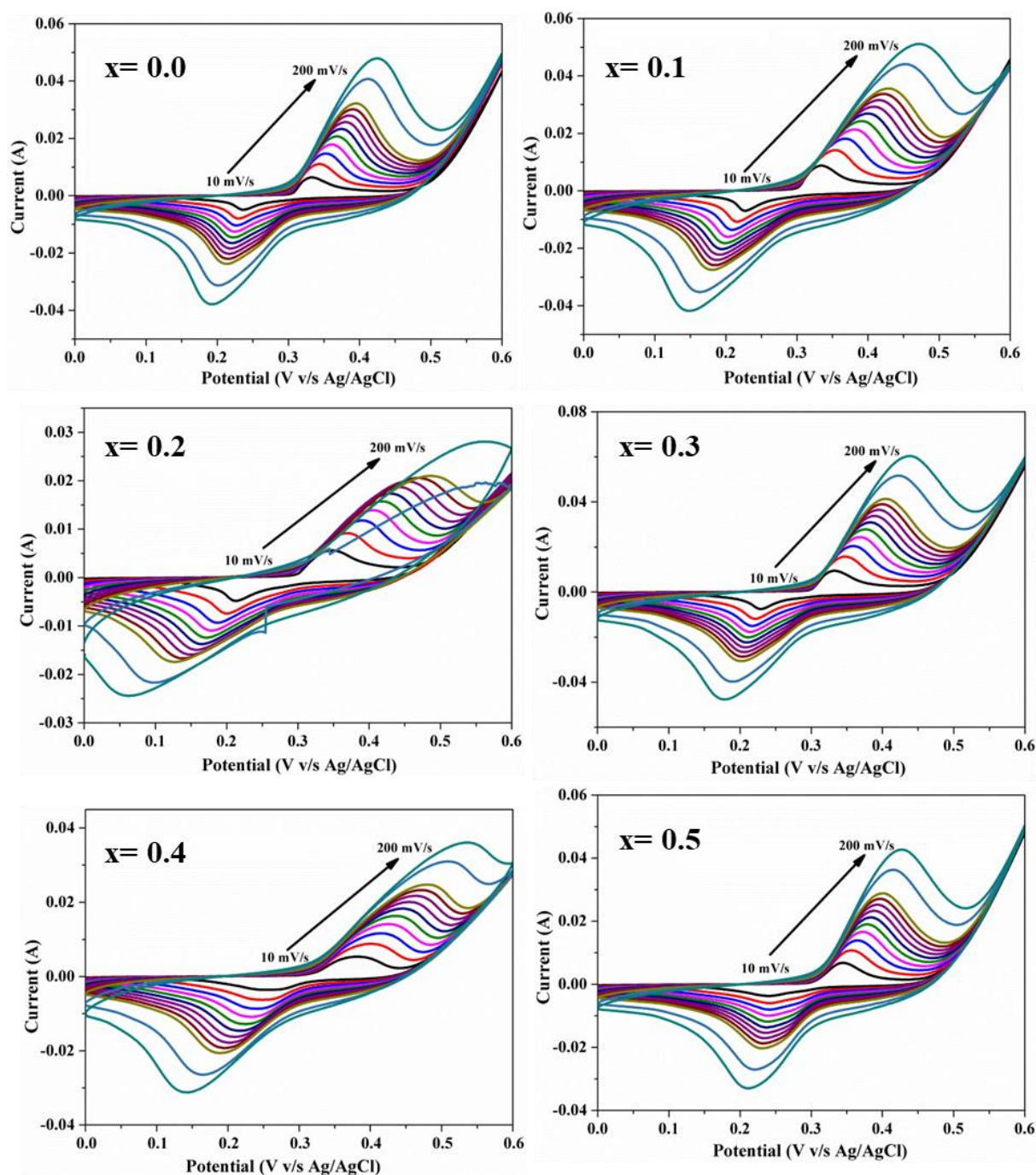


Fig. 3.48 Cyclic voltammograms of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) at varying scan rates ranging from 10 to 200 mV/s, with the potential window between 0-0.6 V.

The pseudocapacitive behavior of all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrite samples was also examined by performing the galvanostatic charge-discharge (GCD) studies at different current densities from 0.1 to 2.0 A/g (Fig 3.51 and Fig. 3.52). All the GCD curves have a non-linear nature and an evident plateau observed at different current densities affirming the pseudocapacitive nature of all the samples [95, 96]. All the GCD curves are non-linear implying pseudocapacitive behavior and this is associated

with the electrochemical adsorption/desorption or quasi reversible redox reactions at the electrode/electrolyte surface [91, 97]. The changes in the C_{sp} values with regards to the current densities for all compositions are shown in Table 3.17.

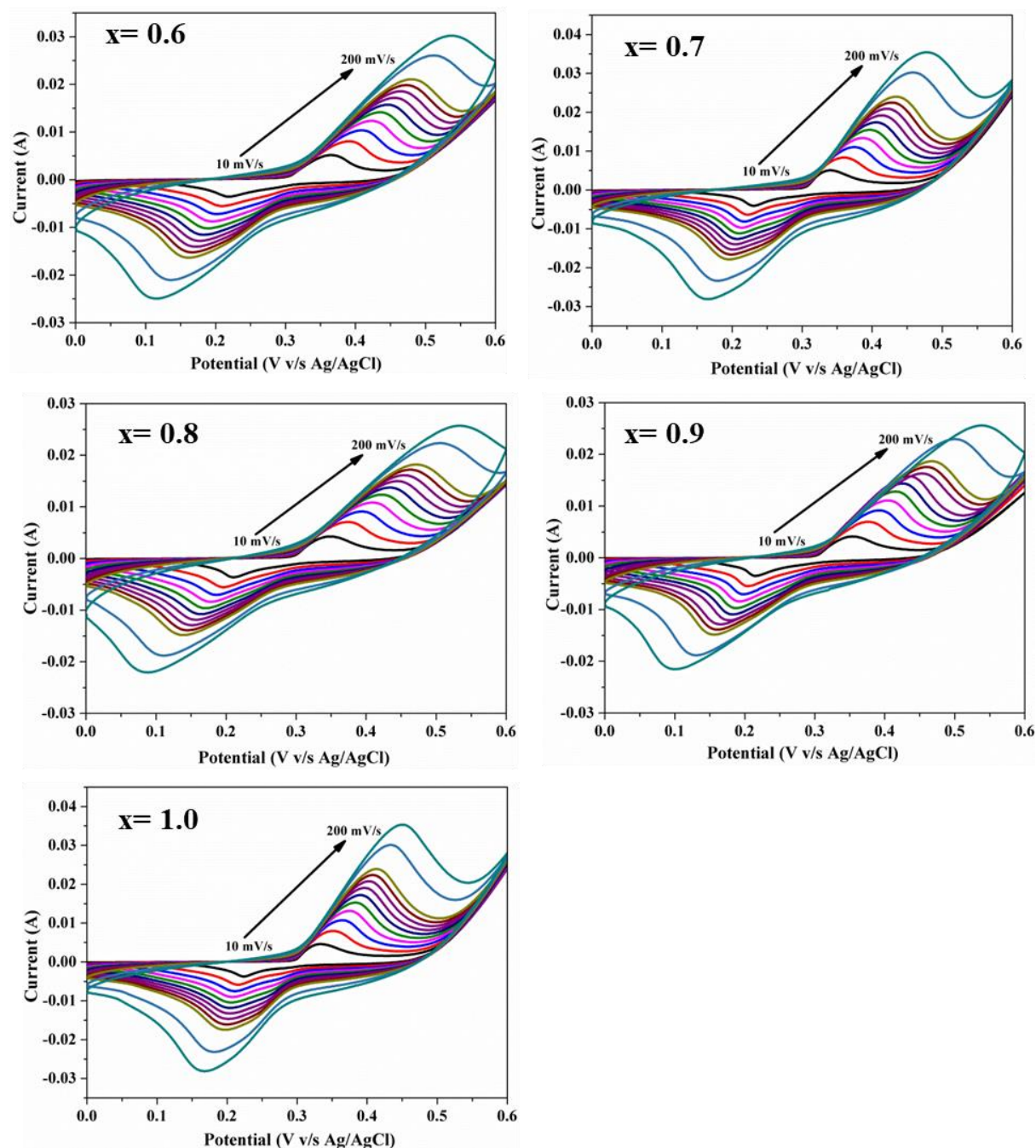


Fig. 3.49 Cyclic voltammograms of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.6-1.0$) at varying scan rates ranging from 10 to 200 mV/s, with the potential window between 0-0.6 V.

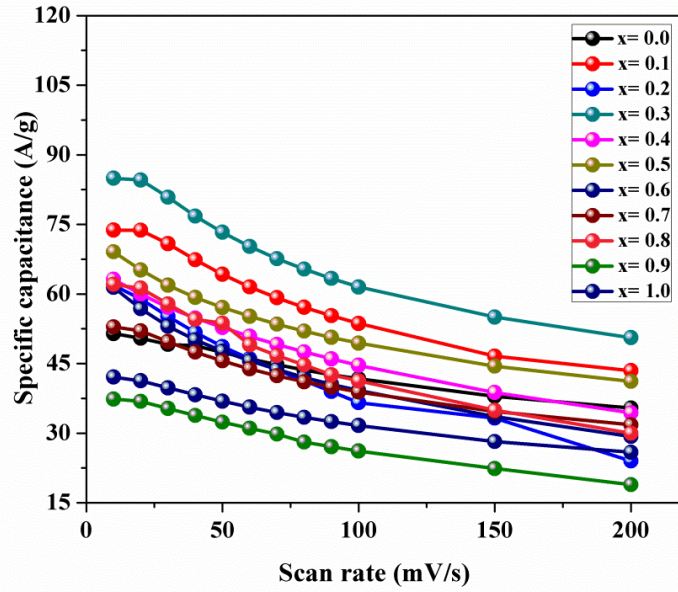


Fig. 3.50 The plot of specific capacitance against the scan rates plots for the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites.

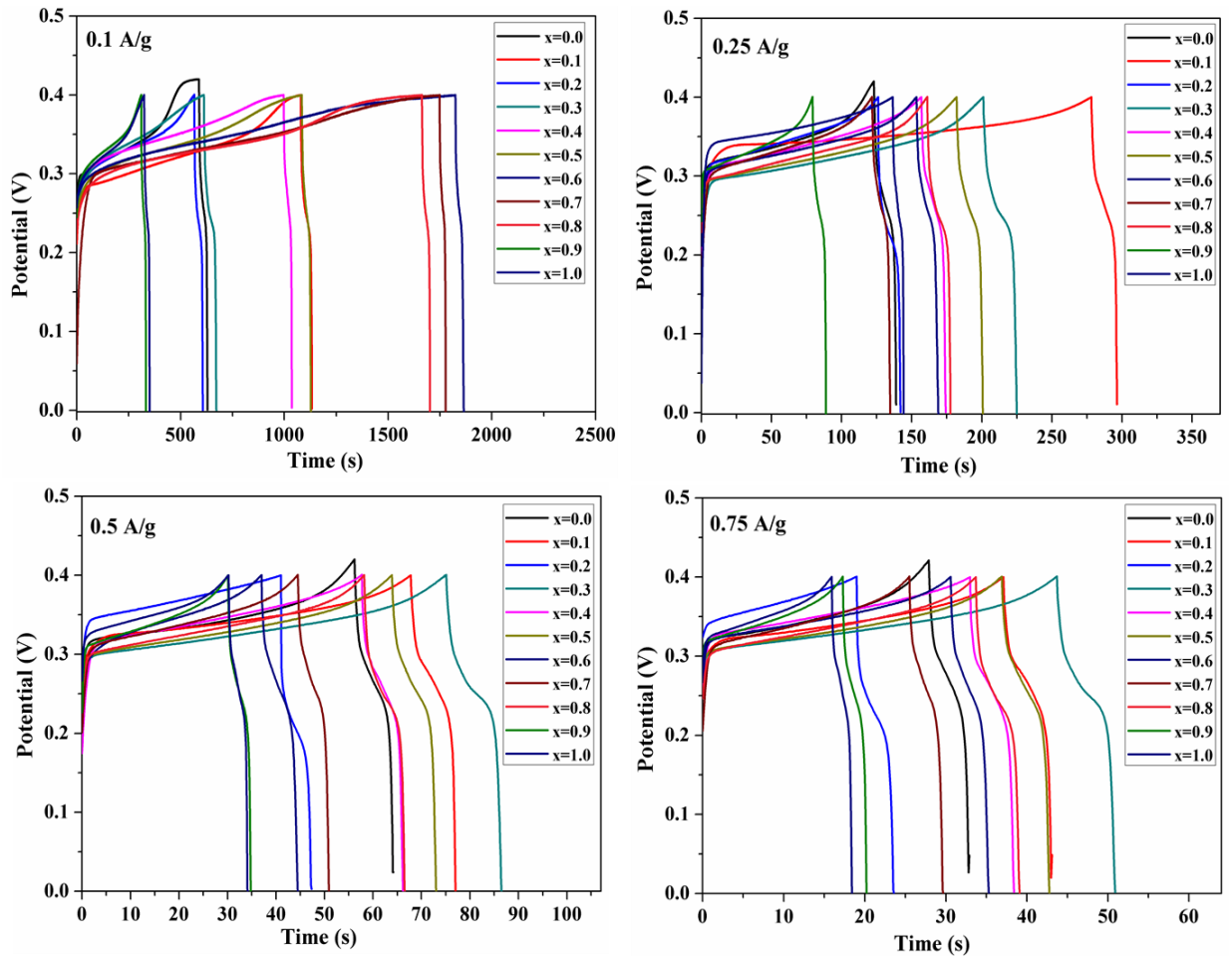


Fig. 3.51 Galvanostatic charge-discharge plots of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at charge-discharge current densities for 0.1, 0.25, 0.5 and 0.75 A/g.

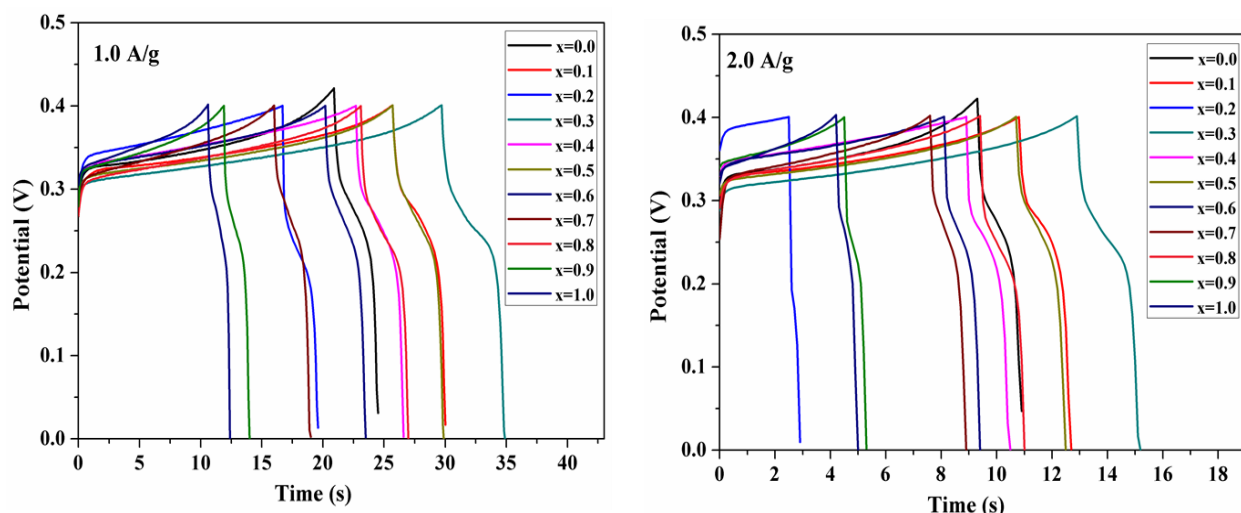


Fig. 3.52 Galvanostatic charge-discharge plots of ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites at charge-discharge current densities for 1.0 and 2.0 A/g.

The C_{sp} significantly decreases with increase in the current densities; this is mainly due to progressive fall in the voltage and insufficient active materials in the redox reactions due to which the electrolyte is poorly diffused inside the material as the current densities are increased [97, 98]. Amongst all the compositions under study, ferrite electrodes having $x=0.3$ composition shows a longer charge-discharge time indicating a good charge storage capacity.

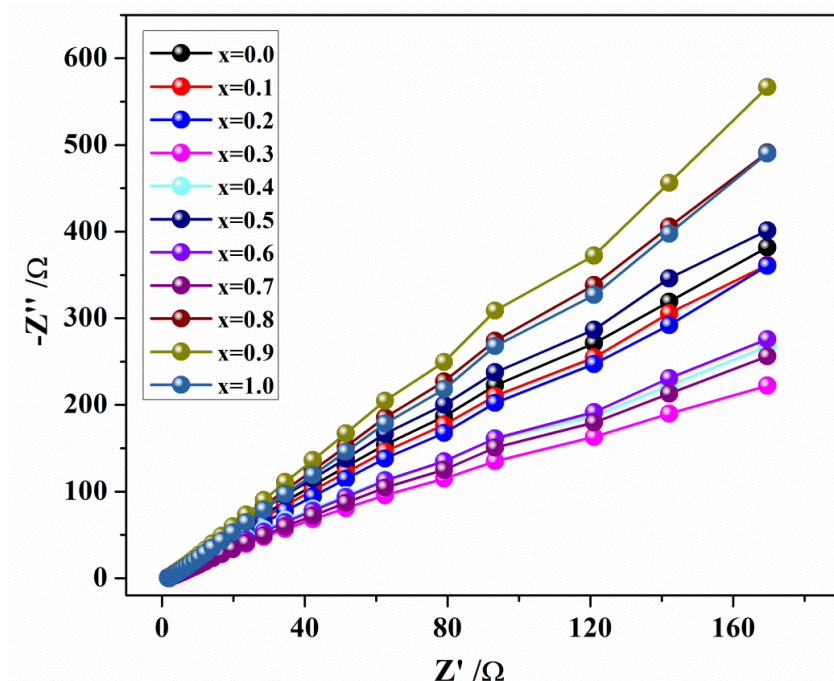


Fig. 3.53 Nyquist plots for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites samples.

Table 3.16 Specific capacitance of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrite samples at different scanning rates (cyclic voltammetry).

Scan rate (mVs ⁻¹)	Specific capacitance (C _{sp}) (in Fg ⁻¹) for ‘as prepared’ Ni _x Co _{1-x} Fe ₂ O ₄ (x= 0.0-1.0) ferrites											
	(x)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
10		51.47	73.76	61.89	84.95	63.16	69.11	61.41	52.91	62.07	37.35	42.11
20		50.45	73.75	58.97	84.57	60.00	65.17	56.82	52.05	61.26	36.86	41.30
30		49.13	70.84	55.16	80.85	57.13	61.89	53.04	49.73	57.83	35.34	39.76
40		48.86	67.38	51.69	76.78	54.83	59.26	50.12	47.48	54.54	33.83	38.27
50		47.44	64.24	48.65	73.31	52.78	57.09	47.71	45.58	53.70	32.40	36.90
60		46.03	61.54	46.04	70.24	50.88	55.19	45.61	43.86	49.04	31.06	35.62
70		44.78	59.19	43.62	67.60	49.12	53.50	43.74	42.38	46.74	29.80	34.45
80		43.62	57.13	41.34	65.36	47.52	52.01	42.05	41.09	44.71	28.08	33.42
90		42.61	55.33	38.99	63.35	46.02	50.65	40.56	39.94	42.57	27.09	32.49
100		41.72	53.65	36.59	61.51	44.62	49.40	39.19	38.88	41.28	26.15	31.67
150		37.96	46.60	33.25	55.02	38.77	44.46	33.59	34.70	34.95	22.38	28.20
200		35.43	43.48	24.01	50.59	34.37	41.16	29.30	31.79	29.99	18.91	25.89

Moreover, another suitable electrochemical technique for the detection of impedance related to redox reactions is the electrochemical impedance spectroscopy (EIS) studied in the frequency range of 100 kHz to 0.1 Hz. This method helps in understanding the characteristics of an electrode/electrolyte interface as supercapacitors by examining the equivalent series resistance and the frequency behavior. It provides information regarding the resistance between electrode and electrolyte and the internal resistance of the electrode material [21]. Fig 3.53 demonstrates the Nyquist plots for all the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites. A straight line is observed at lower frequencies and a distorted semicircle is seen at higher frequencies. The EIS spectra intercept approximately

at 1.76-2.81 Ω of the real part of the impedance (Z') which represents the combined solution resistance (R_s) in the higher frequency region of the plot [99-101]. The distorted semicircle is seen in this region and the estimated diameter of this semicircle is the charge transfer resistance (R_{CT}) at the working electrode-electrolyte interface [94].

However the lower frequency region of all the Nyquist plots showed a straight line curve almost inclined at an angle of 45° with the Z' axis is known as the Warburg impedance (W). The Warburg impedance is related to the transportation and the diffusion of the counter ions in between the electrolyte and the electrode material [95, 100].

Table 3.17 Specific capacitance of the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites samples at different current densities (Galvanostatic charge-discharge)

Current densities	Specific capacitance (C _{sp}) (in Fg ⁻¹) for ‘as prepared’ Ni _x Co _{1-x} Fe ₂ O ₄ (x= 0.0-1.0) ferrites											
	(x)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.1		54.34	91.78	62.64	91.92	72.11	84.57	73.71	61.18	90.12	32.94	32.91
0.25		51.88	72.84	61.91	91.05	72.01	83.68	62.50	47.34	82.01	31.73	27.12
0.5		50.45	69.20	49.16	86.68	68.10	82.79	61.69	47.30	79.65	31.41	24.96
0.75		49.70	65.55	47.34	80.85	67.30	76.56	58.89	45.89	77.30	27.88	24.65
1		49.04	64.10	42.24	74.30	62.50	76.55	52.88	42.24	61.51	28.20	23.11
2		47.77	55.36	39.32	69.93	54.48	64.10	41.66	37.87	60.33	20.51	19.72

3.8.2 Gas sensing properties of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites

The gas sensing properties of pure and nickel substituted nickel cobalt ferrites were examined by focussing on the potential gas sensing factors viz. temperature, concentration after exposing the sensor to a various gases. From the literature we can conclude that the ferrite nanoparticles are very interesting sensing materials which are affected by factors such as structure, morphology, crystallite sizes, and surface area and so on.

The gas sensing properties of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were examined for four different gases like Cl_2 , NH_3 , NO_2 and LPG at temperatures of 30 °C , 50 °C , 100 °C and 150 °C with different concentrations. All the samples showed a highest response towards Cl_2 gas, a good response to NO_2 gas, weaker response towards LPG with the least response towards NH_3 gas. An ideal sensor material is the material with very good sensing properties having shorter response and recovery time, selectivity, sensitivity and a better reproducibility.

3.8.2.1 Effect of operating temperatures on the gas sensing response

The optimum operating temperature was confirmed by the gas sensing response of all the ferrite thick films concerning various concentrations of the oxidizing gases (Cl_2 and NO_2) and reducing gases (NH_3 and LPG) and are shown as a function of temperature. Fig. 3.54, Fig. 3.55, Fig. 3.56 and Fig. 3.57 represents the plots of the sensor responses against the operating temperature at concentrations of 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm for Cl_2 , NO_2 , LPG and NH_3 gases, respectively. From these plots, it was observed that the gas sensing response was found to increase as the operating temperature increases from 30 °C to 50 °C. But further increase in the temperature from 50 °C to 150 °C results in the decrease in the gas sensing response. These results obtained are very similar to the findings obtained by Dang et al. [102]. They reported that at a certain concentration of Cl_2 gas for ZnO nanowires, the gas sensing response was found to increase with increase in temperature and with further increase in temperature the sensor response was found to decrease.

The adsorption phenomenon in the ferrite samples is significantly responsible for the rise in sensor response at low temperature while the decreased responses can be justified by

the desorption reactions (confirmed by the adsorption-desorption isotherm in BET) [102-103].

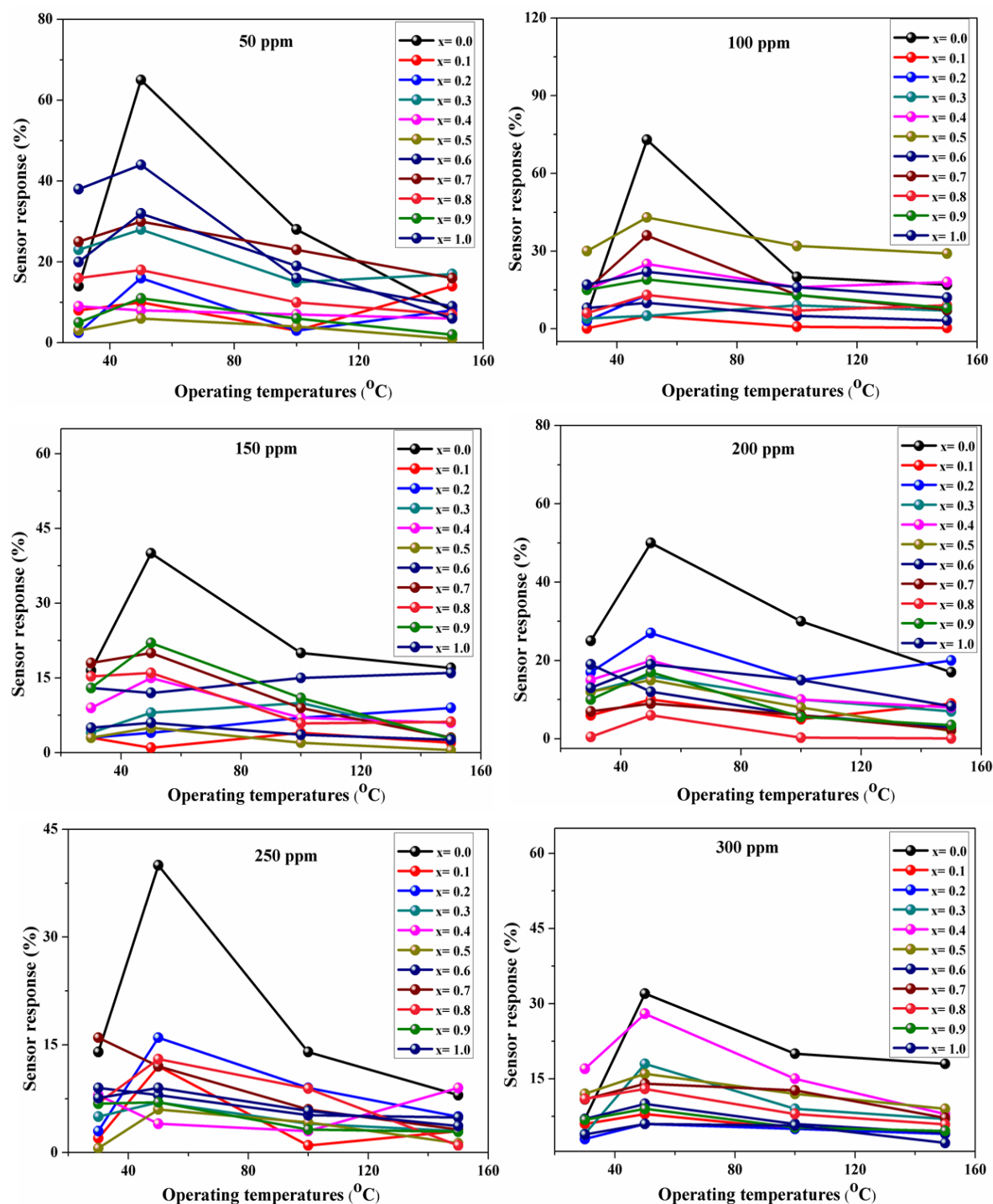


Fig. 3.54 The plot of sensor response v/s operating temperature at 50 ppm , 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm concentrations for Cl_2 gas.

Fig. 3.54 demonstrated that all the ferrite samples showed the best responses for different concentrations of Cl_2 gas at operating temperatures of 30 °C, 50 °C, 100 °C and 150 C.

However the highest response of 73 % was observed for $x = 0.0$ composition at 50 °C for 100 ppm concentration of Cl_2 .

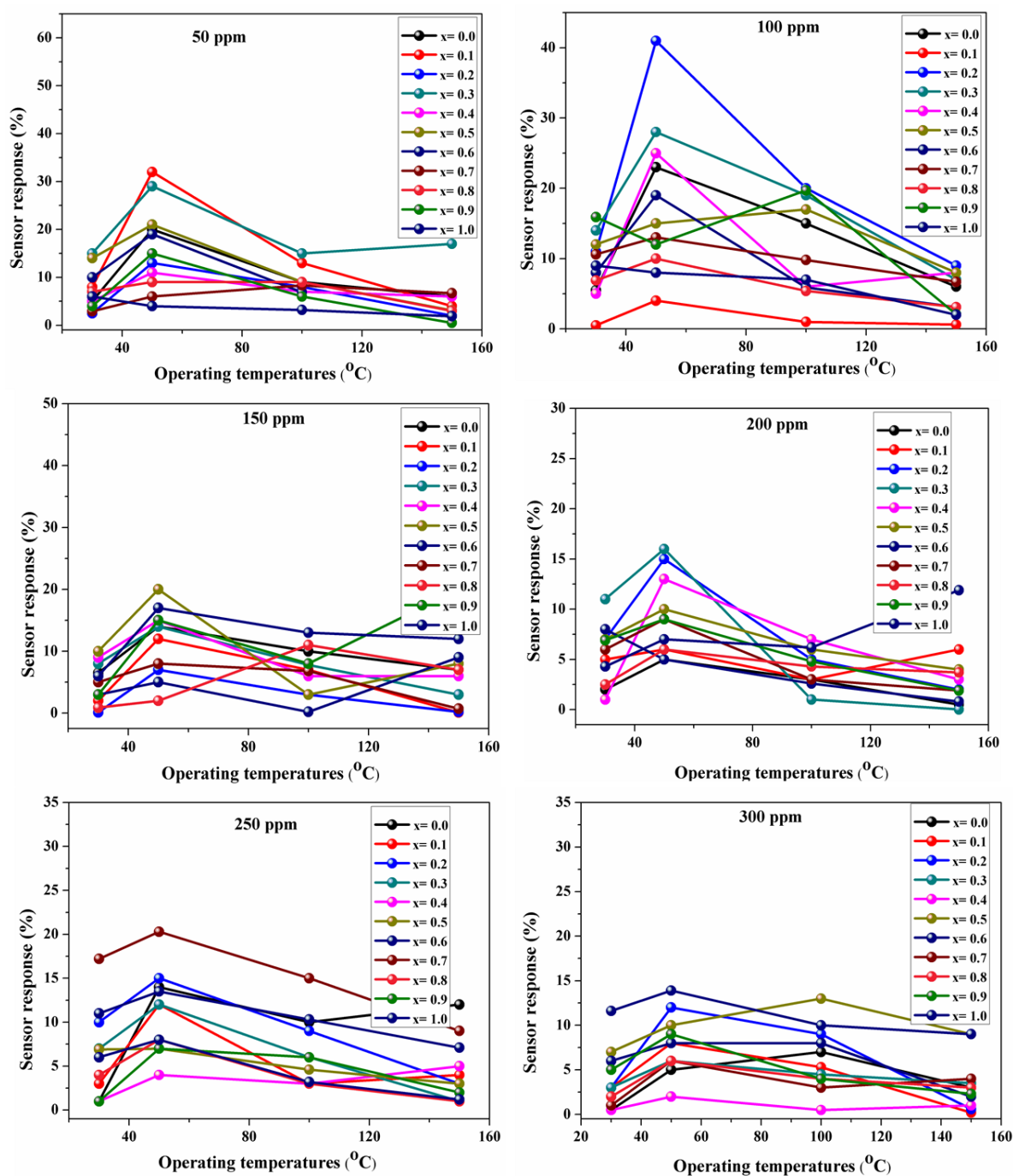


Fig. 3.55 The plot of sensor response v/s operating temperature at 50 ppm , 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm concentrations for NO_2 gas.

From Fig. 3.55 it was observed that all the ferrites thick films exhibited a good response towards NO_2 gas towards different concentrations of the gas. However the most response

of 41 % was obtained by $x = 0.2$ thick film composition at 50 °C for 100 ppm of NO_2 concentration.

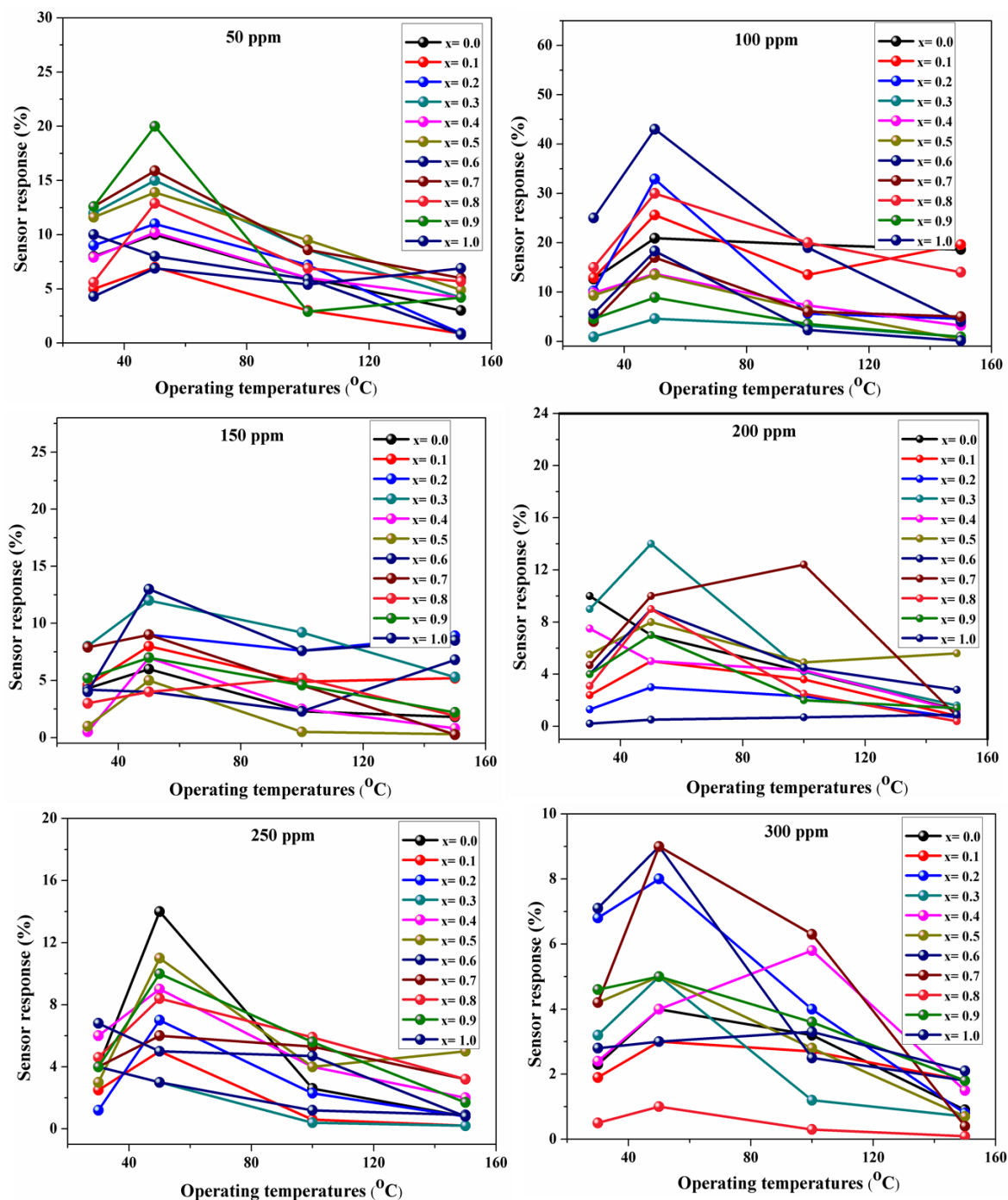


Fig. 3.56 The plot of sensor response v/s operating temperature at 50 ppm , 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm concentrations for LPG gas.

Fig. 3.56 showed some response of ferrite thick films for LPG gas but the response was weaker as compared to that shown for Cl_2 and NO_2 gases. However, at 100 ppm of LPG concentration a considerable gas sensing response was shown by the ferrite thick films.

The thick film $x = 0.6$ showed highest response of 43 % at 50 °C for 100 ppm concentration of LPG gas.

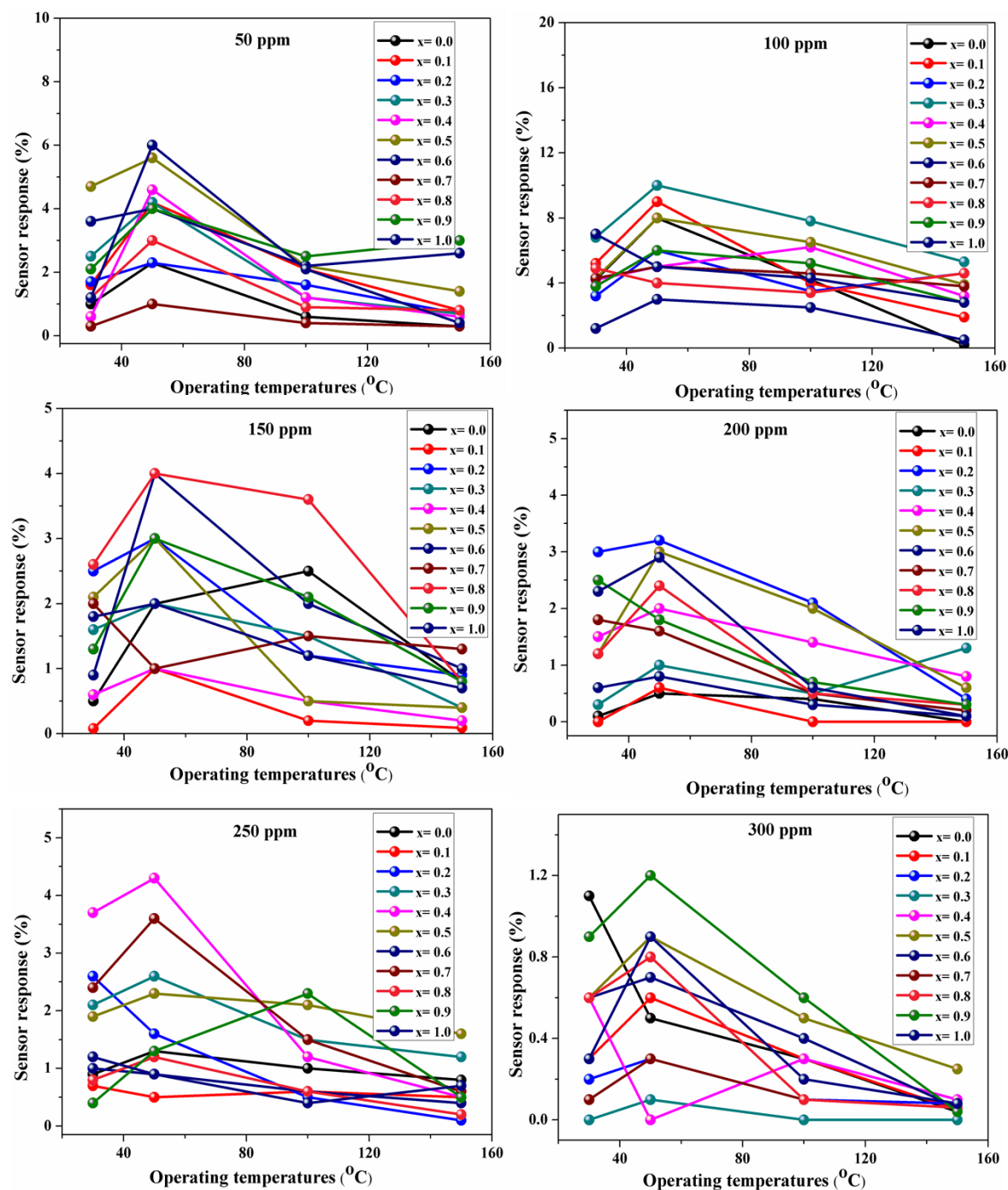


Fig. 3.57 The plot of sensor response v/s operating temperature at 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm concentrations for NH_3 gas.

Weak gas sensing responses were observed towards different concentrations of NH_3 gas for all the ferrite thick films and the highest response of 10 % was observed for composition $x = 0.3$ for 100 ppm concentration of NH_3 at 50 °C (Fig. 3.57).

3.8.2.2 Effect of gas concentration on the gas sensing response

Most of the literature reports show an increase in the gas sensing response with increase in the concentration of gases [104-105]. However, when we studied our ferrite thick films for gas sensing applications we found a deviation in the results. In almost all the compositions we found that the gas sensing response was higher at 100 ppm concentration for all the samples but the response subsequently decreases with increasing concentrations and then remain saturated or even decreases with further increase in the gas concentrations. This possibly could be due to the unimolecular gas layer formation on the ferrite surface (from 50 ppm to 100 ppm) showing better sensing responses. However, beyond 100 ppm concentration it gets saturated due to increased surface layers i.e. because of many gas molecule layers. R. P. Powar et al. [106] also reported similar behaviour for the gas sensing studies conducted of zinc substituted cobalt ferrite thick films for ethanol gas concentration where initially it increases and then remained saturated above 100 ppm concentration of gas. Besides, this decreasing response with increasing gas concentration can also be justified by saturation of the surface active sites by the surface gas molecules.

Fig. 3.58 demonstrate the 3D plots of sensor response against concentration of gas (50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.1$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards Cl_2 gas. From this figure it can be concluded that the maximum gas sensing response is shown by $x = 0.0$ composition at 50 °C for 100 ppm of the Cl_2 gas with shortest response time of ~ 3 seconds and recovery time of ~ 5 seconds. The ferrite thick film $x = 0.6$ also exhibited a good response for 50 ppm of Cl_2 at room temperature. However this showed the response time of ~ 23 seconds and recovery time of ~ 16 seconds which was found to more than the composition $x = 0.0$. As we studied the gas sensing response at higher temperature for Cl_2 gas, it was observed that sensing response was decreasing. The ferrite thick film $x = 0.5$ showed response of 25 % and 20 %, respectively for 50 °C and 100 °C at 100 ppm concentration of gas. It showed the response and recovery time of ~ 15 seconds and ~ 5 seconds at 50 °C and ~ 7 seconds and ~ 13 seconds at 100 °C.

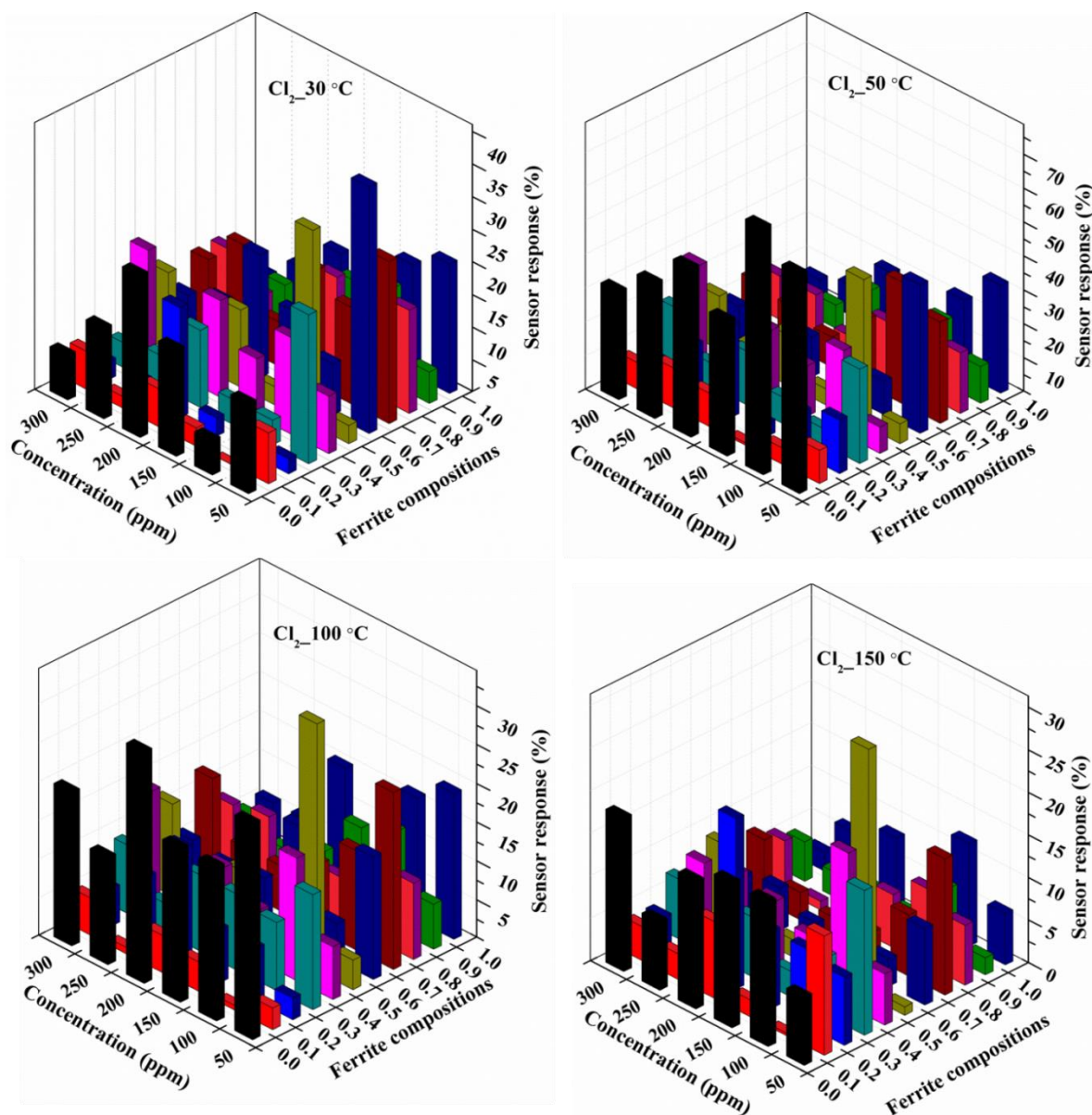


Fig. 3.58 The 3D plots of sensor response v/s concentration for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards Cl_2 gas.

Fig. 3.59 displayed the 3D plots of sensor response against concentration of gas (50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-0.1$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards NO_2 gas. The plots imply that the highest gas sensing response was observed for $x = 0.2$ composition for 100 ppm of NO_2 gas having shortest response and recovery time of ~ 4 seconds and ~ 6 seconds, respectively at 50 °C. Besides the thick film $x = 0.9$ also showed a response of around 19 % with the response time of approximately 15 seconds and the recovery time of ~ 20 seconds for 150 ppm concentration of NO_2 gas at 150 °C. In general the lowest sensing responses were seen at the temperature 150 °C. At room temperature the ferrite thick

film $x = 0.7$ showed a better response of around 15 % with the response time of ~ 5 seconds and the recovery time of ~ 10 seconds.

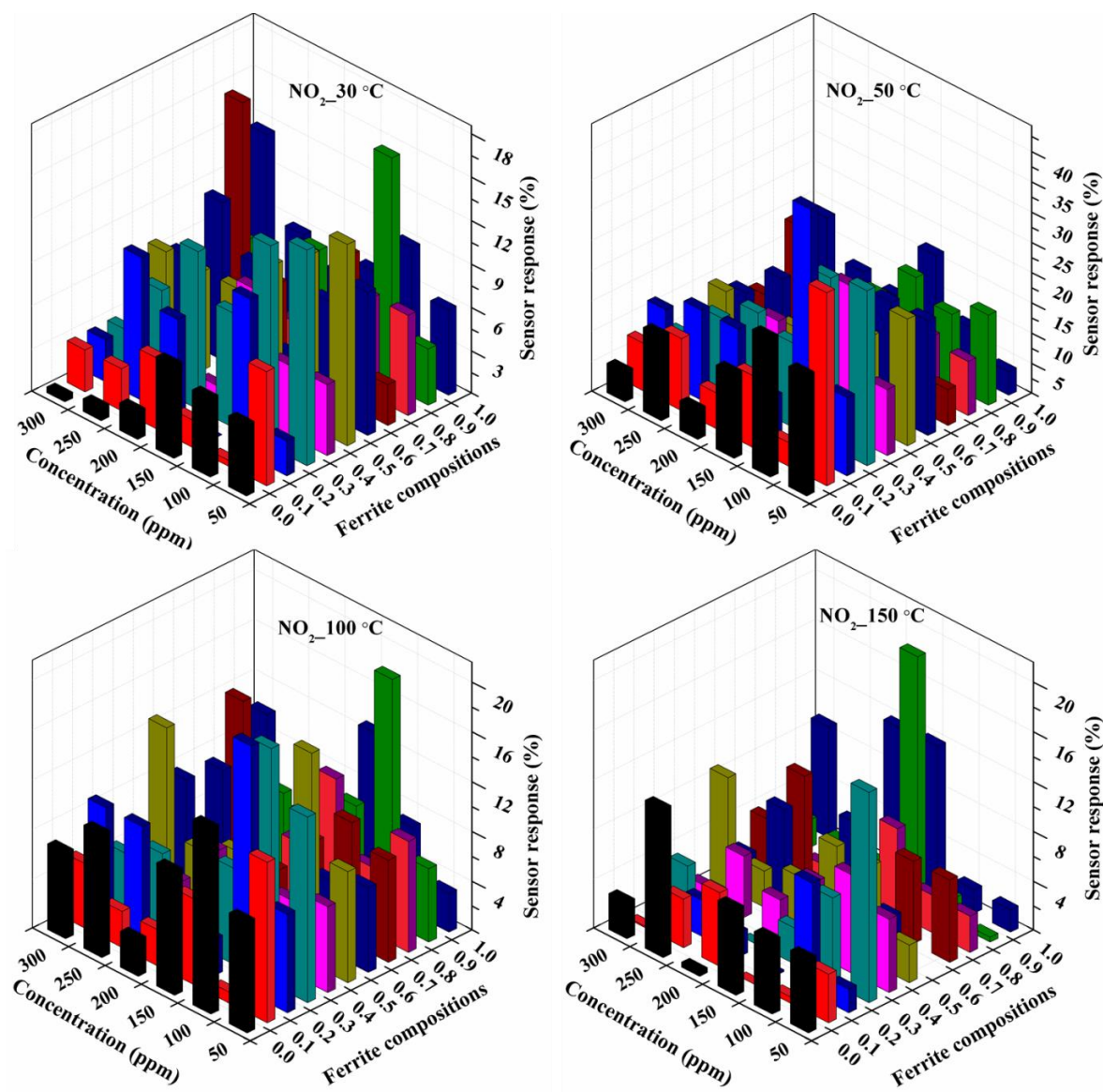


Fig. 3.59 The 3D plots of sensor response v/s concentration for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards NO_2 gas.

The 3D plots of sensor response against concentration of gas (50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards LPG gas has been shown in Fig. 3.60. We encountered less gas sensing response for the LPG gas in comparison with Cl_2 or NO_2 . Again in this case as well, we saw better response at 50 °C for 100 ppm concentration of gas. The ferrite thick film $x = 0.6$ showed the highest gas sensing response of 40 % towards LPG gas at 100 ppm gas concentration at 50 °C. The response and recovery time were found to be ~ 5 seconds and ~ 10 seconds, respectively. The same

composition shows the sensing response of around 20 % for 100 ppm of LPG at 30 °C with response and recovery time of ~15 seconds and ~ 8 seconds, respectively. Moreover, it was seen that upon increasing temperature to 150 °C there is a drastic decrease in the sensing response and the highest response at this temperature was shown by $x = 0.1$ thick film for 100 ppm concentration having response time of 14 seconds and the recovery time of 20 seconds.

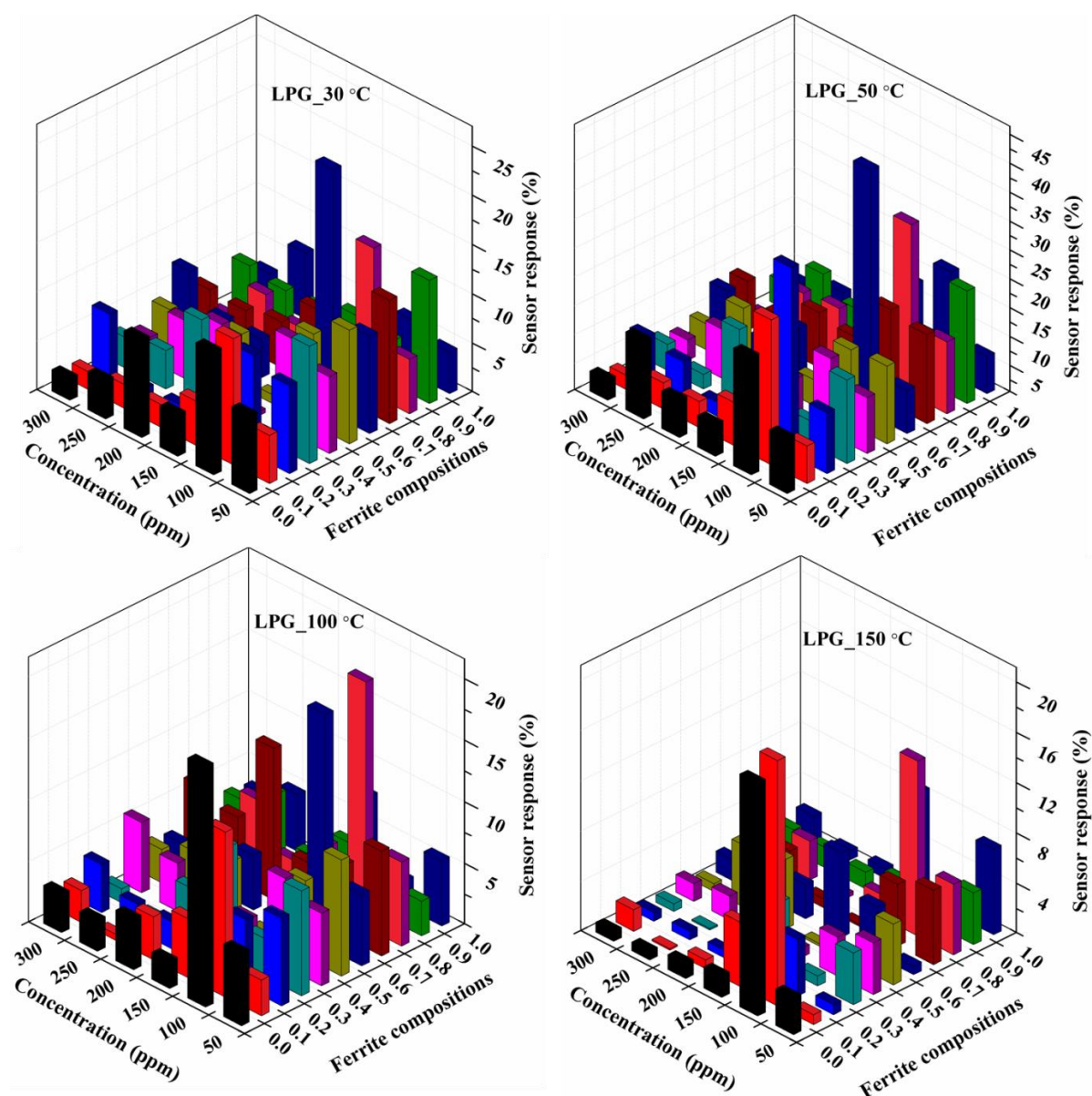


Fig. 3.60 The 3D plots of sensor response v/s concentration for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards LPG gas.

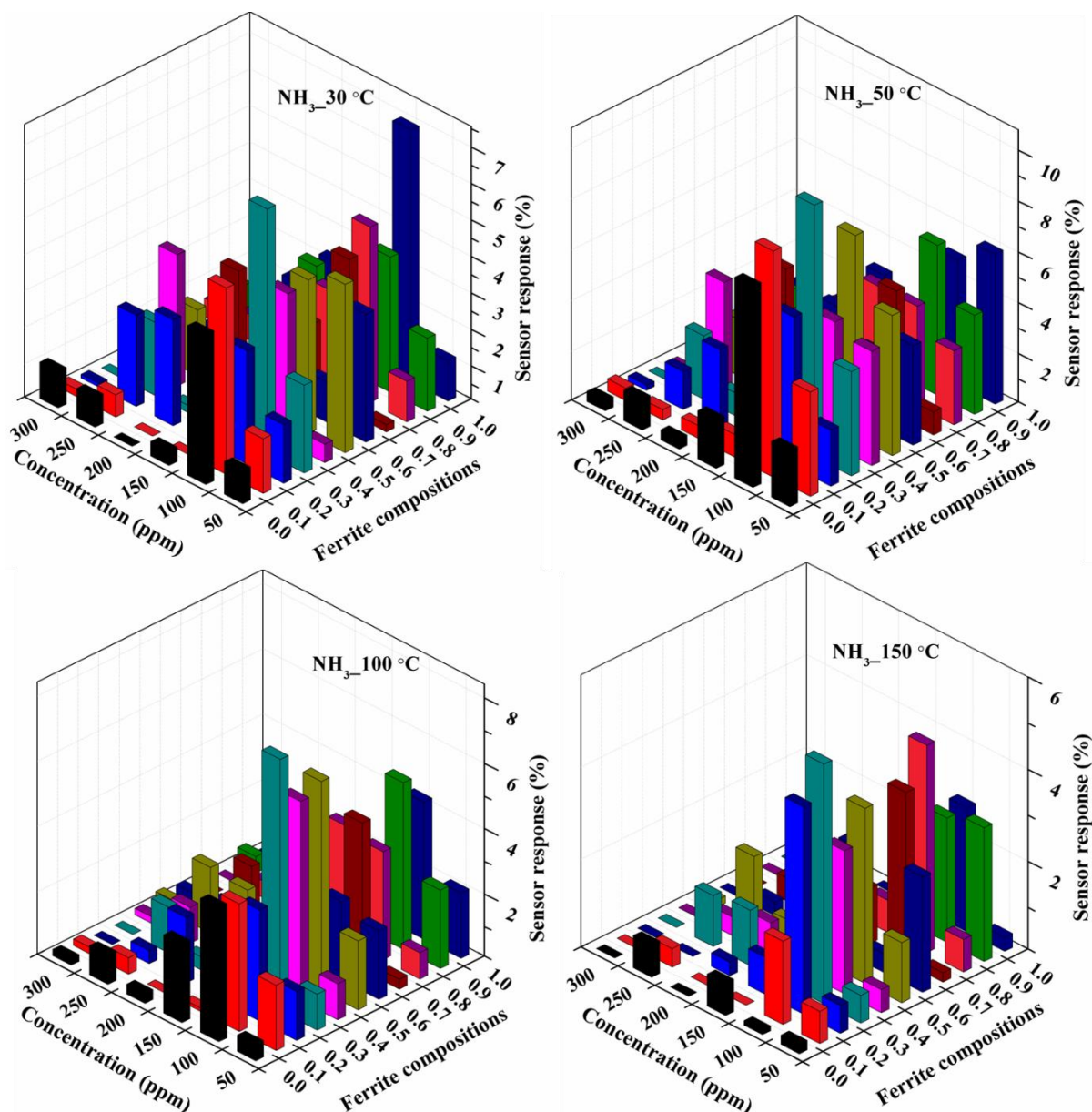


Fig. 3.61 The 3D plots of sensor response v/s concentration for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C towards NH_3 gas.

We also studied gas sensing response of ferrites for NH_3 gas and we found out that NH_3 shows the least response amongst all the test gases for all the samples. Fig. 3.61 shows the sensor response against concentration of NH_3 gas (50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at 30 °C, 50 °C, 100 °C and 150 °C. The highest response for NH_3 was shown by ferrite thick film $x = 0.3$ for 100 ppm of gas concentration. This composition shows the highest response of 8 % with the response and recovery time of ~ 15 seconds and 25 seconds, respectively. Also at other temperatures the gas responses for all the compositions at all the concentrations were found to be almost negligible.

3.8.2.3 Response-recovery and reproducibility

As confirmed from the plots, $x = 0.0$ sensor thick films at 30 °C, 100 °C 150 °C show some response towards NO_2 , and a small response towards LPG and NH_3 . However the response is not that prominent and also it doesn't have any selectivity. While at 50 °C the sensing response towards Cl_2 gas at 100 ppm concentration for $x = 0.0$ is very high close to 75 % with a short response time of ~ 3 seconds and recovery time of ~ 5 seconds. Likewise for $x = 0.2$ concentration we did not get any appreciable response for Cl_2 gas, but good response (41 %) was observed towards NO_2 gas at 50 °C for 100 ppm concentration with high selectively. In this case as well LPG, NH_3 and Cl_2 showed certain response but the less selective. The thick film of $x = 0.2$ had a response time of ~ 4 seconds and recovery time of ~ 6 seconds. High response, shorter response time and shorter recovery time are indeed the key factors necessary for a material to act as good sensor. Fig. 3.62 and Fig. 3.63 assessed the response-recovery plots for reproducibility of the gas sensors developed at 50 °C for 100 ppm concentration for $x = 0.0$ towards Cl_2 gas and for $x = 0.2$ for NO_2 gas respectively.

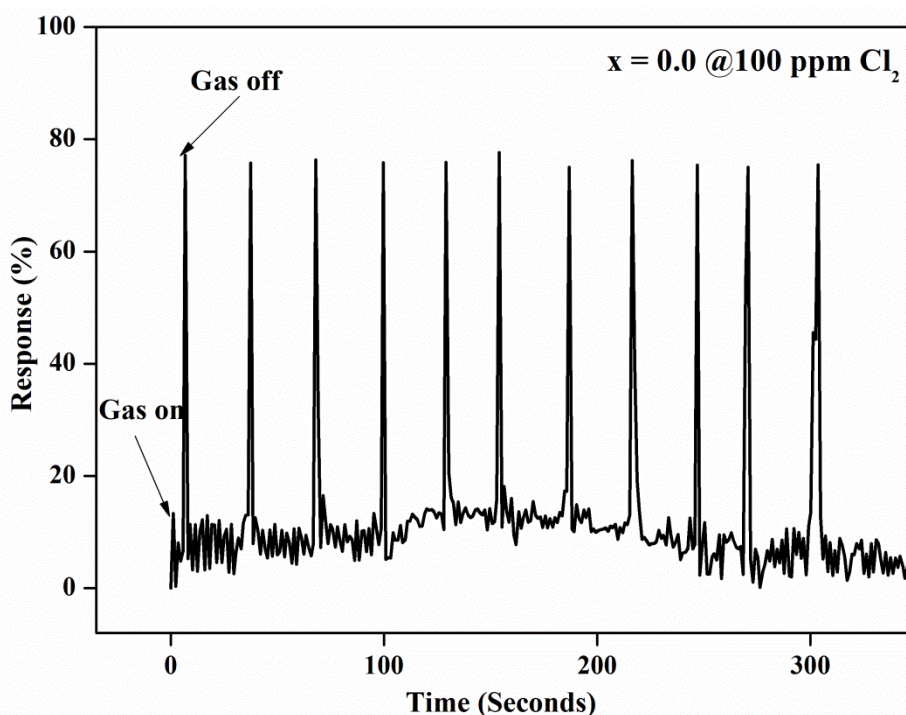


Fig. 3.62 The reproducibility plots of response-recovery against time for $x = 0.0$ ferrite thick film towards Cl_2 gas at 100 ppm at an operating temperature of 50 °C.

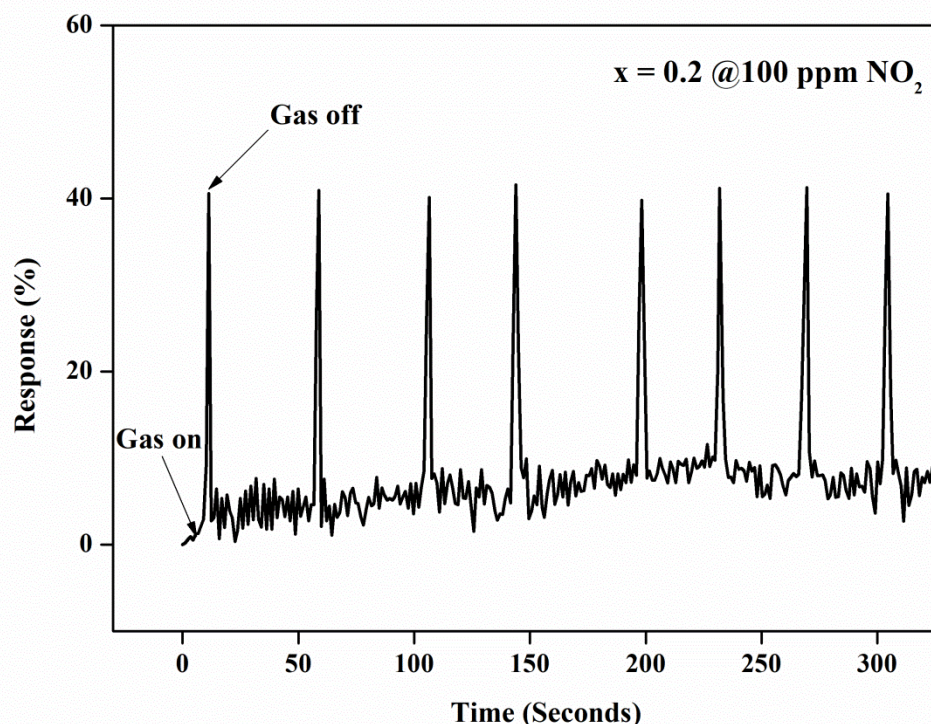


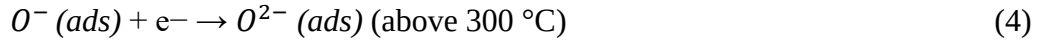
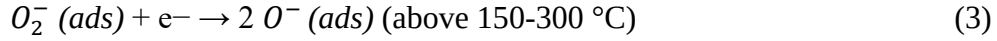
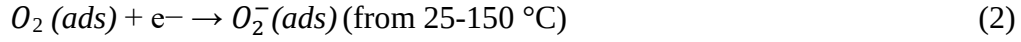
Fig. 3.63 The reproducibility plots of response-recovery against time for $x = 0.2$ ferrite thick film towards NO_2 gas at 100 ppm at an operating temperature of 50°C .

3.8.2.4 Gas sensing mechanism

It is familiar that the gas sensing mechanism of the semiconductor is explained mainly based on the surface controlled mechanism. The metal oxide mechanism of gas sensing is predominantly based on the change in the electrical resistance or conductance on exposure to a certain target gas (oxidizing or reducing) of the sensor thick film. On exposing the metal oxide semiconducting material to numerous oxidizing and reducing gases, either the contact between the previously adsorbed oxygen species on the surface of thick film with the target gases or the straight interaction of the target gases with semiconducting surfaces is responsible for the change in the resistance [25, 28]. The reaction between the oxygen species and the gas adsorbed is favoured if large quantity of gas is adsorbed, thus getting a good sensing response [107].

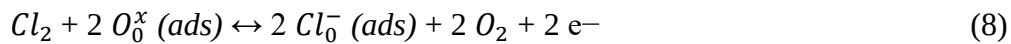
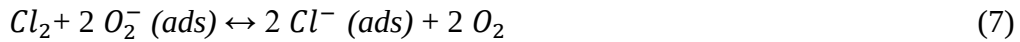
Exposure of the sensor to air leads to adsorption of atmospheric oxygen molecules on the sensor surface which subsequently captivates the electron from conduction band of sensor forming chemisorbed oxygen species as shown in the equations 1-3 [30, 108-109]. The adsorption of O_2^- species occurs at low temperatures while O^- or O^{2-} species adsorb at elevated temperature as seen in the equations [30, 110-111]. The plausible chemisorbed

oxygen species engaged in our work would be O_2^- since the optimum operating temperature in our study towards the gases is 50 °C.



The higher potential barrier is formed near the sensor thick film surface which hinders the oxygen molecules from further capturing the free electrons whilst the sensor resistance was comparatively lesser due to presence of a thick holes accumulation layer near sensor surface. On gases exposure, the gas molecules are oxidized by oxygen anions, the released electrons from conduction band are combined with holes thus decreasing the height of potential barrier and thickness of holes accumulation layer [108] leading to increase in conductance and thus consequently reducing the resistance of the sensor [30].

The four reactions below are responsible for the gas sensing response of the oxide sensors in case of Cl_2 gas [112, 113].



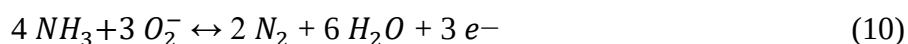
The equations 5 and 6 claim the capturing of the electrons by Cl_2 causing an increased number of holes, while equation 7 indicates that O_2^- ions are consumed by Cl_2 thus resulting in decrease in resistance in the p-type semiconductor (equations 5, 6 and 7). However, in case of equation 8, the released electrons lead to a decrease in the number of holes due to partial electron-hole neutralization causing an increase in resistance [112].

When NO_2 gas (oxidizing) comes in contact with the O_2^- species of p-type semiconducting sensor, it captures the electrons from sensor leading to a decrease in resistance [88]. The equation for the same can be given as follows [114].

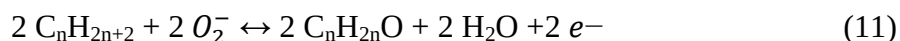


Owing to the electron accepting nature of NO_2 gas, most of the charge carriers are holes thus increasing its density. Hence the sensor conductivity increases with decreased resistance.

For NH_3 sensing when the surface of the ferrite thick film comes in contact with the gas, the gas molecules interacts with O^{2-} species and they release the electrons back to the sensor hence causing decrease in the resistance. The equation for the same can be written as



The equation for the sensing mechanism of LPG gas can be given as



It is observed that when the gas comes in contact with sensor thick film there is a reaction between the gas and the chemisorbed oxygen species after its interaction with the hydrocarbon in LPG. Thus, there is formation of water vapour (gaseous species) since the adsorbed oxygen is removed. The electron concentration on the ferrite surface is increased thus resulting in increase in electron from the conduction band of sensor thus leading to decrease in resistance.

3.9 Conclusions

This chapter presents the synthesis, characterization, properties, and applications of $Ni_xCo_{1-x}Fe_2O_4$ ($x = 0.0-1.0$) ferrites. The ferrites were synthesized using a combustion method with tartaric acid as fuel, and the process was optimized using various oxidizer:fuel ratios. An optimal ratio of 1:0.75 yielded single-phase cubic spinel ferrites with smaller crystallite sizes and single-domain particle nature. Structural confirmation and stoichiometry were established using powder XRD, ICP-AES, IR, Raman, and XPS analyses. Morphological studies using SEM and HR-TEM revealed agglomerated nanocrystalline particles. Electrical and dielectric studies confirmed the semiconducting nature of the ferrites, while magnetic investigations showed an increase in Curie temperature and a decrease in saturation magnetization and coercivity with increasing nickel content. Sintering enhanced crystallinity and the particle sizes. The ‘as prepared’ ferrites demonstrated promising performance in gas sensing and supercapacitor applications, with the composition $x = 0.3$ exhibiting the highest specific capacitance.

Finally, the ‘as prepared’ ferrites were successfully tested for supercapacitor and gas-sensing applications, with the composition $x = 0.3$ showing the best electrochemical performance and good sensitivity toward various gases highlighting their multifunctional potential.

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Chapter 4

*$Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x= 0.0-0.5$) ferrites: Synthesis,
characterization, solid state properties and their applications*

4.1 Introduction

The literature reports of the nanostructured ferrites demonstrate the advancement of appreciable interest in comprehending the numerous physical and chemical properties particularly in the nanoscale region because of their extensive applications.

Nevertheless, the smaller crystallite sizes of the nano structured ferrites highly influence various properties of the ferrites. It is observed that the chemical and the physical properties of the nano ferrites are generally different from their bulk analogues and many advanced applications such as data storage require smaller crystallite size particles [1]. The substituted magnesium ferrites are found to be used appreciably in applications such as magnetic recordings, magnetic sensors, transformers, etc. [2]. The main cause of the variety of applications is associated with the numerous transition metal cations that can be embodied into the spinel lattice of the pristine structure.

The element magnesium is environmentally friendly and biocompatible and accounts for numerous applications such as high performance vehicles [3], defense constructions [4] and other such practical uses. Considering efficient and sustained energy storage appliances, supercapacitors (SCs) demonstrate rapid charge-discharge behavior, long cycle life and greater energy densities in comparison with the conventional batteries [5-7]. Energy storage in the SCs is done by using fast surface redox reactions [8-9] and hence there is a need to develop the electrode material involving large redox sites and high surface area in order to promote better SCs performance [10].

In the present work we have investigated the impact of cobalt and magnesium substitution on nickel ferrite. The ferrite system $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites was synthesized by combustion method using L-tartaric acid dihydrazide as a novel fuel. In this case, we have synthesized the fuel in the laboratory and did the characterization of the same. The exact procedure for the ferrites synthesis and the synthesis and characterization of the fuel synthesized has been already discussed in chapter 2. This chapter briefs about the characterization of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites along with their ‘sintered’ analogues in addition to the study of ‘as prepared’ ferrite as supercapacitors.

4.2 Optimization of combustion method for synthesis of $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites using novel L- Tartaric acid dihydrazide fuel

This method of synthesis has been fully illustrated in chapter 2 wherein the middle composition of this particular series i.e. $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ has been synthesized. The ferrite sample $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ was chosen for the optimization studies and was prepared using 5 different oxidizer (O: F) to fuel ratios. $(Ni(NO_3)_3 \cdot 6H_2O)$, $(Co(NO_3)_3 \cdot 6H_2O)$, $Mg(NO_3)_3 \cdot 6H_2O$ and $(Fe(NO_3)_3 \cdot 9H_2O)$ were the oxidizers used and the novel fuel used was L-tartaric acid dihydrazide. The L-Tartaric acid dihydrazide was synthesized in the laboratory and was used as a fuel for the first time in synthesis of any ferrite. There are no reports reported in the literature on use of the L-Tartaric acid dihydrazide as a fuel for synthesis of ferrite. A thorough characterization of L-Tartaric acid dihydrazide was carried out before employing it as a fuel in the synthesis of $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrite. The reaction of this fuel with the oxidizers employed in this synthesis is highly exothermic and as a result only fuel deficit ratios have been used for the optimization of this synthesis method. The amount of oxidizers and the fuel used for the synthesis of $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ compound has been depicted in Table 4.1.

Table 4.1 The amount of various metal nitrates and the fuel taken and the metal nitrate: fuel ratio which was taken for optimization.

Sr. No.	$Ni(NO_3)_2 \cdot 6H_2O$ (g)	$Co(NO_3)_3 \cdot 6H_2O$ (g)	$Fe(NO_3)_3 \cdot 9H_2O$ (g)	$Mg(NO_3)_3 \cdot 9H_2O$ (g)	L-Tartaric acid dihydrazide $C_4H_{10}N_4O_6$ (g)	Oxidizer: Fuel Ratio
1	1.7623	1.0582	9.8938	0.6215	0.3563	1:0.075
2	1.7623	1.0582	9.8938	0.6215	0.8313	1:0.175
3	1.7623	1.0582	9.8938	0.6215	1.187	1:0.25
4	1.7623	1.0582	9.8938	0.6215	1.7815	1:0.375
5	1.7623	1.0582	9.8938	0.6215	2.3753	1:0.5

4.3 Characterization of $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrite as a representative sample obtained from different fuel

4.3.1 Thermal analysis (TG-DTA) of $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrite synthesized using the optimization ratio 1: 0.175

The autocatalytic behaviour of the combustion synthesis method wherein the metal nitrates behave as oxidizer and L-Tartaric acid dihydrazide act as fuel was inspected using the TG-DTA measurements. The TG-DTA measurements were carried out of the solidified melt of metal nitrate and fuel and the results for the same are presented in Fig 4.1. It is observed from Fig. 4.1 that over the temperature from 30 °C to 800 °C, the solidified melt shows weight loss initially at around 110 °C which can be attributed to the loss of moisture (water molecules) from the solidified melt which is accompanied by a small endotherm in the corresponding DTA plot.

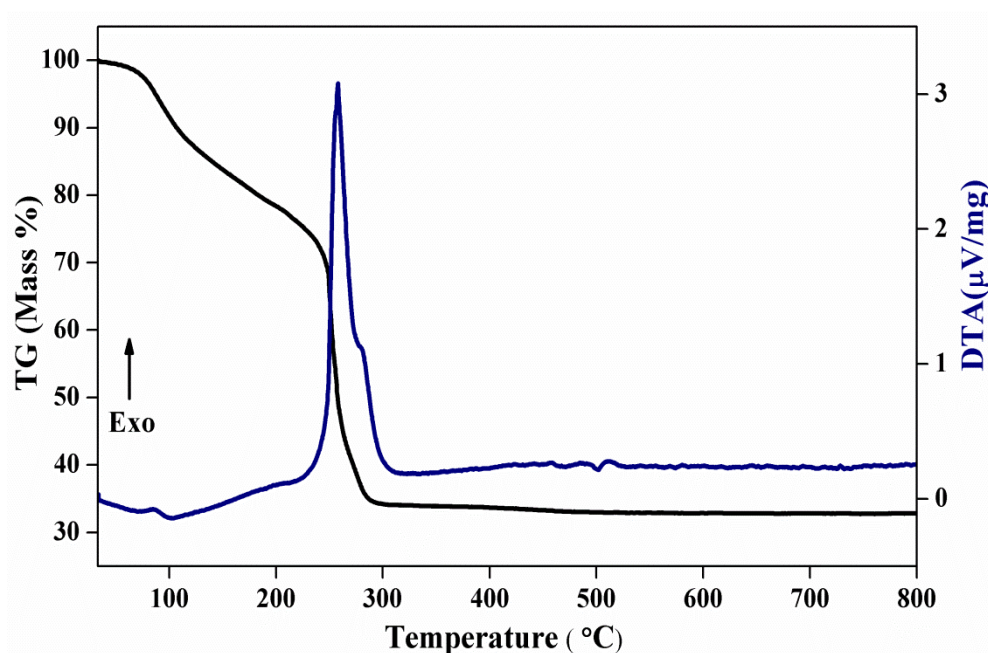


Fig. 4.1 The TG-DTA plot of solidified melt of oxidizer and fuel with the optimization ratio 1:0.175 of $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrite.

The second mass loss is observed at around 300 °C in the TG plot pertaining to the combustion of the metal nitrates with the fuel. It releases large amount of heat in order to form the mixed metal oxide. A concomitant DTA exothermic peak is observed at this step which indicates the exothermic nature of this reaction. After 300 °C there is no particular weight loss observed in the TG-DTA plot. Taking into consideration the TG-DTA

analysis, it can be deduced that Ni-Co-Mg ferrites can be synthesized by calcining the compounds at a temperature higher than 300 °C to ensure total elimination of any carbon impurities. In our present work, we have employed 500 °C as the calcining temperature to ensure the complete elimination of carbon impurities. The results are persistent with the findings obtained for the thermal analysis of $CoFe_2O_4$ and $MgFe_2O_4$ using glycine-nitrate precursor gel [11-12].

4.3.2 Powder XRD studies of the $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrite obtained by using different oxidizer: fuel ratios

The $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrites synthesized using the different fuel deficit ratio's i.e. 1:0.075, 1:0.175, 1:0.25, 1:0.375 and 1:0.5 were calcined at 500 °C and the powder XRD patterns of the same are depicted in Fig 4.2. Powder XRD studies corroborate the phase purity of all the oxidizer: fuel ratios upon calcination.

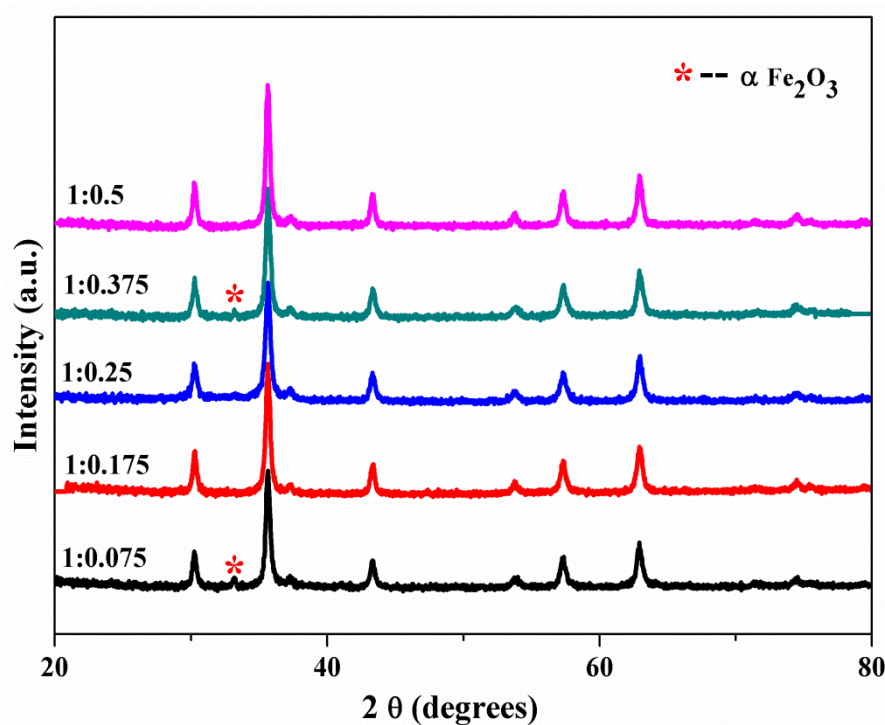


Fig. 4.2 Powder XRD patterns for $Ni_{0.5}Co_{0.3}Mg_{0.2}Fe_2O_4$ ferrite synthesized using different optimization ratios after calcination at 500 °C.

The powder XRD patterns revealed that the ferrite synthesized using the ratios 1:0.075 and 1:0.375 shows an extra impurity peak of α - Fe_2O_3 along with the spinel peaks. This impurity peak may be attributed to either very high exothermic reaction or not enough generation of heat for the formation of the metal oxide. The ferrite synthesized using the remaining optimization ratios viz. 1:0.175, 1:0.25 and 1:0.5 showed formation of the

monophasic cubic spinel structure without any impurity peak. Using the Scherrer's formula, the crystallite sizes (D) of this ferrite synthesized using different ratios was determined and their values along with the lattice parameter values are shown in Table 4.2. The lattice parameter (a) values range from 8.3476 Å–8.3534 Å for all the optimization ratios. It appears that the fuel ratio 1: 0.175 possess a lower crystallite size without any impurity peak. Thus, this ratio was chosen for the further synthesis of main series of the 'as prepared' and 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

4.3.3 Infra-red studies of $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite obtained by optimizing different oxidizer: fuel ratios

The room temperature IR spectra of $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite synthesized using different optimization ratios is depicted in Fig. 4.3 The IR spectra was recorded from 4000 cm^{-1} to 350 cm^{-1} . The absorption peaks observed at 600 cm^{-1} relate to the M–O stretching vibration at the tetrahedral sites and the vibrational band at 400 cm^{-1} is due to metal-oxygen bond vibration at the octahedral sites of the cubic spinel ferrite [13-14]. The values for the characteristic peaks for all the optimization ratios are tabulated in Table 4.2.

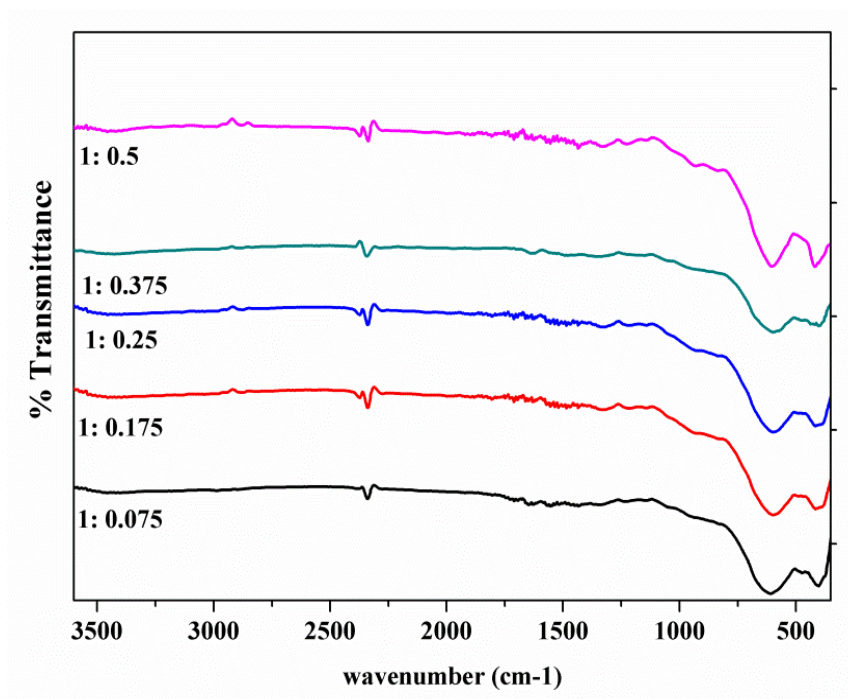


Fig. 4.3 The IR spectra for $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite after calcination at $500\text{ }^{\circ}\text{C}$ by fuel deficit ratios 1:0.075, 1:0.175, 1:0.25, 1:0.375 and 1:0.5.

4.3.4 The normalized A.C. susceptibility studies of $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ obtained by optimizing different oxidizer: fuel ratios

Fig. 4.4 depicts the normalized A.C susceptibility plots with respect to temperature which explored the Curie temperature of $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ obtained by varying the oxidizer: fuel ratios. The transformation of any material from ferromagnetic/ferrimagnetic to paramagnetic is called its Curie temperature; specifically, the transition from the organized arrangement of the magnetic spins to its randomized order [15]. The Curie temperatures obtained for $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite synthesized at varied optimization ratios are given in Table 4.2.

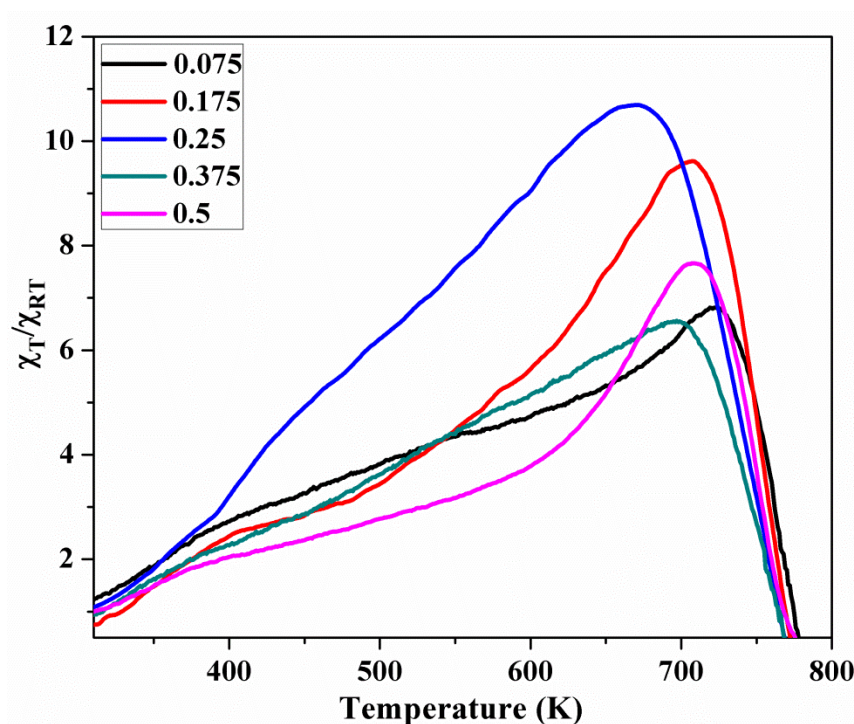


Fig. 4.4 Plots of variation of normalized AC susceptibility as a function of temperature for $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite synthesized using varying fuel deficit ratios (1:0.075, 1:0.175, 1:0.25, 1:0.375 and 1:0.5).

A.C susceptibility technique typically introduces the three types of magnetism domains viz. the superparamagnetic (SP), single-domain (SD), and multi-domain (MD) [16]. Contribution of SP nanoparticles to magnetization is limited due to the random arrangement of the magnetic domains with rising temperature which produces chaos. In case of MD nanoparticles increasing temperature increases the magnetization as arrangement of the magnetization domain is in single direction. Nevertheless, the magnetization of SD nanoparticles is in between SP and MD. The ferrite synthesized

using varied oxidizer: fuel ratio 1:0.075, 1:0.25 and 1:0.375 displayed a blend of SD-MD particles with SD particles having its majority. However, ferrites synthesized using the fuel ratios 1:0.175 and 1:0.5 show single domain particle nature. Thus, the ferrite synthesized using ratio 1:0.175 was chosen for the further synthesis of the main series considering several other parameters such as its lower crystallite size [Table 4.2].

Table 4.2 IR frequencies (ν_1 and ν_2), Curie temperature (T_c), average crystallite size (D) and lattice parameter ($\text{\AA}$) for $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite synthesized by varying metal nitrates: fuel ratios.

Metal nitrate: Fuel ratio	IR frequency		T_c (K)	Average crystallite size (D) (nm)	Lattice parameter ($\text{\AA}$)
	M-O _{tet} ν_1 (cm^{-1})	M-O _{oct} ν_2 (cm^{-1})			
1:0.075	602	410	783	24	8.3528
1:0.175	600	435	777	20	8.3476
1:0.25	600	405	774	21	8.3514
1:0.375	596	400	777	23	8.3496
1:0.5	598	398	789	26	8.3534

4.4 Characterization of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.4.1 Chemical analysis of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The elemental stoichiometry for all the elements i.e. nickel, cobalt, magnesium and iron for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites has been determined using ICP-AES technique. Table 4.3 depicts the exact values of all the elements present experimentally and theoretically in the ferrite samples. From the table it is concluded that the experimental percentages of all the ‘as prepared’ samples match closely with the theoretical percentages affirming the stoichiometric ferrite formation.

Table 4.3 Theoretical and experimental percentages of nickel, cobalt, magnesium and iron present in ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Composition	Ni%		Co%		Fe%		Mg%	
	(theor.)	(expt.)	(theor.)	(expt.)	(theor.)	(expt.)	(theor.)	(expt.)
x= 0.0	12.51	12.35	12.56	12.63	47.63	47.87	-	-
x= 0.1	12.70	12.55	10.20	10.38	48.34	47.84	1.05	0.99
x= 0.2	12.89	12.91	7.76	7.80	49.08	49.35	2.13	2.32
x= 0.3	13.09	12.96	5.25	4.99	49.83	49.80	3.25	3.11
x= 0.4	13.29	12.99	2.67	2.63	50.62	50.89	4.40	4.46
x= 0.5	13.51	13.25	-	-	51.42	51.28	5.59	5.62

4.4.2 Structural characterization of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites by powder XRD studies

Fig. 4.5 illustrates the room temperature powder XRD patterns for all the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites in the range from 20° to 80° . The XRD patterns for all the ferrite compounds show clearly defined diffraction peaks and better crystallinity in the samples. There is absence of any secondary phase like the impurity peak such as the α - Fe_2O_3 peak thus affirming the formation of single phasic cubic structure. The diffraction peaks are indexed to the (h k l) planes (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) confirming the formation of spinel structure and the peaks match with the standard PDF card No. 01-088-0380 [17]. Table 4.4 shows the lattice parameter (a), crystallite sizes (D), measured density (d_m), theoretical density (d_x) and porosity (P) of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites obtained from the powder XRD patterns.

From the table, it is noted that the lattice parameter values are in the range of 8.3442-8.3593 Å and the values were found to increase with increasing magnesium substitution. The lower values of the lattice parameter for lower concentration of magnesium is due to the replacement of the smaller ionic radius of Ni^{2+} (0.69 Å) ions and in the octahedral B-sites by the larger Mg^{2+} (0.72 Å) ions. This substitution results in expanding the unit cell thus causing larger lattice constant with increasing Mg^{2+} content [17-20]. The crystallite sizes were found to be in the range 17-20 nm and were found to decrease as magnesium

concentration was increased. The theoretical density was found to decrease with increasing Mg content while the measured density did not exhibit any trend. The porosity calculated by this method is found to be in the range of 33.86-45.15 %

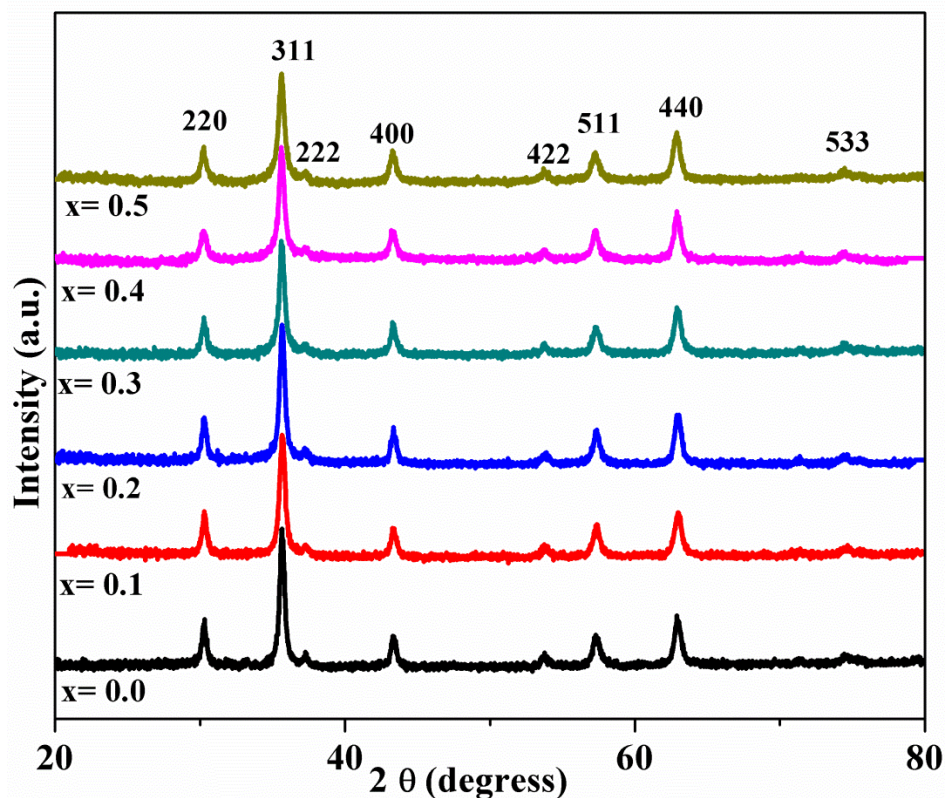


Fig. 4.5 The powder XRD patterns for the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Table 4.4 The lattice parameter (a), measured density (d_m), theoretical density (d_x) porosity (P) and crystallite sizes (D) of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	Lattice parameter (a) Å	Measured density (g/cm^3)	Theoretical density (g/cm^3)	Porosity (%)	Crystallite size (D) in nm
0.0	8.3442	3.1450	5.3637	41.36	21
0.1	8.3458	2.8951	5.2791	45.15	20
0.2	8.3476	2.9856	5.1966	42.54	20
0.3	8.3519	2.4978	5.1097	51.11	20
0.4	8.3569	3.3000	5.0217	34.28	17
0.5	8.3593	3.2663	4.9386	33.86	18

4.4.3 Infra-red (IR) spectroscopy studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

Fig. 4.6 shows the Infra-red spectra for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites. The two characteristic vibrational frequency bands are present in all the samples; the lower frequency band at approximately 400 cm^{-1} (ν_1) which is due to the intrinsic vibrations of the octahedral sites and the higher frequency absorption band at $\sim 600\text{ cm}^{-1}$ (ν_2) is due to the intrinsic vibrations at the tetrahedral sites [21]. Table 4.5 shows the exact values of the IR frequency obtained for the different ferrites.

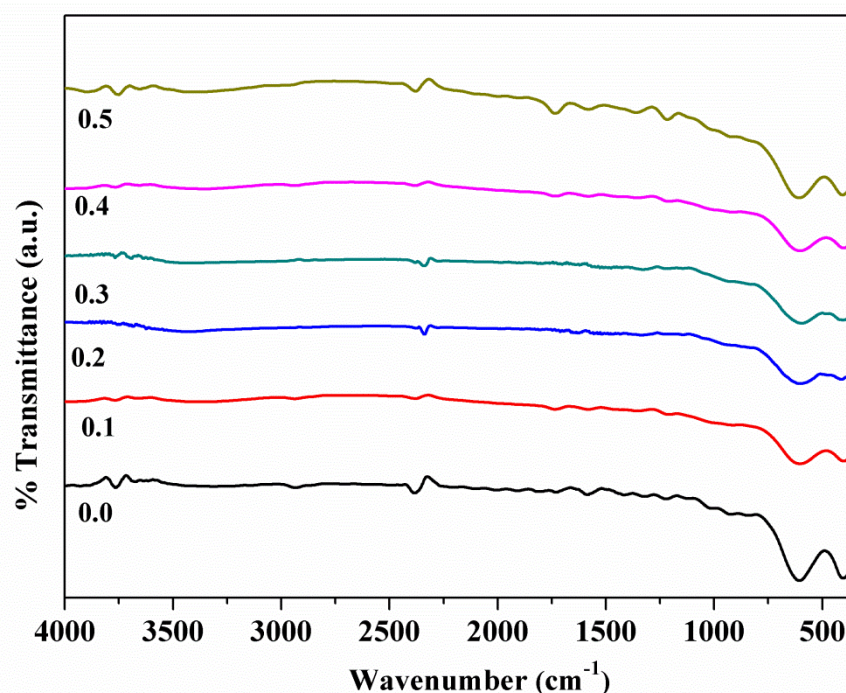


Fig. 4.6 The IR spectra of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

Table 4.5 The ν_1 and ν_2 values in the IR spectra of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Composition	Wavenumbers obtained from IR spectra of ‘as prepared’ ferrites (cm^{-1})	
	ν_1	ν_2
0.0	598	398
0.1	596	384
0.2	586	402
0.3	577	400
0.4	602	389
0.5	601	388

4.4.4 Raman spectroscopy studies of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

Raman spectroscopy is an innovative, non-destructive, spectroscopic determination method used for gaining understanding into the vibrational energy states and the structural information of the compounds. Fig. 4.7 demonstrates the Raman spectra of all the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites. The group theory indicates the presence of 42 vibrational modes which are observed in the spinel ferrites structure as depicted in the equation below.

$$\Gamma = A_{1g} (R) + E_g (R) + T_{1g} (In) + 3T_{2g} (R) + 2A_{2u} (In) + 2E_u (In) + 4T_{1u} (IR) + 2T_{2u} (In)$$

Wherein, ‘R’ and ‘IR’ and ‘In’ indicate the Raman and the infrared vibrations and the inactive modes respectively predicting the presence of cubic phase inverse spinel having $Fd-3m$ space group. They have five Raman active modes i.e. $A_{1g} + E_g + 3T_{2g}$ [22].

Generally, above the frequency 600 cm^{-1} the vibrational modes are attributed to the symmetric stretching of M–O bond at the tetrahedral sites (A) and the modes below 600 cm^{-1} is as a result of symmetric and asymmetric M–O bond bending at the octahedral sites [23]. Besides, absence of sharp spikes around 240 or 300 cm^{-1} in the Raman spectra confirms formation of monophasic ferrite samples without any $\alpha\text{-Fe}_2\text{O}_3$ impurity [24]. As per the Raman active modes, the symmetric stretching of the M–O bond is represented by the A_{1g} mode that appears as a result of the symmetric bond bending of oxygen atom with the metal is the E_g mode. A band (small shoulder peak) towards a little left of the A_{1g} band indicates mixed spinel nature of the ferrites. The T_{2g} (3) and T_{2g} (2) modes occur due to asymmetric bond bending and asymmetric bond stretching of the M–O bonds respectively at the octahedral sites. Also, the T_{2g} (1) mode is ascribed to the translational movement of the metal ions with the four oxygen atoms at the tetrahedral site [25]. The approximate frequency band values for all the Raman modes have been given in the Table 4.6.

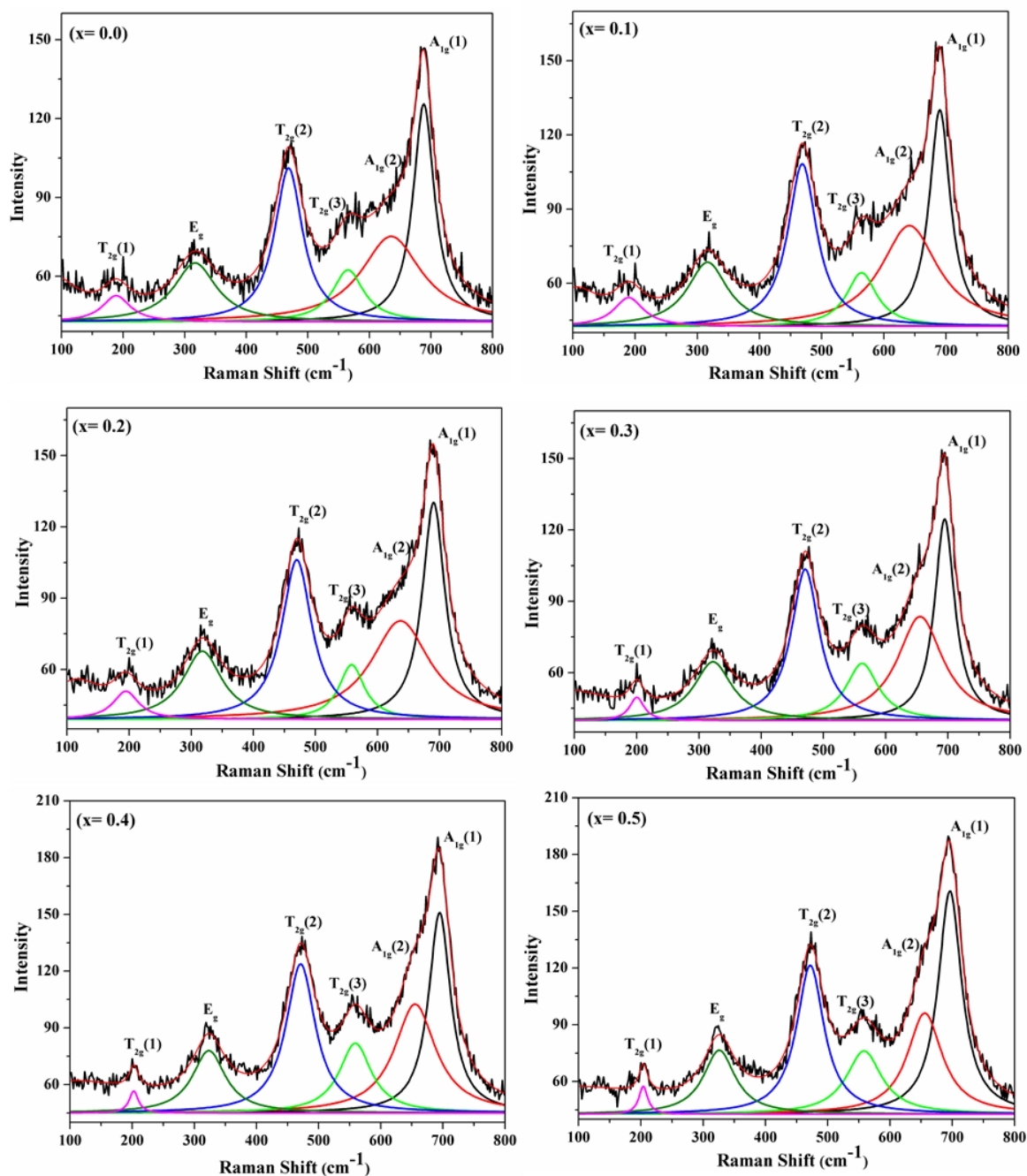


Fig 4.7 The Raman spectra of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

There is a huge distribution of the Fe–O or Co–O or Mg–O arrangements that affirms the differences in the ionic radii of Co^{2+} , Mg^{2+} and Fe^{3+} ions in the Raman spectroscopy. Substitution of the magnesium ions in the cobalt ferrites has a shift in the Raman frequency band to the higher frequency range because of lower atomic masses of Mg^{2+} ions than for Co^{2+} ions [22].

Table 4.6 The Raman shifts observed for the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Composition	$A_{1g}(1)$ cm^{-1}	$A_{1g}(2)$ cm^{-1}	$T_{2g}(3)$ cm^{-1}	$T_{2g}(2)$ cm^{-1}	E_g cm^{-1}	$T_{2g}(1)$ cm^{-1}
$x = 0.0$	686	663	555	467	310	184
$x = 0.1$	687	665	568	467	315	196
$x = 0.2$	688	667	562	470	317	198
$x = 0.3$	693	669	559	475	323	199
$x = 0.4$	694	672	554	476	322	202
$x = 0.5$	696	673	555	477	323	204

As can be seen from the Fig. 4.7 the peak at $\sim 690\text{ cm}^{-1}$ (for A_{1g}) are eminent along with the shoulder peak which confirms the mixed spinel nature of the ferrites. At tetrahedral sites the Mg^{2+} ions causes the A_{1g} peak to split in which the higher wavenumber was attributed to magnesium ions and the peak with lower wavelength is assigned to Fe^{3+} ions [26-27].

4.4.5 X-Ray phototelectron spectroscopy (XPS) studies of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

XPS technique was used to explore the bonding, composition and the valence states (oxidation states) of Ni, Co, Mg, Fe and O for all the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites. The core level deconvoluted XPS spectra for all the individual elements like Ni 2p, Co 2p, Mg 2s, Fe 2p and O 1s for all the ferrite samples has been plotted using the XPS PEAK 41 software. For all the samples, the full scan range was calibrated for carbon 1s peak at a set value (284.8 eV) before deconvolution. All the deconvoluted core level spectra of the corresponding elements for the ferrites are shown in Fig. 4.8 ($x = 0.0$), Fig. 4.9 ($x = 0.1$), Fig. 4.10 ($x = 0.2$), Fig. 4.11 ($x = 0.3$), Fig. 4.12 ($x = 0.4$) and Fig. 4.13 ($x = 0.5$). The binding energy for all the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites have been mentioned in Table 4.7 and the full scan XPS spectra has been depicted in Fig. 4.14.

The XPS core level spectra of Fe 2p for all the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites shows that the binding energy peaks positioned at $\sim 710\text{ eV}$ and $\sim 724\text{ eV}$

are ascribed to the $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$ respectively for Fe in the trivalent oxidation states [28-29]. The $\text{Fe } 2p_{1/2}$ peak at approximately 724 eV has a satellite peak at roughly 8 eV more than this peak at around 718 eV suggestive of the iron present in trivalent oxidation state hence affirming presence of Fe^{3+} [30-31] ions. The binding energy peaks approximately at 710 eV and 724 eV [29] are due to distribution of Fe^{3+} in the octahedral sites whereas the binding energies at roughly 712 eV and 726 eV appear due to occupancy of tetrahedral sites in Fe^{3+} [32-33]. Besides, the ionic state of Fe^{3+} is represented by the $\text{Fe } 2p_{1/2}$ peak that has a satellite peak at the binding energy of roughly 732 eV [34].

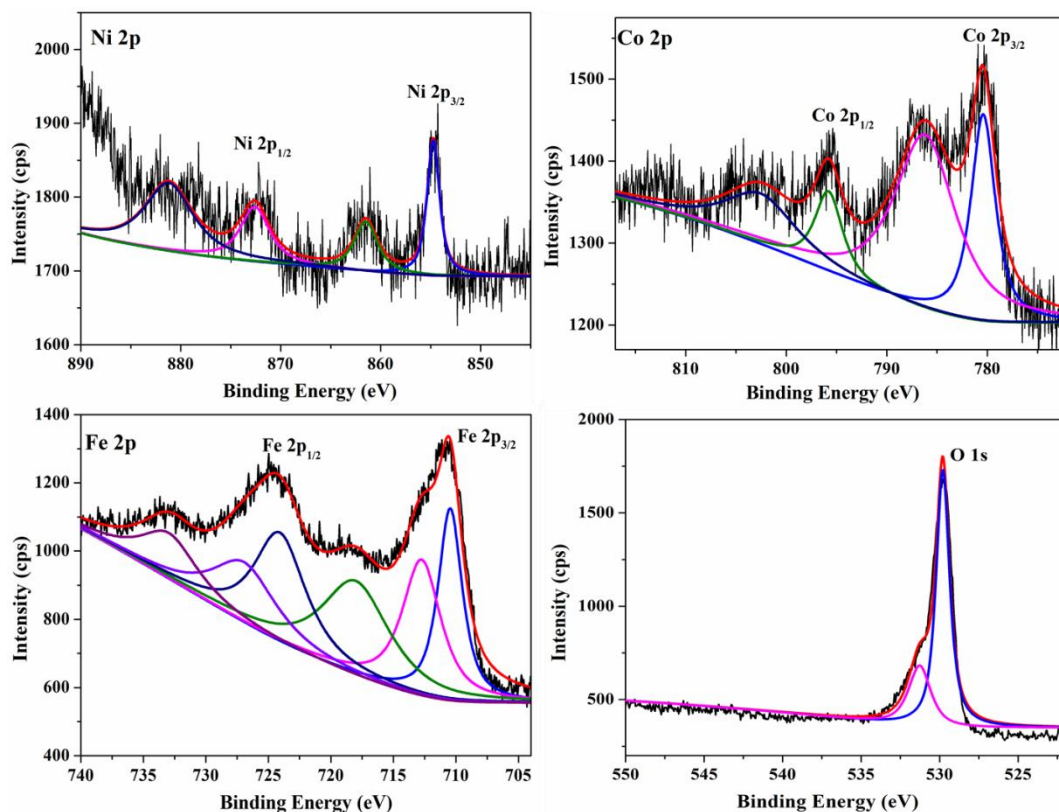


Fig. 4.8 High resolution deconvoluted XPS spectra corresponding to Ni, 2p, Co 2p, Fe 2p and O 1s of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0$) ferrites.

The deconvoluted spectra of Mg 2s peak for the samples is shown and it is observed at the binding energy of ~ 93 eV which represents that Mg^{2+} is present in the ionic state [35-36]. In all the cases, peak broadening is seen in the Mg^{2+} spectra due to presence of Mg ions at the octahedral sites [35, 37-38]. In case of deconvoluted spectrum of Ni 2p the two

main peaks are seen for Ni 2p_{1/2} and Ni 2p_{3/2} at the binding energy of ~ 872 eV and ~ 855 eV, respectively [39-40]. The satellite peaks observed at ~ 861 eV and ~ 880 eV are analogous to Ni 2p_{3/2} and Ni 2p_{1/2} and validate that nickel is present in its divalent oxidation state for all the ferrite samples [39, 41]. Besides, the probability of NiO formation is excluded due to absence of satellite peak (1.2 eV) with the main peak [42].

The Co 2p deconvoluted spectra shows binding energy peaks at ~780 eV and ~ 795 eV for Co 2p_{3/2} and Co 2p_{1/2} respectively. Further, the existence of cobalt in divalent oxidation state is validated by the binding energy peaks at ~ 786 eV and 802 eV [24]. The deconvoluted spectra for O 1s show binding energy peak equivalent to roughly 529 eV which is attributed to the lattice oxygen contribution. Whereas the peak approximately at 531 eV is ascribed to lower coordinated lattice oxygen that indicate structural defects in the ferrites [34, 43-44].

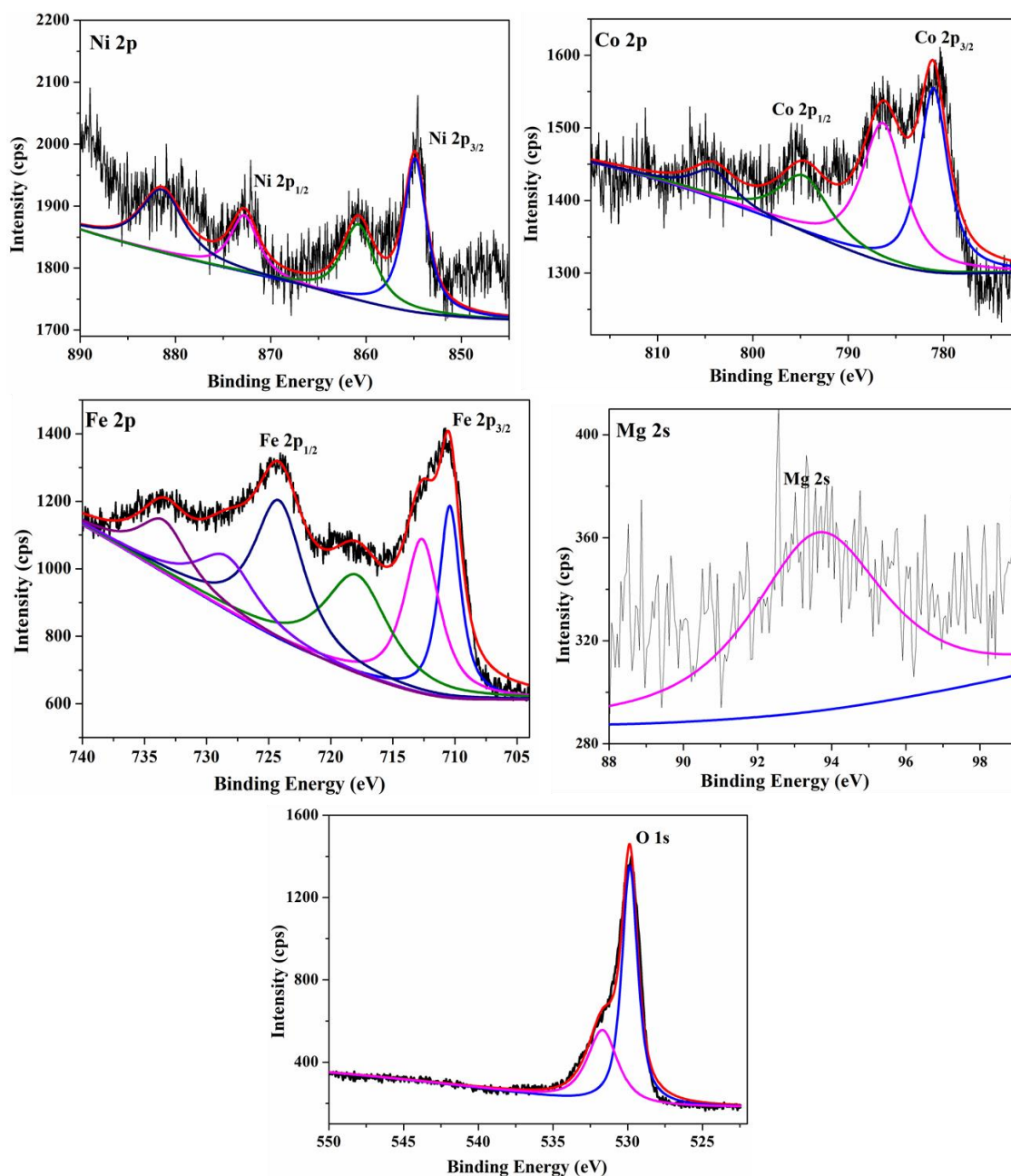


Fig. 4.9 High resolution deconvoluted XPS spectra corresponding to Ni, 2p, Co 2p, Fe 2p, Mg 2s and O 1s of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.1$) ferrite.

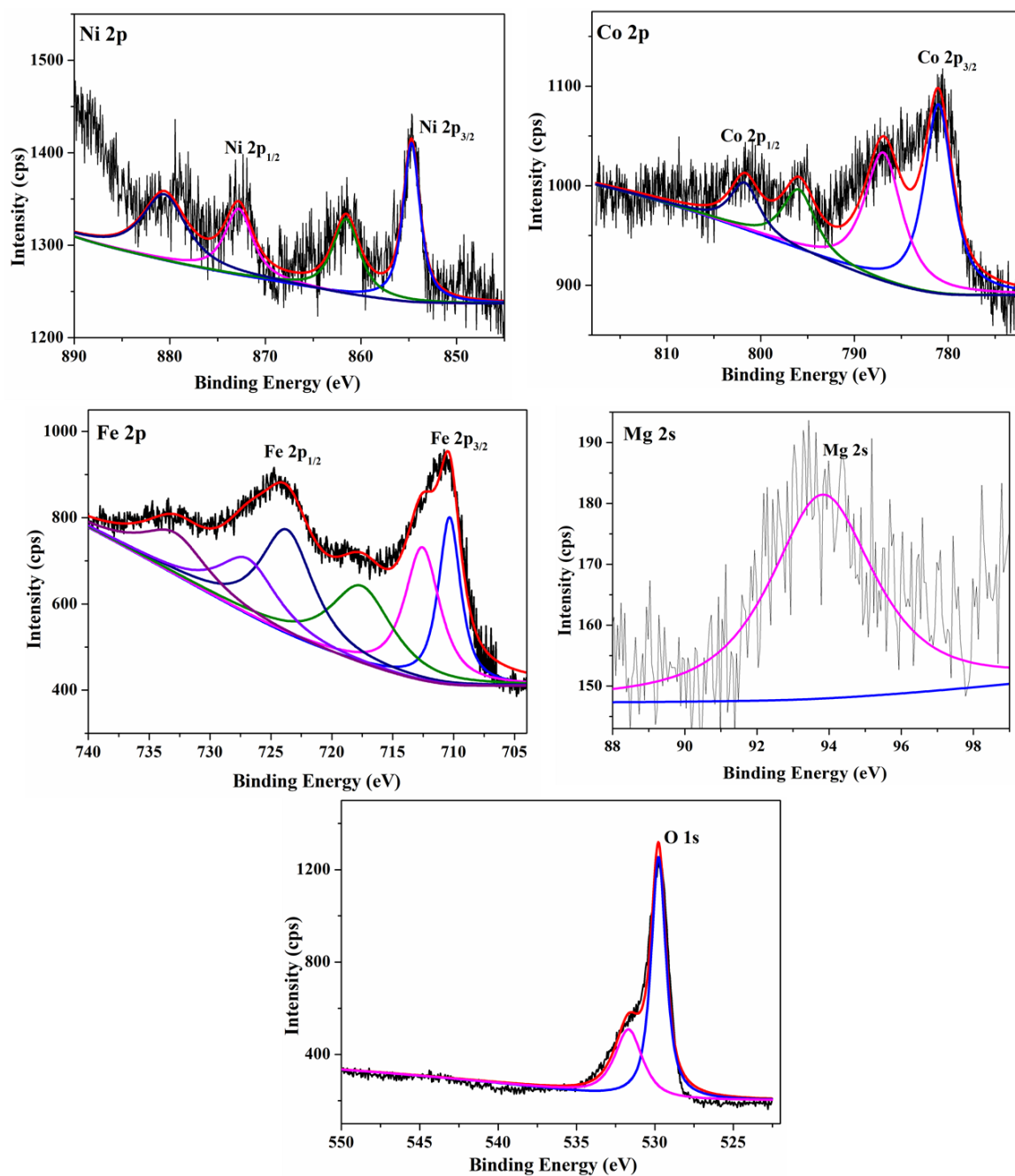


Fig. 4.10 High resolution deconvoluted XPS spectra corresponding to Ni, 2p, Co 2p, Fe 2p, Mg 2s and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.2$) ferrite.

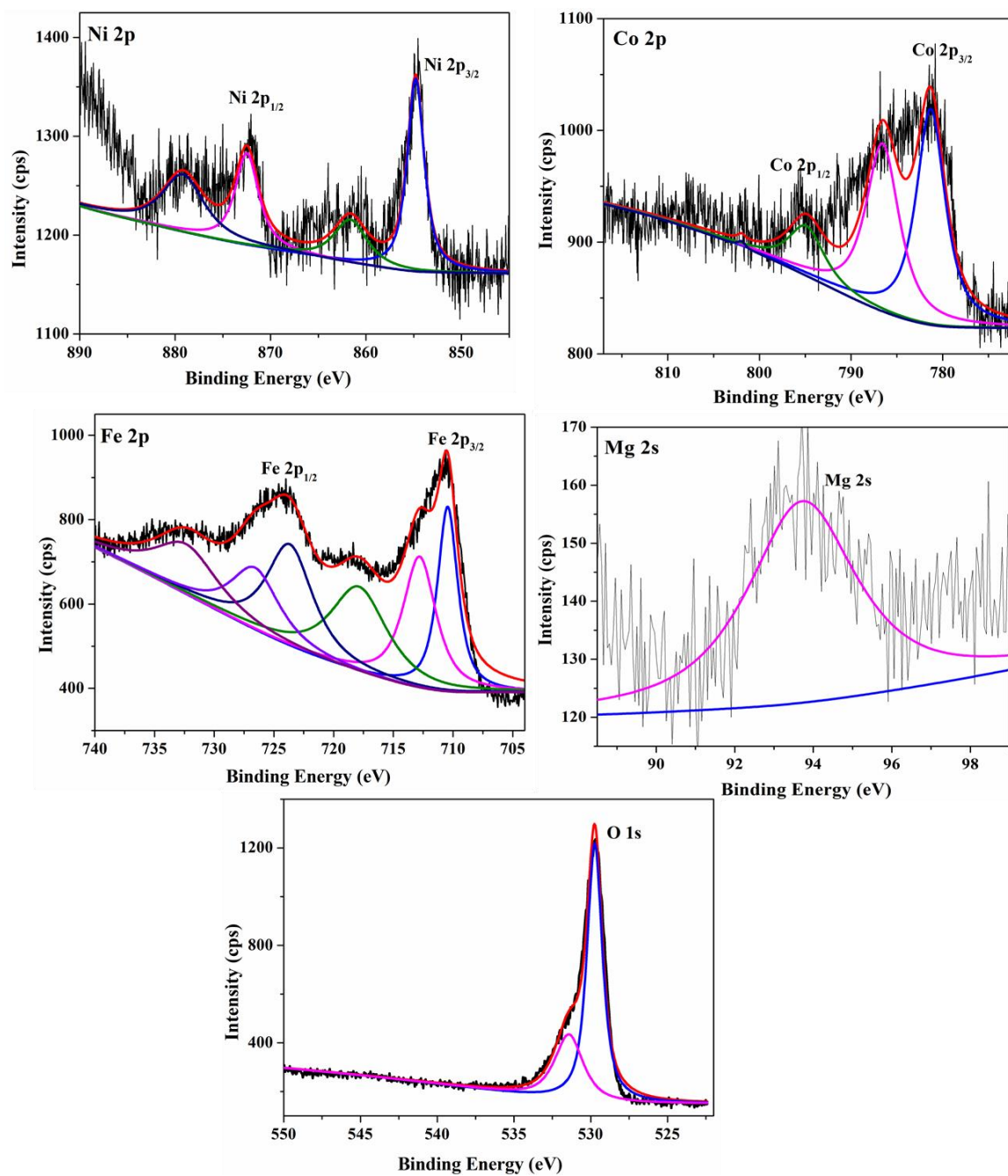


Fig. 4.11 High resolution deconvoluted XPS spectra corresponding to Ni, 2p, Co 2p, Fe 2p, Mg 2s and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.3$) ferrite.

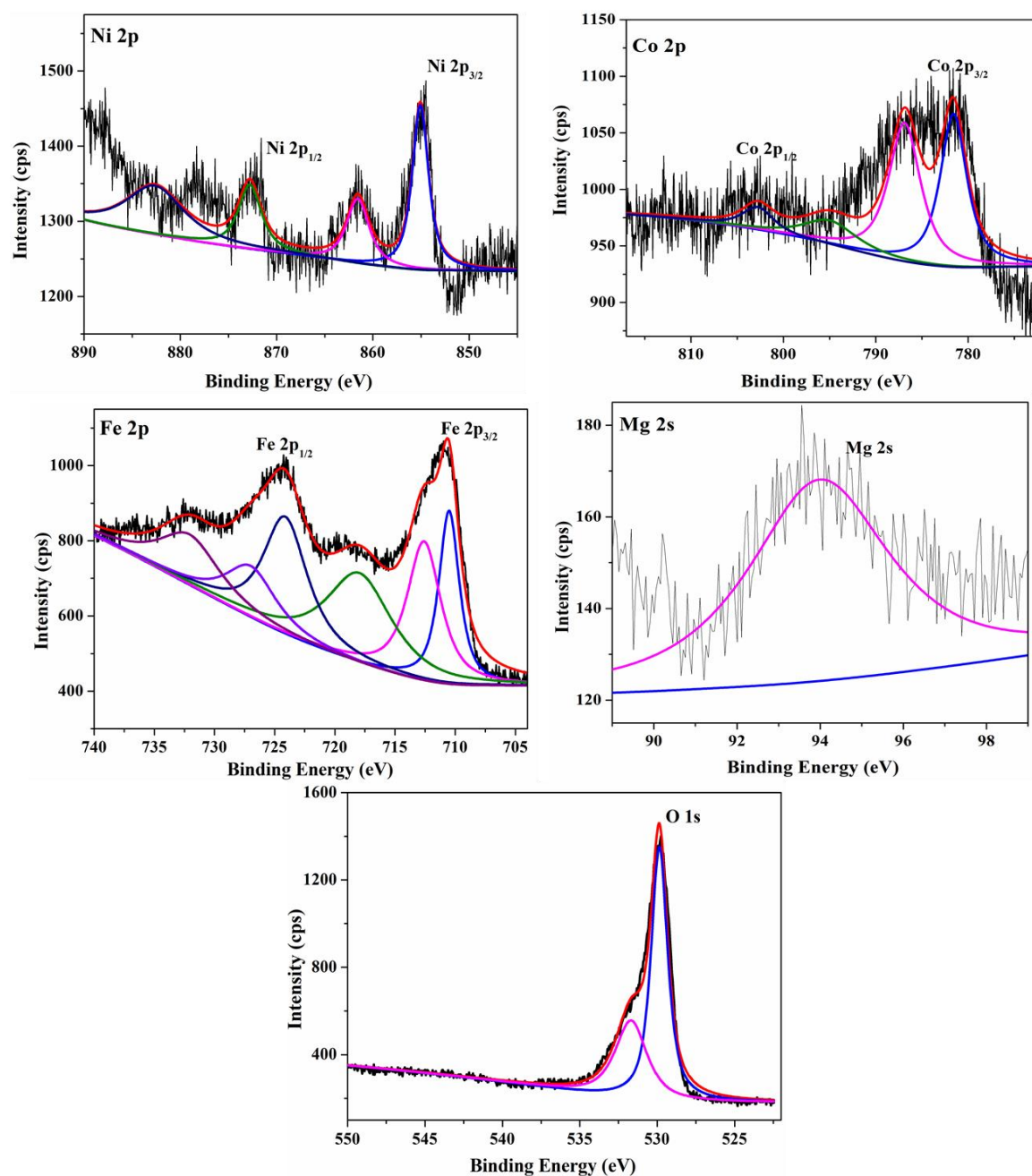


Fig. 4.12 High resolution deconvoluted XPS spectra corresponding to Ni, 2p, Co 2p, Fe 2p, Mg 2s and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.4$) ferrite.

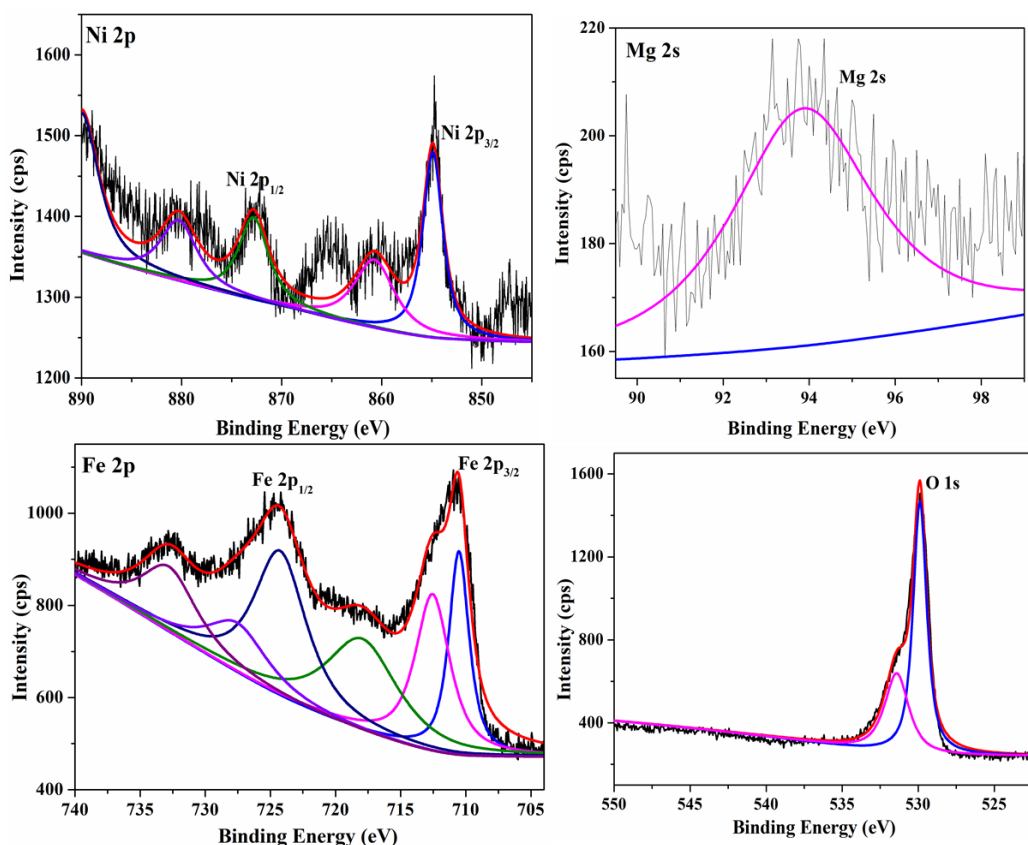


Fig. 4.13 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p, Mg 2s and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.5$) ferrite.

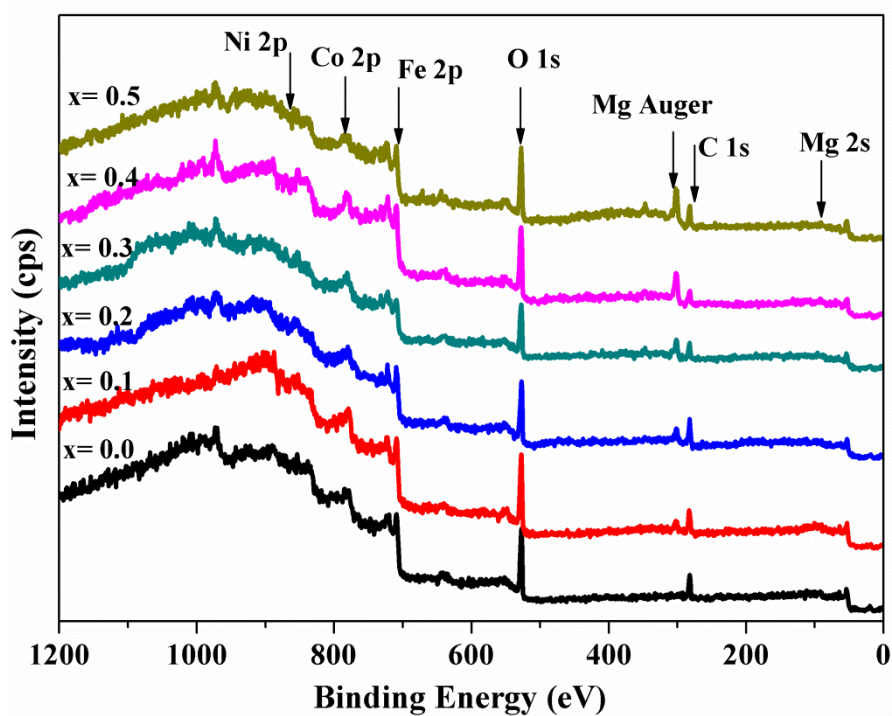


Fig. 4.14 The full scan XPS spectra of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

Table 4.7 The binding energies of all the elements obtained from deconvolution of XPS peaks of 'as prepared' $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Compositions (x)	0.0	0.1	0.2	0.3	0.4	0.5
Binding Energy (eV)						
Ni 2p _{3/2}	854.5	854.7	855.0	855.2	855.1	854.8
Satellite	861.5	861.2	860.5	860.6	861.2	861.3
Ni 2p _{1/2}	872.3	871.7	871.8	872.6	872.5	872.4
Satellite	880.4	880.1	879.9	880.3	879.5	880.2
Co 2p _{3/2}	780.5	780.8	780.2	780.8	780.4	-
Satellite	786.2	785.2	786.0	786.1	786.2	-
Co 2p _{1/2}	796.2	795.8	796.2	796.0	795.6	-
Satellite	803.2	802.6	803.1	802.8	803.2	-
Fe 2p _{3/2} (oct)	710.5	710.3	710.4	710.4	710.3	710.6
Fe 2p _{3/2} (tetra)	713.3	713.2	713.9	713.1	712.8	713.0
Satellite	717.9	718.1	718.3	718.3	718.1	718.0
Fe 2p _{1/2} (oct)	724.8	725.7	724.6	724.8	725.0	724.9
Fe 2p _{1/2} (tetra)	726.4	726.5	726.4	726.8	726.5	726.7
Satellite	732.3	732.5	732.4	732.8	732.5	732.3
O 1s (lattice)	529.6	529.7	529.7	529.6	529.9	529.6
O 1s (surface)	531.1	531.2	531.4	531.3	531.3	531.4
Mg 2s	-	93.67	93.81	93.71	93.94	93.89

4.4.6 Surface area characterisation of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.4.6.1 Brunauer-Emmett-Teller (BET) surface area measurements of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

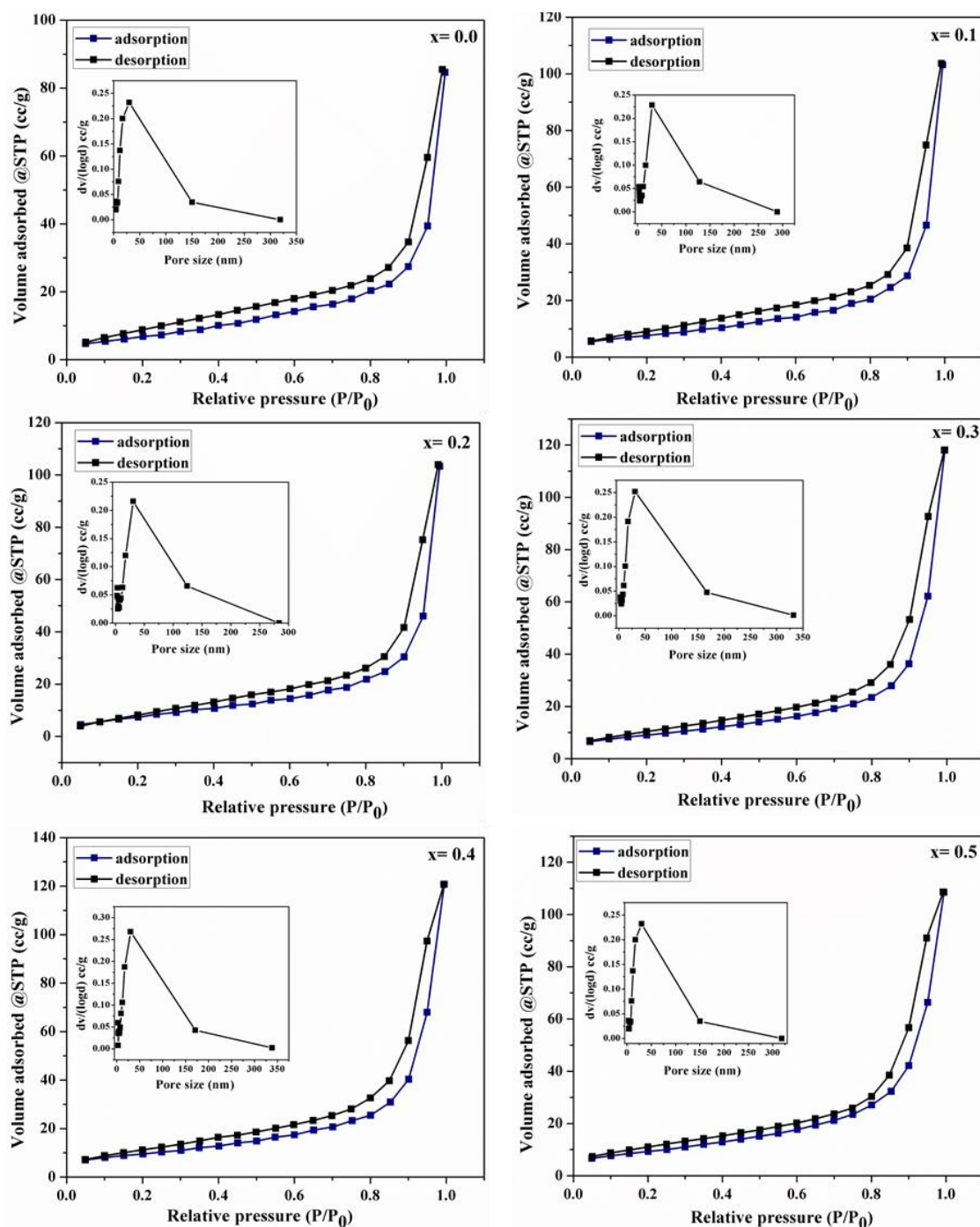


Fig. 4.15 The N_2 adsorption-desorption isotherms of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites [Inset figure: plot of $[dV/d(\log d)]$ cc/g against pore size (nm)].

To examine the specific surface area, total pore volume and pore sizes of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites, the Brunauer–Emmett–teller (BET) measurements were carried out and the results are shown in Fig. 4.15. The figure represents the N_2 -adsorption desorption isotherm of N_2 adsorbed volume against partial vapour pressure per saturated pressure (P/P_0) of the adsorbate gas along with corresponding BJH pore size distribution plots of all the ‘as prepared’ samples. From the plots it is confirmed that all the ferrite samples show type IV isotherm with small hysteresis loop [45-46].

Table 4.8 BET surface area, average pore sizes and the pore volume of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	BET surface area (m^2/g) $\pm 1 \text{ m}^2/\text{g}$	Average pore size (nm)	Total pore volume (cc/g)
0.0	27.00	30.80	0.130
0.1	27.88	31.04	0.159
0.2	30.20	30.24	0.159
0.3	32.90	33.52	0.182
0.4	34.20	30.26	0.186
0.5	34.45	31.56	0.167

The initial part of the isotherm (lower relative pressure range) is composed of monolayer-multilayer adsorption accompanied by pore filling mechanism which later reaches saturation at further higher pressure [47]. An insignificant steep of N_2 -adsorption-desorption occurs at pressure of 0.6 to 0.97 thus confirming the presence of mesopores in all the ferrite nanoparticles [48-49]. The occurrence of the mesopores in particles is determined using the pore size distribution curve (figure inset). Comparing the total pore volume with mesoporous nature of the sample, it is obvious that pores of samples are filled with mesopores which are able to enhance the electrochemical properties of these materials. Table 4.8 demonstrates the specific surface area, average pore size and total pore volume for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites nanoparticles. The surface area was found to be in the range of 27.00-34.45 $\pm 1 \text{ m}^2/\text{g}$. Furthermore, the nanostructured $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites with high magnesium content garnered a larger surface area as compared to the ones with lower

magnesium concentration which probably might lead to better electrochemical properties. The total pore volume and the average pore sizes did not show any trend in particular with increase in magnesium concentration as can be seen from the Table 4.8.

4.4.6.2 Study of acid base properties by temperature programmed desorption (NH_3 -TPD) and (CO_2 -TPD) of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

NH_3 -temperature programmed desorption (NH_3 -TPD) profiles from the surface of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites are presented in Fig. 4.16 for all the ferrite samples. This TPD profiles show that all the ferrite samples have presence of both acidic as well as basic sites.

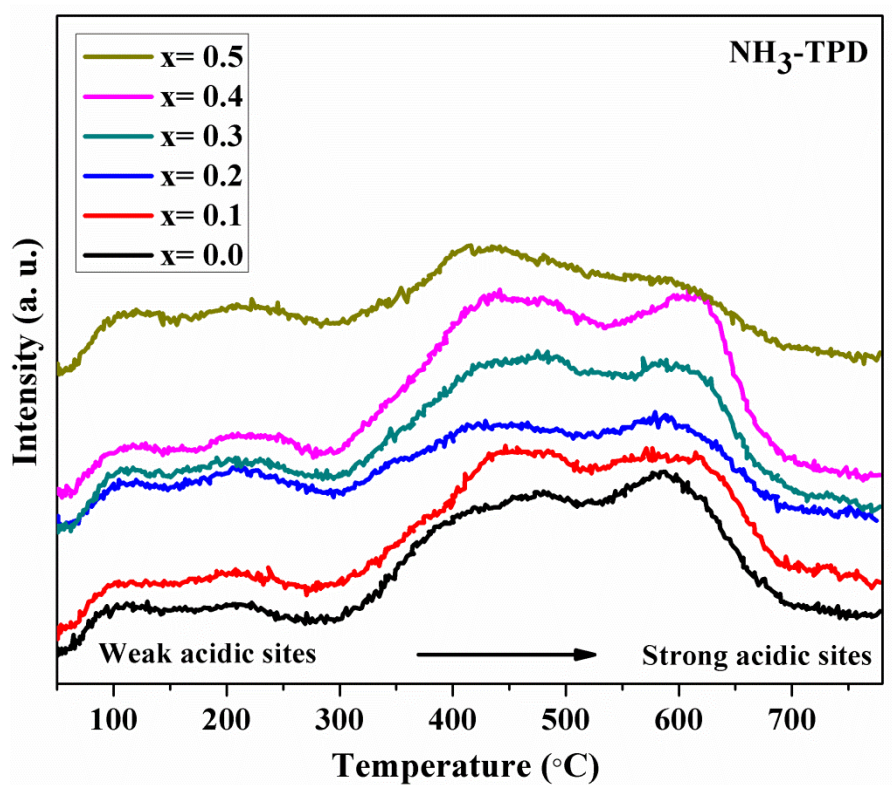


Fig. 4.16 NH_3 -temperature programmed desorption profiles of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

In all the samples four desorption peaks of ammonia are seen implying evolution of ammonia at these four different temperature regions. It is familiar that there is a reaction of NH_3 with metal oxide surface with $-\text{OH}$ group participating (presence of Bronsted acidic sites) and consistently unsaturated metal cations (Lewis acidic sites) [50-51]. The initial smaller peak is seen at $\sim 100-124$ °C in the NH_3 -TPD temperature profile followed

by another little hump at around $\sim 206-222$ °C. The third eminent desorption peak is seen at the temperature range of $\sim 425-440$ °C and the final peak is prominently observed within the temperature range of $\sim 580-615$ °C in the NH_3 -TPD desorption profiles. The first and the second smaller humps are due to the presence of weakly acidic sites which are weakly adsorbed and need lesser temperature for desorption. The third desorption peaks within $\sim 425-440$ °C is because of presence of medium acidic sites in ferrite samples. Finally, the peak $\sim 580-615$ °C with the highest temperature is ascribed to the strongly adsorbed NH_3 molecules at the ferrite surfaces which needs higher energy for desorption [52-54]. At lower temperatures, the weak acidic sites or Bronsted sites are observed while at higher temperatures strong acidic sites (Lewis sites) are seen in the NH_3 -TPD profiles [55-58].

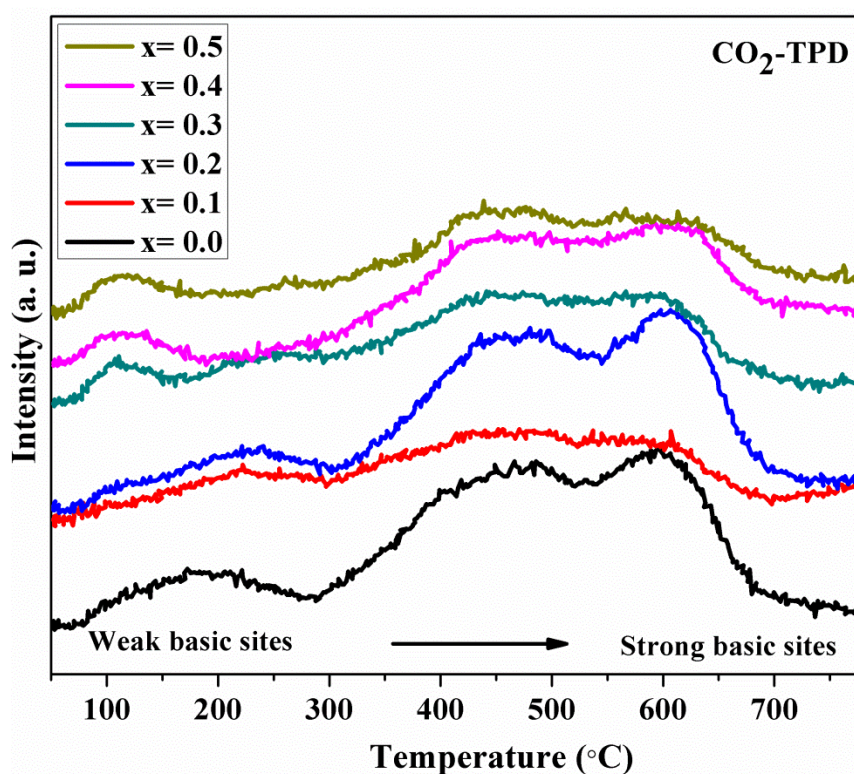


Fig. 4.17 CO_2 -temperature programmed desorption profiles of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

CO_2 temperature programmed desorption (CO_2 -TPD) profiles of all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites surfaces are shown in the Fig. 4.17. The shape of the temperature profiles shows desorption of CO_2 at various basic sites at the ferrite surface. The initial peak at the temperature range of $117-182$ °C is attributed to weakly active basic sites whereas the peaks in the range ~ 448 to 462 °C is due to existence of

medium active basic sites. The prominent peaks at 592-614 °C at a higher temperature range is due to the presence of strongly adsorbed CO_2 which indicates presence of strong basic sites [50, 55, 59].

The NH_3/CO_2 –TPD studies confirmed that all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites have presence of weak, medium and strongly active acidic sites and weak, medium and strongly active basic sites [60-61].

4.4.7 Morphological studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.4.7.1 High Resolution Transmission Electron microscopy (HR-TEM) studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

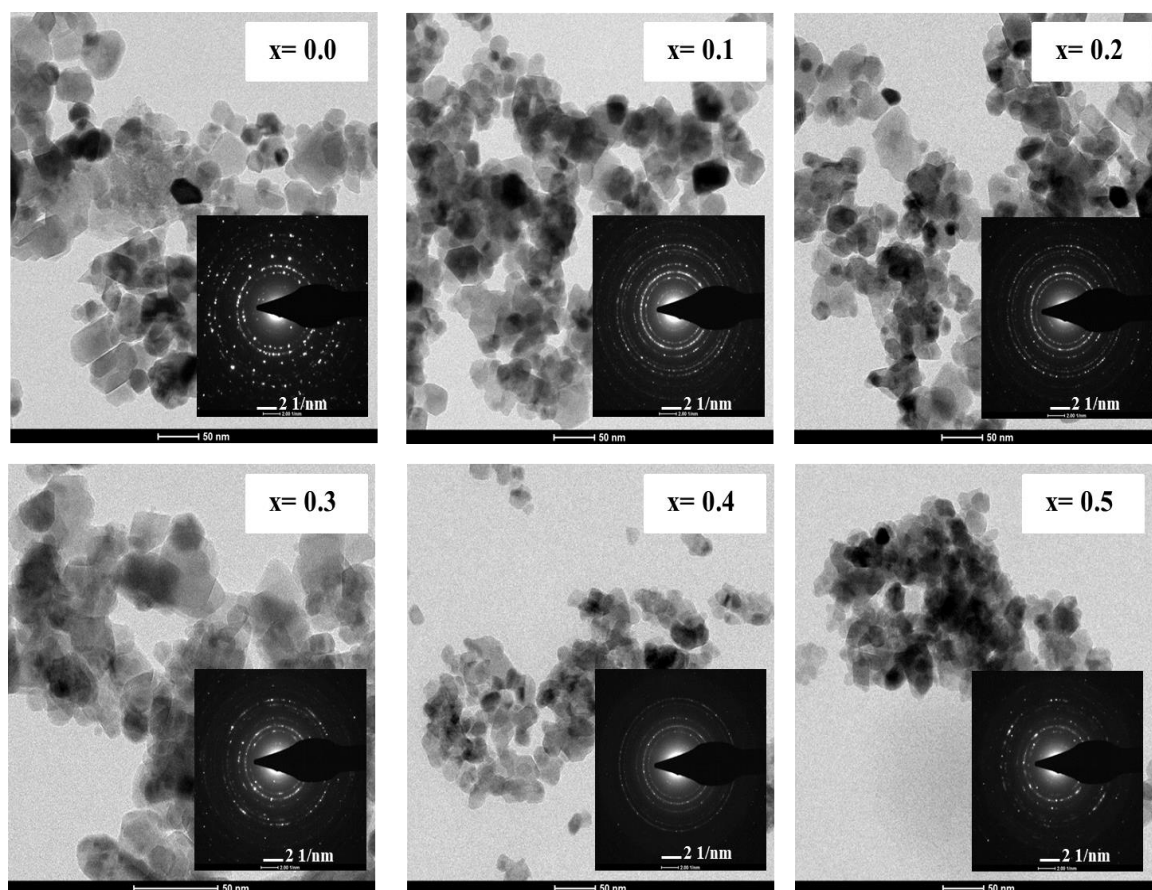


Fig. 4.18 The HR-TEM micrographs and SAED pattern of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

The morphology of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites nanoparticles was studied by HR-TEM and the Fig. 4.18 demonstrates their HR-TEM

images with their Selected Area Electron Diffraction (SAED) patterns. All the images show the presence of ferrite nanoparticles that are almost distorted hexagonal in shape and appear as loose agglomerates. This aggregation is ascribed to the strong magnetism of the samples which leads to the particles to come together [62].

All the SAED patterns have concentric rings with the brightest spot in the diffraction pattern (for 3 1 1) affirming nanocrystalline nature of the nanoparticles [63-64].

4.5 Solid state studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.5.1 Dielectric properties of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.5.1.1 Dielectric measurements as a function of frequency for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The variation in the dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites as a function of frequency from 20 Hz to 10 MHz at room temperature are depicted in Fig 4.19a and Fig. 4.19b respectively. Fig. 4.19 shows variation of dielectric constant and loss tangent as a function of composition at 20 Hz. All the ‘as prepared’ ferrite samples were found to depict the frequency-dependent behaviour in which the dielectric constant values were found to decrease upon increasing frequency up to around 1 KHz and further remain constant at higher frequencies demonstrating a normal ferrimagnetic behaviour in the ferrites. The independent behaviour of the ferrites at higher frequency can be justified on the basis of Koop’s phenomenological theory which is in agreement with the Maxwell-Wagner interfacial polarization [18, 65-66]. The dielectric polarization in the ferrites is same as the conduction hopping mechanism, for instance hopping amongst the Fe^{3+} and Fe^{2+} occurs in the applied field direction and these electrons determine polarization. At a certain higher frequency, the electron exchange of $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ cannot follow alternating field hence there is a decreasing polarization with increasing frequency and later reaching a constant value [18, 67]. However, at lower frequencies dielectric constant values appear to be very large due to dominance of certain species like Fe^{2+} ions, oxygen vacancies, pile up of interfacial dislocation, grain boundary defects and so on [65-66]. Normally, electronic, ionic, dipolar and space charge polarizations are the contributing factors to the dielectric constant of any material. Interfacial and dipolar polarizations are vital to the dielectric constant at lower frequencies but at higher frequencies, electronic polarizations

is effective and the contribution due to dipolar polarization is non-crucial [68, 69] No trend as such was seen for the dielectric constant upon increasing magnesium concentration but the sample with $x = 0.3$ exhibited highest value of dielectric constant.

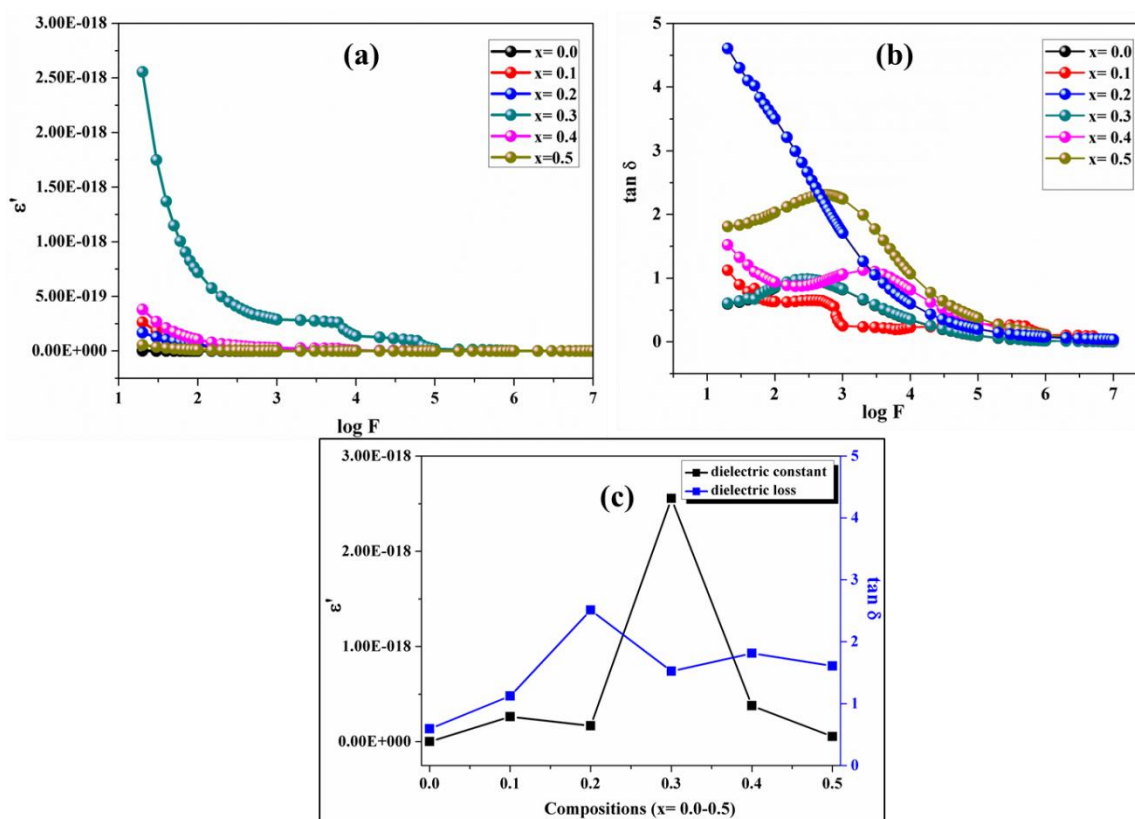


Fig 4.19 The plots of (a) Dielectric constant against log frequency (b) dielectric loss tangent ($\tan \delta$) against log frequency (c) Plot of dielectric constant and loss tangent as a function of composition at 20 Hz of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x=0.0-0.5$) ferrites.

The energy which is dissipated (rate of energy loss) due to dielectric relaxation or electric conduction of the electrical energy is known as the dielectric loss tangent ($\tan \delta$). A decrease in the loss tangent values was seen with increasing frequency; the decrease was sharp at lower frequencies (up to 2 KHz) and later the values remained constant at higher frequencies. A strong interconnection between the conduction mechanism and the dielectric behaviour was pointed out by some researchers [70-72]. The electron-hopping is the key reason for conduction in ferrites between Fe ions in various oxidation states over the octahedral sites. During hopping, there can be abrupt formation of Fe^{2+} ions in the ferrites involving Co^{2+}/Co^{3+} to Fe^{2+}/Fe^{3+} hopping in turn contributing to the dielectric properties [73-74]. Since magnesium exhibits only one oxidation state, the substitution of magnesium causes a decrease in the hopping process hence leading to a decrease in the

dielectric constant with increase in magnesium. As observed for the dielectric constant the dielectric loss tangent also did not show any specific trend but sample with the highest dielectric constant was $x = 0.2$. Also, some samples exhibited the relaxation peaks which can be attributed to the two reasons i.e. interfacial polarization and multiple valances of the ionic relaxations [75].

4.5.1.2 Dielectric measurements as a function of temperature for the 'as prepared' $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

Fig 4.20 depicts the plots for variation of dielectric constant against room temperature for the 'as prepared' $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites performed at constant frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from 30 °C to 500 °C. At first, the dielectric constant remained constant at lower temperatures but as the temperature increases (after around 380 °C) the dielectric constant was found to increase drastically.

With increase in the temperature hopping between Fe^{2+} and Fe^{3+} ions is thermally activated causing these strongly localized d-shell leading to local displacements in the direction of the applied AC field. The dielectric constant remains constant at a lower temperature region since it is independent of temperature whereas with rise in temperature it shows temperature dependent behaviour [76]. The atoms or molecules in many samples do not align themselves at lower temperature regions. However with increase in temperature this dipole alignment is facilitated which increases dielectric polarization. At substantially higher temperatures the thermal oscillations of the molecules are intense and the dielectric constant has the maximum values [77]. The dielectric constant values were found to decrease with increase in the magnesium concentration and the highest value was found to be for composition $x = 0.0$.

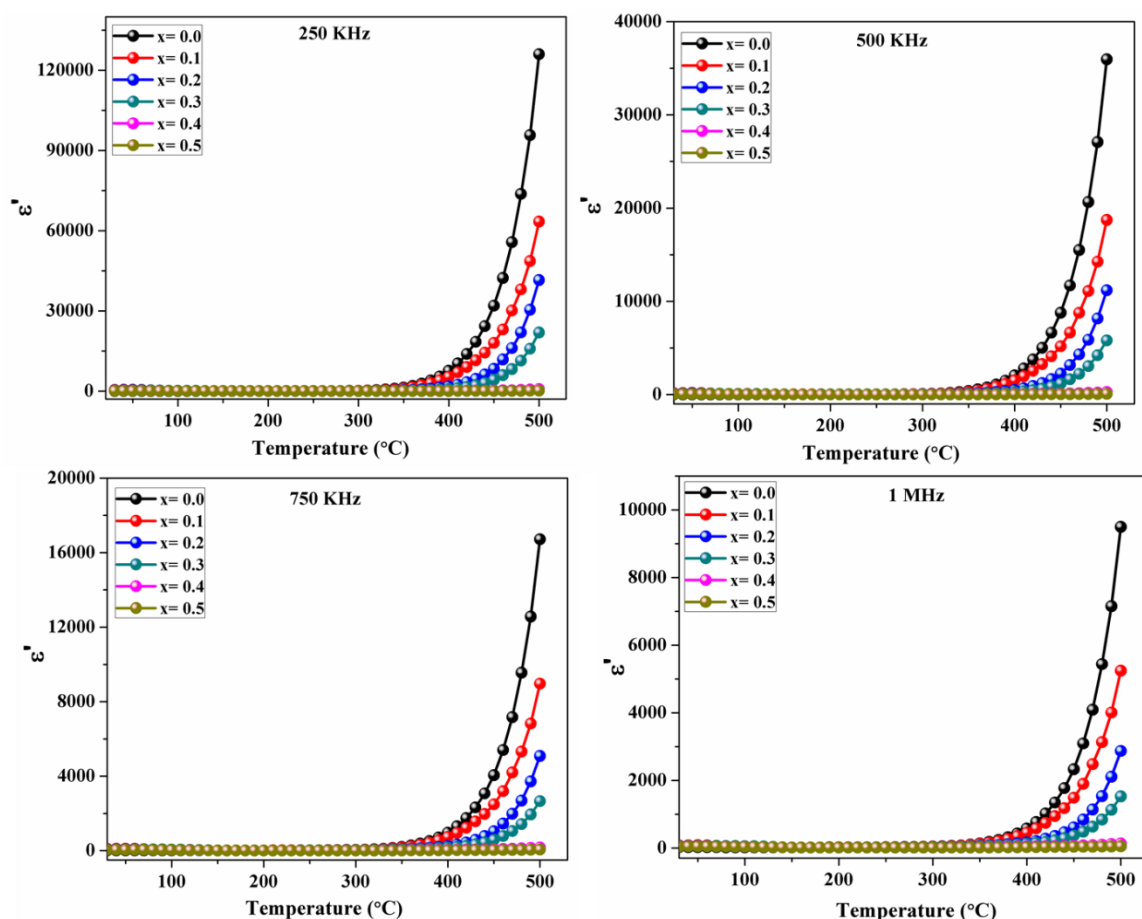


Fig. 4.20 The plots representing variation of dielectric constant as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz)

Any ferrite material exhibits four types of polarizations viz. electronic, ionic, space charge and dipolar polarizations [78]. The most prominent polarizations at lower frequencies are dipolar and interfacial which play a key role and both are temperature dependent. In this case, the interfacial polarization increases with temperature and dipolar polarization decreases with increasing temperature. This prompt increase in the dielectric constant at low frequencies is suggestive of the more pronounced impact of temperature on the interfacial polarization than that for the dipolar polarization. Contrarily, electronic and ionic polarizations contribute to higher frequencies and their temperature dependency is almost not important. The dielectric constant values are extremely large at lower frequencies (250 KHz) and it is comparatively lower with increase in frequency (1 MHz).

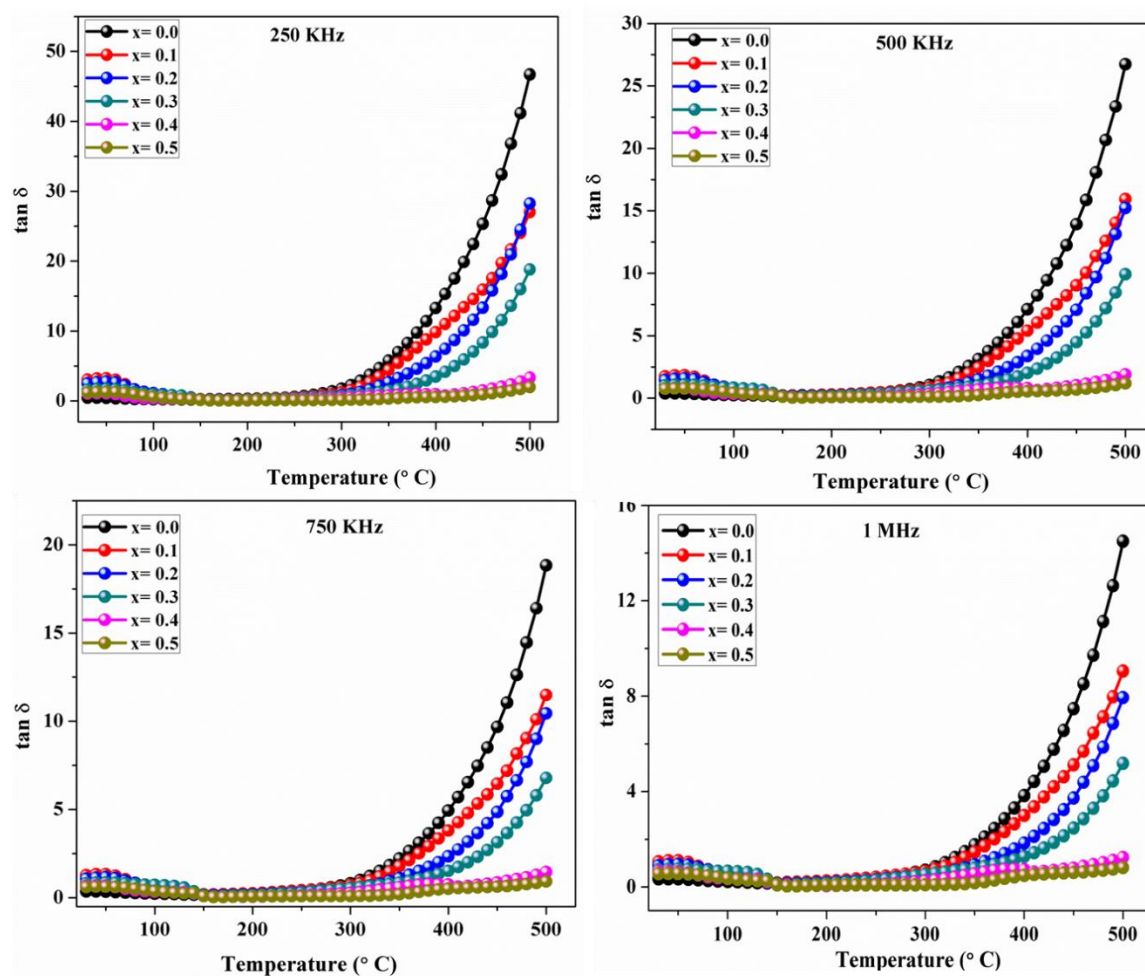


Fig. 4.21 The plots representing variation of dielectric loss tangent as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz)

Fig 4.21 shows the dielectric loss tangent with respect to temperature for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites. The same trend as that of dielectric constant has been seen in case of the dielectric loss tangent as the temperature increases. At lower frequencies (250 KHz) $\tan \delta$ values were found to be greater than at a higher frequency (1 MHz). The dielectric loss tangent values were found to be more for composition $x = 0.0$ and the values were found to decrease with increase in the magnesium concentration $x = 0.5$. The Mg^{2+} ions substitution leads to reordering of cations at the crystallographic sites. Thus, fraction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions are present at the octahedral sites for electron exchange and the $\text{Ni}^{3+}/\text{Ni}^{2+}$ ions for hole transfer, thus leading to the difference in polarization with increase in magnesium substitution [79-80].

4.5.2 The magnetization studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.5.2.1 The normalized A.C. susceptibility studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The variation of the normalized A.C. susceptibility of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites has been measured till 850 K and is depicted in Fig. 4.22. Normally, the Curie temperature (T_c) is assigned as the transition from ferrimagnetic to the paramagnetic state and the magnetic properties results as an effect of both the type of substituents and microstructure [18, 81].

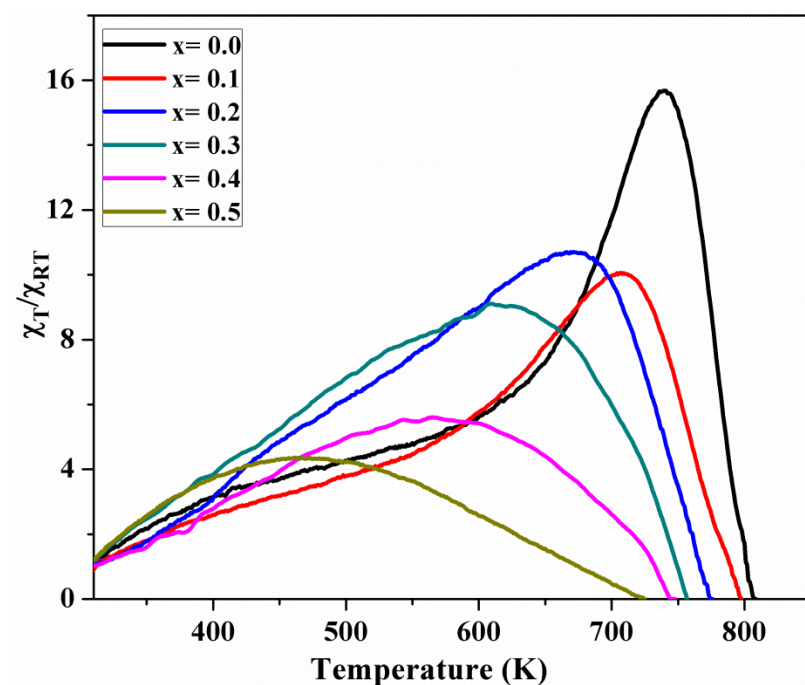


Fig. 4.22 Plots of normalized AC susceptibility against temperature of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) samples

The composition $x = 0.0$ with the highest concentration of cobalt exhibit single domain nature with a distinct hump with maximum susceptibility which upon further increase in temperature there is a sharp fall till the T_c . The hump in the peaks is known as the Hopkinson’s peak. Ferrite sample with composition $x = 0.1$ to $x = 0.4$ shows a mixture of superparamagnetic and single domain particles in which there is a steady increase in the susceptibility at low temperatures and upon increasing the temperature there is a gradual fall in the T_c . However, $x = 0.5$ composition exhibits a superparamagnetic nature which

initially shows a slow increase in the susceptibility and later slowly decreases the magnetic susceptibility upon increase in temperature till T_c . The exact values of the Curie temperatures observed for all the ferrite samples are given in Table 4.9.

Table 4.9 The Curie temperature of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites determined using AC susceptibility studies

Composition (x)	Curie Temperature (K)
0.0	809
0.1	798
0.2	773
0.3	757
0.4	748
0.5	725

The nature of the susceptibility curves as depicted in Fig.4.22 with respect to temperature indicates the domain behavior of the nanoparticles and represents the variation in the T_c with increase in magnesium content. A decrease in the value of T_c is observed upon addition of Mg^{2+} ions from 809 K to 725 K. This behavior of the ferrite samples [82-84] is because Mg^{2+} ions partially occupies the A-sites and have strong preferences for the B-sites and as a result of which at low concentrations of magnesium the total magnetization is equivalent to the difference between the magnetization of B and A respectively i.e. $M_{AB} = M_B - M_A$. Upon magnesium substitution some of the Mg^{2+} ions replace Fe^{2+} ions on the A sites that change to Fe^{3+} ions and move to the B sites. Thus, the remaining Fe^{3+} ions will not orient their moments antiparallel at the B site due to opposition by the B-B interaction this is unaffected [18].

4.6 Characterisation of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.6.1 Structural characterization of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites by powder XRD studies

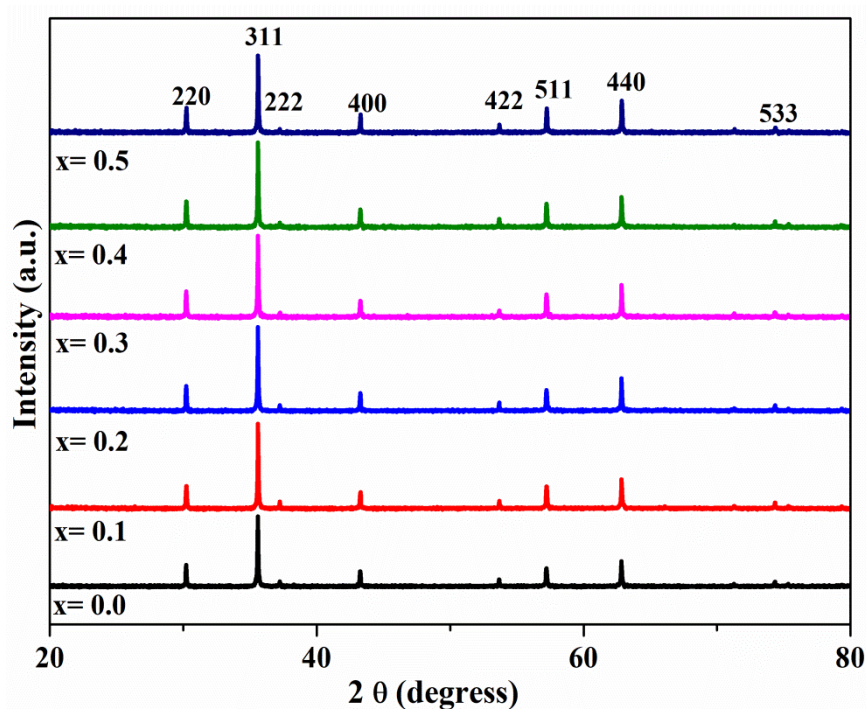


Fig. 4.23 The powder XRD patterns for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

All the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were examined for their phase purity using the powder XRD technique and the diffraction patterns are specified in Fig. 4.23. All the ferrites show the formation of monophasic spinel cubic structure with no noticeable impurity peaks detected upon sintering the ferrites at 1000 °C for 10 h. The crystalline nature of the diffraction patterns is indexed to spinel ferrites, matching with JCPDS card no. 79-1744 and 73-2410 respectively for the end ferrites i.e. CoFe_2O_4 and MgFe_2O_4 [22] and JCPDS card no. 74-2081 for the NiFe_2O_4 [85]. However, all the diffraction peaks are quite sharp and narrow as compared to their ‘as prepared’ analogues indicating high crystallinity and low porosity in the ‘sintered’ samples. Table 4.10 tabulates the exact values of lattice parameter (a), crystallite sizes (D), measured density (d_m), theoretical density (d_x) and porosity (P) of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites obtained from the powder XRD diffraction patterns.

As discussed before in section 4.4.2 for the ‘as prepared’ samples the ionic radii of Mg^{2+} and Ni^{2+} are 0.72 Å and 0.69 Å, respectively [18-19]. A linear increment in the lattice constant was observed with increasing Mg^{2+} substitution and is in agreement with the Vegard’s law [86]. The lattice constant values are found to be in the range of 8.3622-8.3670 Å. From the table, it is confirmed that the average crystallite size (D) was found to be higher for the ‘sintered’ ferrites as compared to their ‘as prepared’ analogues. Elements like surface pressure and surface tension leading to surface strain and several other factors are accountable for the variation in the crystallite sizes [87-88].

Table 4.10 The lattice parameter (a), measured density (d_m), theoretical density (d_x) porosity (P) and crystallite sizes (D) of the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

Composition (x)	Lattice parameter (a) (Å)	Measured density (g/cm^3)	Theoretical density (g/cm^3)	Porosity (%)	Crystallite size (D) nm
0.0	8.3622	2.928	5.3269	45.03	112
0.1	8.3635	3.4429	5.2456	34.38	120
0.2	8.3647	3.225	5.1503	37.38	115
0.3	8.3658	2.8951	5.0843	43.05	116
0.4	8.3662	3.4429	5.0049	31.20	111
0.5	8.3670	3.9196	4.9250	20.41	117

4.6.2 Raman spectroscopy studies of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

The ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites were also evaluated using Raman spectroscopy and the room temperature Raman spectra for all the ‘sintered’ ferrites is depicted in Fig. 4.24. As already mentioned regarding the Raman spectra in the ‘as prepared’ section, the Raman spectra for the ‘sintered’ samples also show various vibrational modes in the cubic spinel structure that are attributed to the octahedral and the tetrahedral sites. However, the spectra are more intense and distinct upon sintering. Table 4.11 shows the exact positions of all the bands i.e. A_{1g} (1), A_{1g} (2), E_g , T_{2g} (1), T_{2g} (2) and T_{2g} (2) observed for our ‘sintered’ ferrite samples.

The occurrence of the $\alpha\text{-Fe}_2\text{O}_3$ peak is not detected by the sharp peak $\sim 240\text{ cm}^{-1}$ [89] in all the ferrite samples affirming formation of the single phasic nature of the ‘sintered’ ferrites.

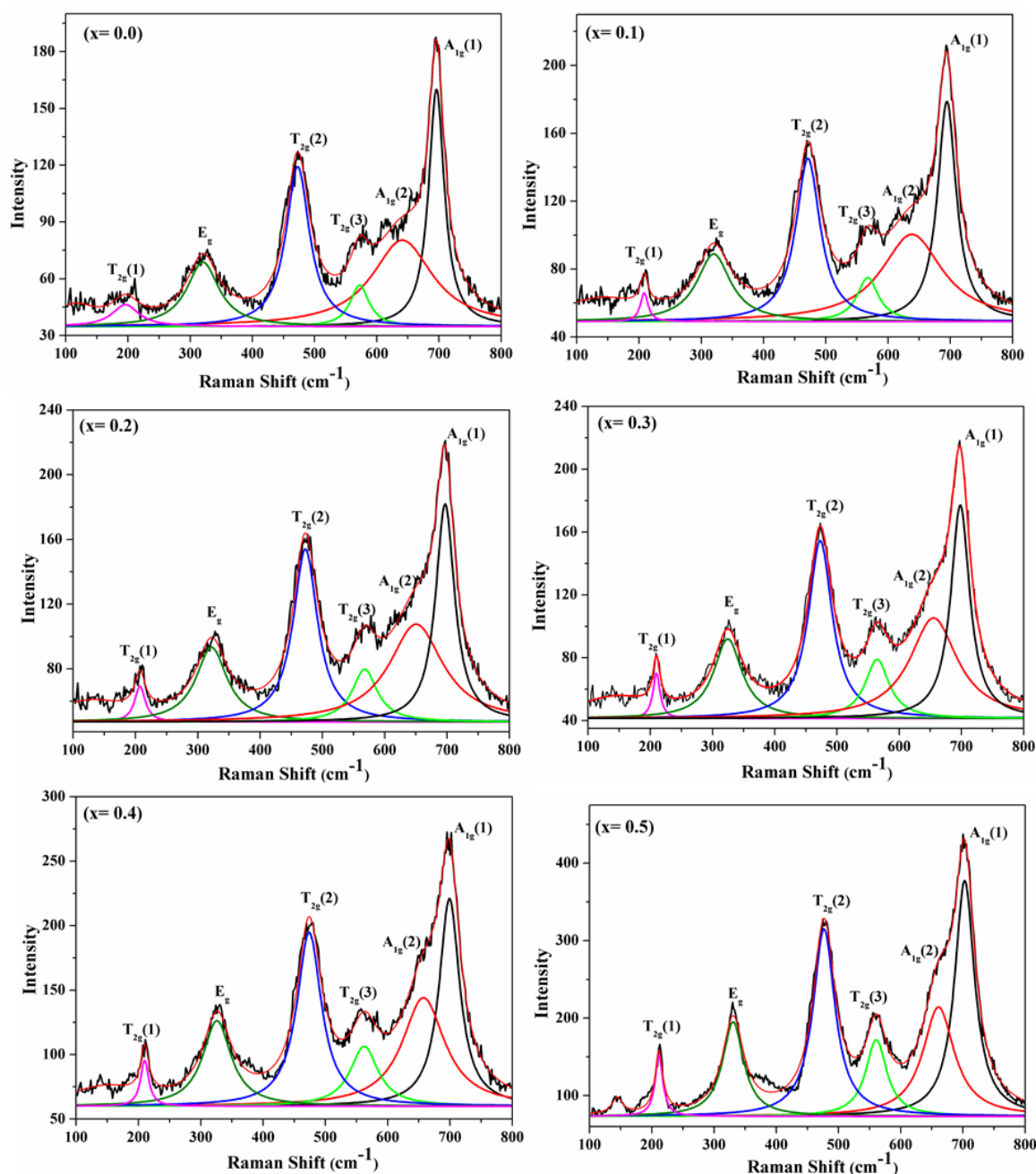


Fig. 4.24 The Raman spectra of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The transformation associated with the increase in the magnesium concentration is indicated by the variation in the intensities and the peak positions in the ferrite samples. The intensities of the Raman modes are in accordance with the inversion degree [90]. From Fig. 4.24 it is evident that there is an increase in the intensity of the A_{1g} peak as the magnesium concentration is increased. As the Mg^{2+} ions are added at the tetrahedral

sites, Ni^{2+} ions are replaced at the octahedral sites the consequent movement of Fe^{3+} ions occur towards the octahedral sites as a result the splitting becomes more eminent.

Table 4.11 The Raman shift obtained for the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	$A_{1g}(1)$ cm^{-1}	$A_{1g}(2)$ cm^{-1}	$T_{2g}(3)$ cm^{-1}	$T_{2g}(2)$ cm^{-1}	E_g cm^{-1}	$T_{2g}(1)$ cm^{-1}
0.0	693	654	561	473	321	208
0.1	694	656	561	475	322	208
0.2	699	657	562	477	323	209
0.3	700	660	562	475	326	209
0.4	703	663	563	477	328	209
0.5	706	664	565	478	330	210

4.7 Solid state studies of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

4.7.1 Dielectric properties of the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

4.7.1.1 Dielectric measurements as a function of frequency for the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

Since the variation of the dielectric properties of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites were greatly dependent on the dielectric properties, thus the dielectric properties for their ‘sintered’ counterparts were investigated for their dielectric properties upon sintering. The room temperature dielectric constant as a function of frequency for all the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites carried out in frequency range from 20 Hz to 10 MHz are depicted in Fig 4.25a. All the ‘sintered’ ferrites demonstrated normal dielectric nature in the frequency range where the dielectric constant was found to decrease promptly till the lower frequency at 1 KHz and thereafter it remained constant at a higher frequency.

As already discussed in the ‘as prepared’ section 4.5.1.1 for dielectric properties, this decrease in the dielectric constant with increase in the frequencies is in agreement with the Koop’s theory in conjunction with the Maxwell-Wagner theory [91-92]. The dielectric properties of the ferrite material comprise of conducting grains that are segregated by the

poorly conducting grain boundaries. The grains are effective at high frequencies whereas the grain boundaries are effective at lower frequencies.

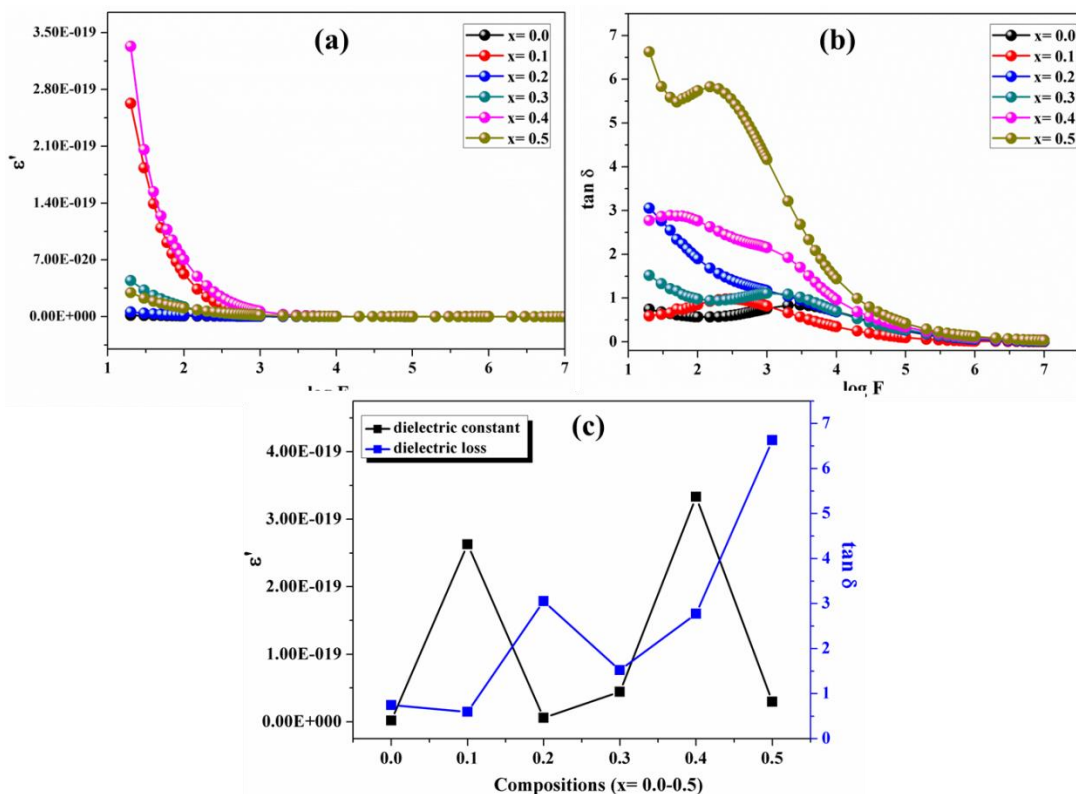


Fig 4.25 The plots of (a) Dielectric constant against log frequency (b) dielectric loss tangent ($\tan \delta$) against log frequency (c) Plot of dielectric constant and loss tangent as a function of composition at 20 Hz of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

During the sintering process there is a formation of the grain boundaries because of oxidation of crystallites in a porous ferrite material. At higher frequencies, the samples show frequency independent behavior of an applied electric field because of charge carriers that are accountable for different mechanisms of polarization and which are below the applied field. Thus, with increase in frequency the carriers do not follow the transformations in the applied electric field over a definite frequency [93-94]. The dielectric constant values were found to be highest for $x = 0.4$ composition. The mechanism of conduction in $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites occur as a result of hopping of electrons between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ ions at the octahedral (B) sites and the hopping of holes between $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$ ions [18, 93]. Fe^{3+} ions are present on both A-sites and B-sites whereas Ni^{2+} and Co^{2+} ions preferentially occupy the B-sites in the spinel ferrite lattice. Upon substitution of Ni^{2+} and Co^{2+} by Fe^{3+} ions and Mg^{2+} ions, some amount of

Mg^{2+} ions prefers A-sites in spinel which displaces the Fe^{3+} ions. The displaced Fe^{3+} ions relocate from A-sites to the B-sites thus causing an increased amount of Fe^{3+} ions at the B-sites. Hence electron hopping further improves the dielectric polarization at the grain boundary leading to a decrease in the dielectric constant [93, 95].

Fig 4.25b displays the dielectric loss tangent ($\tan \delta$) against frequency plot of the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites. The plot showed a decreasing behaviour of the dielectric loss tangent with increased frequency; this decrease was abrupt at low frequency (2 KHz) and finally was found to remain constant with increasing frequencies. The dielectric loss tangent did not show any definite trend but the composition $x = 0.5$ showed the highest value.

4.7.1.2 Dielectric measurements as a function of temperature for the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The dielectric constant plots of the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C has been depicted in Fig 4.26. At first the dielectric constant was found to remain constant and after a certain point an increase in the dielectric constant is observed with increase in temperature. As it is known that there are four types of polarizations, viz. ionic, electronic, interfacial and space charge. All the four types of polarizations are responsible for the contribution at lower frequencies. Also, the dipolar and interfacial polarizations which are temperature dependent are contributing factors for prompt increment in the dielectric constant values with rising temperature. While the higher values of the dielectric constant are a result of contribution of the electronic and ionic polarization that are enormously independent of both frequency and temperature [78]. The lower values of the dielectric constant with increase in frequency (1 MHz) are observed as per the dielectric constant against temperature plot shown in Fig.4.26 (highest for 250 KHz) thus justifying the lowest impact of temperature. It is also noted from the temperature profiles (Fig 4.26) that there is a slight shift in the temperature towards higher temperature as the frequency is increased.

With increase in frequency, the electrons are incapable of keeping the speed with the promptly changing field because of which at higher frequencies the polarization was found to decrease. The shift in the values with increasing temperature is due to higher time lags at higher frequencies and need for high temperature to restore the polarization

[96-97]. The dielectric constant values are found to be highest for $x = 0.0$ composition and the values were found to decrease with increase in magnesium substitution.

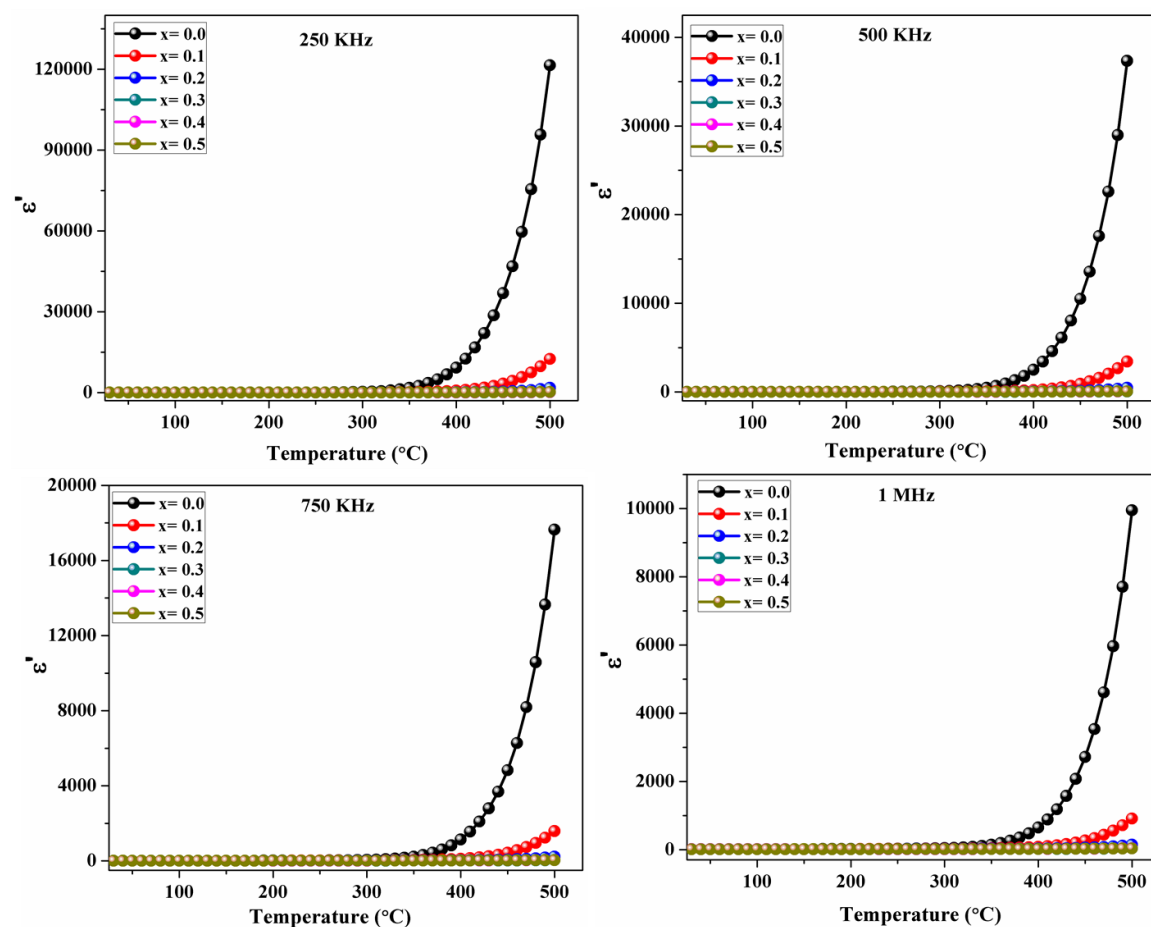


Fig. 4.26 The plots representing variation of dielectric constant as a function of temperature for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz).

A similar trend has been observed in the dielectric loss tangent values as seen for the dielectric constant. Fig 4.27 depicts the dielectric loss tangent values for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz in which the values were found to remain constant at lower temperature and were found to increase swiftly with increase in temperature. The compound with composition $x = 0.0$ showed the highest values and with increasing magnesium concentration the dielectric loss was found to decrease.

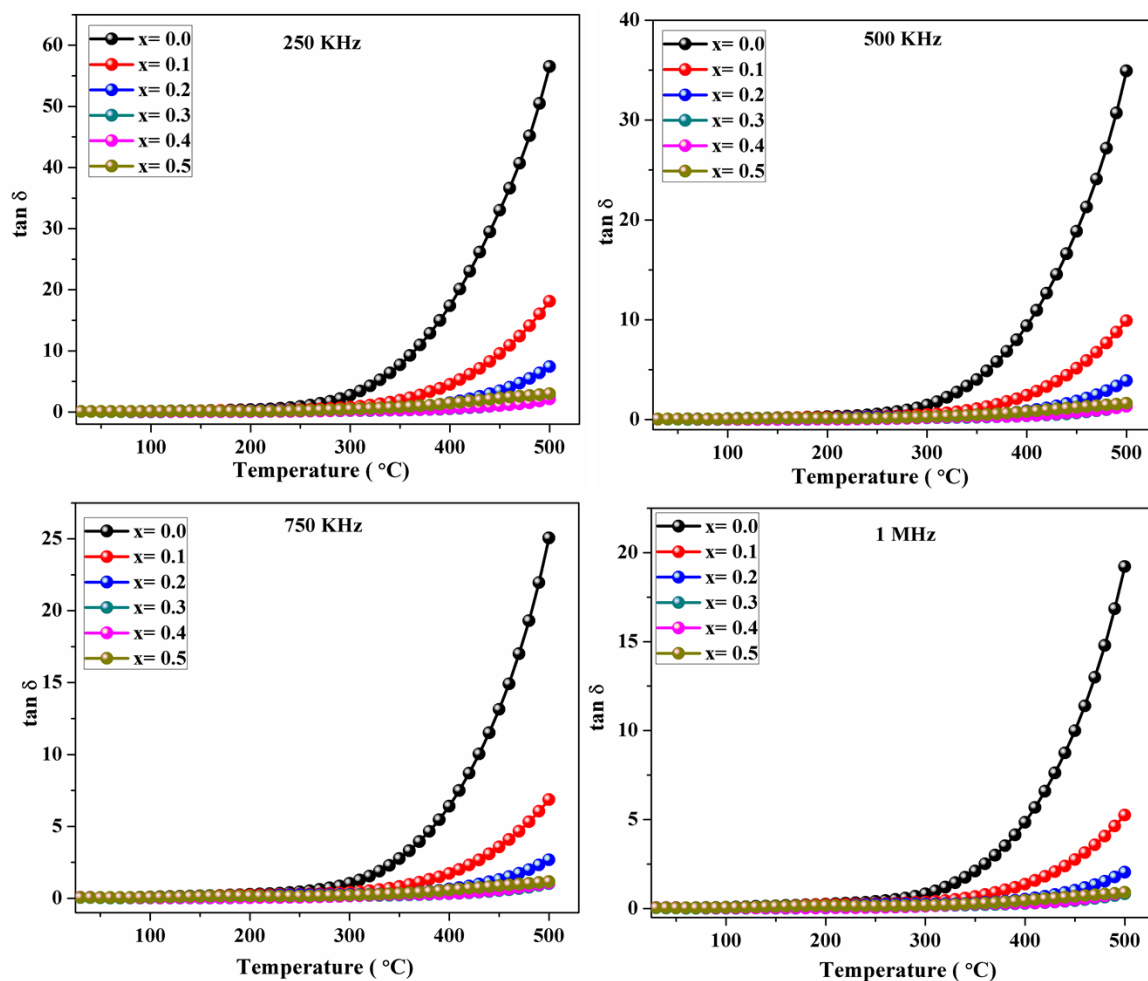


Fig. 4.27 The plots representing variation of dielectric loss tangent as a function of temperature for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz).

4.7.2 The magnetization studies of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.7.2.1 The normalized A.C. susceptibility studies of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The alternating current susceptibility studies for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were also measured till Curie temperature is obtained and the normalised A.C. susceptibility curves for the same are shown in Fig. 4.28. The susceptibility values were found to show a gradual increase forming a peak, which abruptly falls near the Curie temperature (T_c). The fall in the susceptibility is extremely slow as the temperature rises which implies the presence of multi domain particles in all the ferrites [98-100].

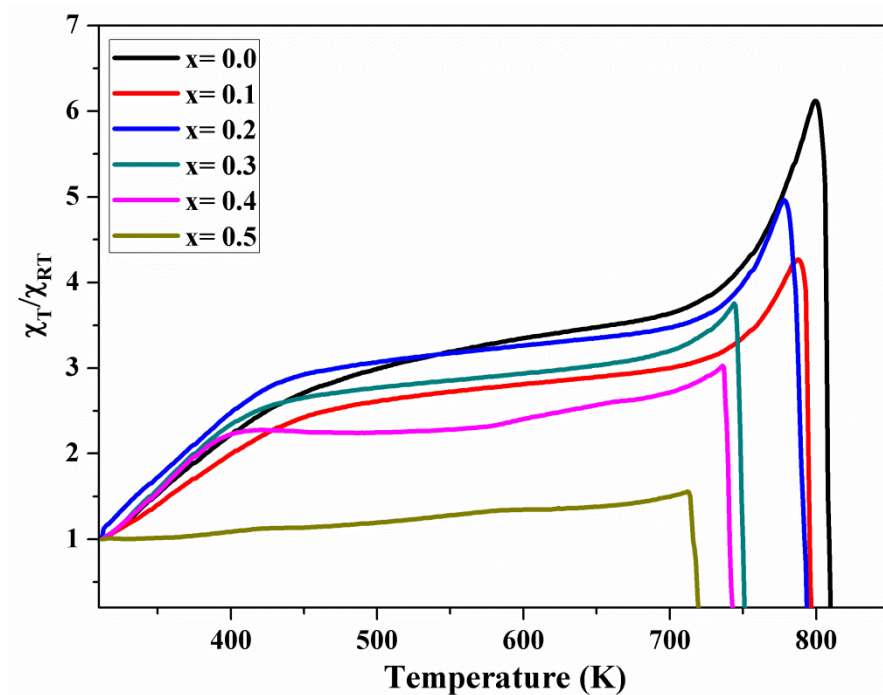


Fig. 4.28 Plots of normalized AC susceptibility against temperature of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) samples

Table 4.12 The Curie temperature of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites determined using AC susceptibility studies

Composition (x)	Curie Temperature (K)
0.0	806
0.1	795
0.2	792
0.3	750
0.4	741
0.5	718

It was determined that the T_c decreases with increase in the magnesium concentration linearly due to the non-magnetic Mg^{2+} ions substitutions in the magnetic nickel cobalt ferrites. The exact values of susceptibility for all the ‘sintered’ samples are tabulated in Table 4.12. As per the Neel’s theory, the variation in T_c is associated with the strength between the magnetic ions at the octahedral and the tetrahedral sites over oxide ions and can be categorised as A-O-B or A-B type interactions. There is a decrease in A-B strength upon Mg^{2+} ion substitution for Ni^{2+} ions and Co^{2+} ions leading to a decrease in the Curie temperature. Besides, the increased lattice parameter (Table X for sintered ferrites) upon

increasing Mg^{2+} substitution increases the magnetic ions distance hence leading to lowering of the T_c [101].

Moreover, T_c for the ‘sintered’ ferrites was found to be lower in comparison with the ‘as prepared’ ferrites which can be justified by the particle size effect, since majority of the particles in the ‘sintered’ samples are dominantly multi domain in nature.

4.8 Applications of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

4.8.1 Electrochemical properties of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The electrochemical properties of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were inspected using the cyclic voltammetry (CV) technique, galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The fabrication of working electrodes for all the ‘as prepared’ samples has been thoroughly discussed in chapter 2.

A well identified redox peak related to transition metal studied by this electrochemical method can provide huge knowledge to reveal the various active species at the metal oxide surfaces. All the ‘as prepared’ ferrite samples of this series were tested for cyclic voltammetry (CV) by using a three-electrode system. The electrolytic solution of 3 M KOH was used and the study was performed at varying scan rates of 10–200 mV/s. Fig 4.29 depicts the CV curves of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites in the potential window of 0.0-0.6 V at varying scan rates.

The anodic and cathodic peaks are observed corresponding to the redox reaction that are characteristic features of pseudocapacitors and are known to show pseudocapacitive behaviour [102-103] which means presence of an oxidation and a reduction peak implying that a reversible redox reaction has occurred on the working electrode and this is a reversible process [45, 104].

The reduction peak is observed roughly at around 0.2 V and the oxidation peak at around 0.4 V in the positive potential range for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites [105]. With increase in the scan rates, the voltammograms appeared to be rectangular and more symmetrical implying highly reversible redox processes at the electrode surface [106]. Besides, a slight shift in the potential towards higher side is also seen with increased scan rates that can be attributed to electrochemical polarization which

demonstrates that the process is quasi reversible or diffusion controlled charge transfer process [92, 107].

Table 4.13: Specific capacitance of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites samples at different scanning rates (cyclic voltammetry).

Scan rate (mVs^{-1})	Specific capacitance (C_{sp}) (in Fg^{-1}) for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites					
(x)	0.0	0.1	0.2	0.3	0.4	0.5
10	72.89	55.76	72.63	127.32	48.77	35.05
20	72.41	55.68	71.7	124.19	48.03	34.62
30	69.85	55.55	69.78	123.17	47.96	34.51
40	67.06	54.78	67.6	120.72	47.58	33.97
50	64.54	53.68	65.73	118.32	47.05	33.45
60	62.45	52.81	64.01	116.09	46.55	32.82
70	60.52	51.9	62.46	113.99	45.95	32.22
80	58.9	51.04	61.01	111.84	45.37	31.66
90	57.39	50.26	59.66	110.14	44.8	31.08
100	56.06	49.54	58.48	108.41	44.25	30.55
150	50.6	45.82	53.43	99.81	41.11	27.9
200	46.78	43.14	49.87	93.41	38.7	26

The extent of the area under the curve (cyclic voltammogram) is accountable for calculating the specific capacitance values [45, 108]. The C_{sp} values found to decrease at a faster scan rate for all the samples as shown in Table 4.13. This decreasing trend with high scan rate is because of the fact that the movement of electrolytic ions and the time of diffusion are confined to shorter duration of time which affects assess of electrolytic ions on some of the active sites of the working electrodes [109].

The specific capacitance values for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites are depicted in Table 4.13 and it was seen that the samples show good specific capacitance values ranging from 35.05 to 127.32 F/g. However, the composition $x = 0.3$ is found to exhibit highest value of specific capacitance at the scan rate of 10 mV/s thus implying a better pseudocapacitive nature. Fig. 4.30 shows the plot of specific capacitance against the scan rates for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

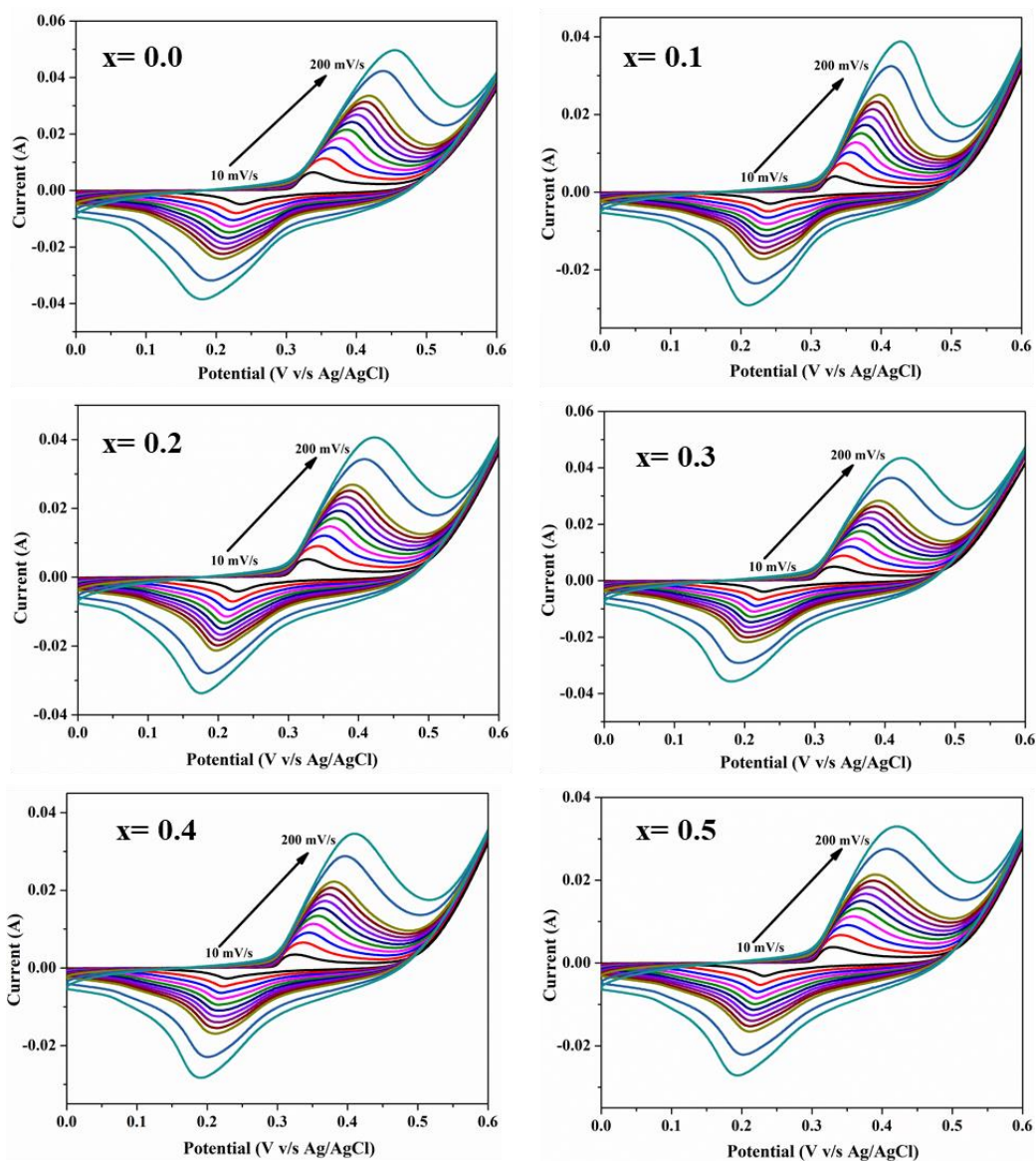


Fig. 4.29 Cyclic voltammograms of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at varying scan rates ranging from 10 to 200 mV/s, with the potential window between 0.0-0.6 V.

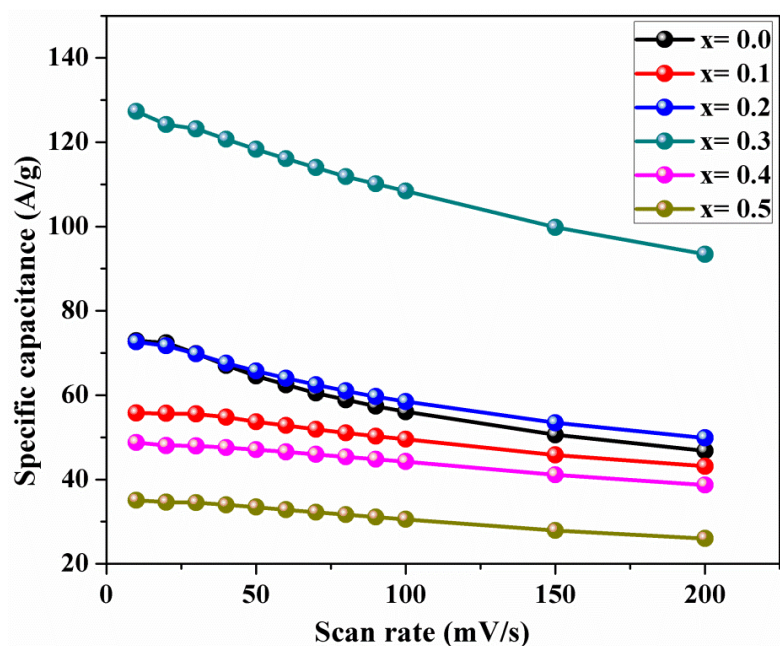


Fig. 4.30 The plot of specific capacitance against the scan rates plots for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

For better comprehension of the nature of Mg substitution on the nickel cobalt doped ferrite samples for the super capacitive applications, the galvanostatic charge-discharge (GCD) measurements were carried out at varying current densities. Fig. 4.31a and Fig 4.31b indicate the current densities investigated by GCD from 0.1 to 2.0 A/g (0.1 A/g , 0.25 A/g, 0.5 A/g, 0.75 A/g, 1 A/g and 2 A/g) for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites. As can be seen from the GCD measurements, it indicates a decreasing trend in the discharge time with increase in the current density which justifies that all the active sites cannot be assessed for the electrolytic ions at higher current densities to carry out the electrochemical reactions [110].

As can be seen from the fig. 4.31a and b the GCD curves are not linear (forms a plateau) indicating pseudocapacitive nature allied to the adsorption/desorption or quasi reversible redox reactions at electrolyte/electrode surface [111-112]. As the current densities increases the C_{sp} values were found to decrease which is attributed to the drop in the voltage and inadequate active material in the redox reactions because of which there is poorly diffused electrolyte at higher current densities [112-113]. These findings are suggestive of enhanced C_{sp} due to better surface area, mesoporous nature (confirmed from BET) which is also probably due to diffusion effects of ions within Mg substituted nickel cobalt ferrites [114-115]. The exact C_{sp} values for all the ‘as prepared’ samples are shown in Table 4.14 for varying current densities. Amongst all the samples the sample with

composition $x = 0.3$ has found to show a longer charge-discharge time thus indicating better charge storage capacity.

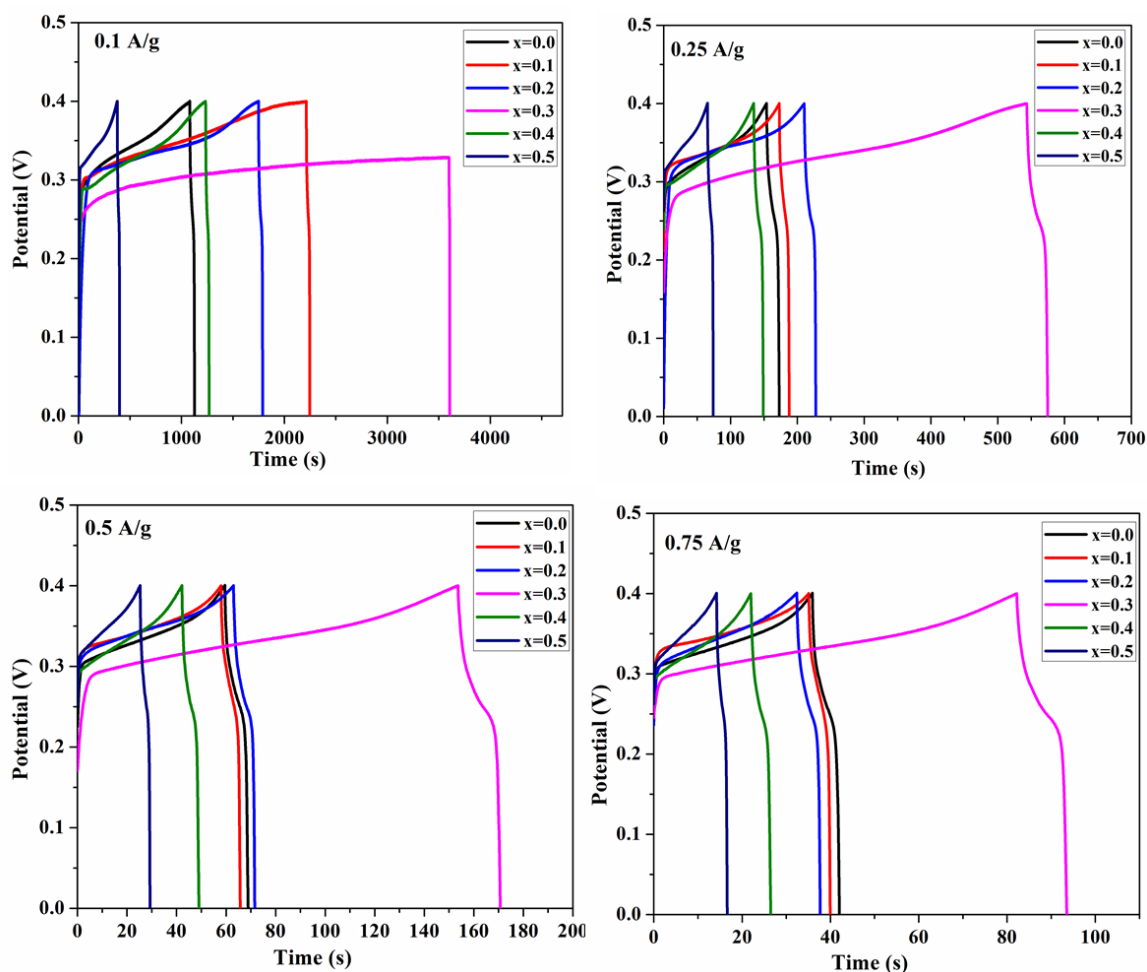


Fig. 4.31a Galvanostatic charge-discharge plots of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at charge-discharge current densities for 0.1, 0.25, 0.5 and 0.75 A/g.

The investigation of the electrolyte resistance (R_s) and the charge transfer resistance (R_{CT}) over electrode/electrolyte interface was examined using the electrochemical impedance spectroscopy (EIS). The investigation was performed within the frequency range of 100 kHz to 0.1 Hz. The Nyquist plot is depicted in Fig 4.32 for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites electrodes which shows the impedance (Z') and the imaginary (Z'') part. The plot displays the slight semicircles in the high frequency region and a straight line at the low frequency region. The semicircle region at the high frequency is associated with the porosity of nanocrystalline Mg substituted nickel cobalt ferrites and the reaction kinetics at the electrode/electrolyte interface.

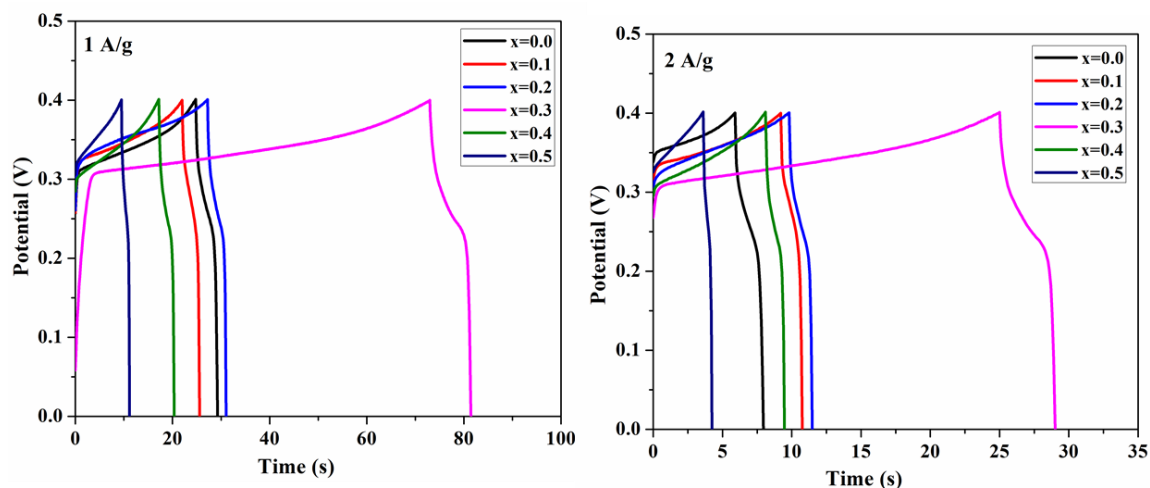


Fig. 4.31b Galvanostatic charge-discharge plots of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at charge-discharge current densities for 1.0 and 2.0 A/g.

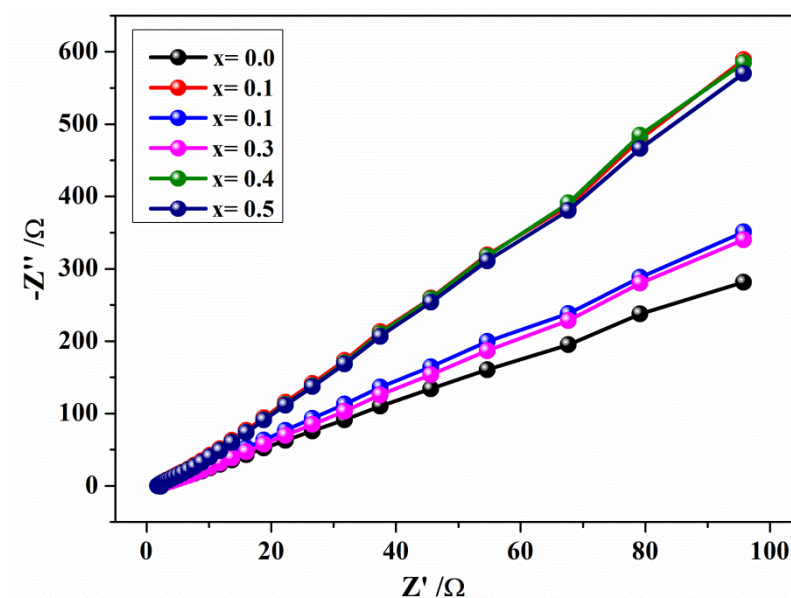


Fig. 4.32 Nyquist plots for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites samples.

From Fig. 4.32, it is observed that there is an intercept nearly in the range of 1.21-3.23 Ω for the real impedance part (Z') which shows total solution resistance (R_s) with increasing frequencies [116-117]. Moreover, at low frequencies a straight line is seen inclined at an angle of 45° with Z' -axis which is known as the Warburg impedance (W) related to transportation and diffusion of the counter ions in electrode/electrolyte interface [117].

Table 4.14 Specific capacitance of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites samples at different current densities (Galvanostatic charge-discharge)

Current densities (x)	Specific capacitance (C_{sp}) (in Fg^{-1}) for ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites					
	0.0	0.1	0.2	0.3	0.4	0.5
0.1	79.95	100.42	95.65	316.95	75.98	29.33
0.25	77.52	81.19	88.14	311.60	74.47	27.73
0.5	76.12	83.33	86.13	309.82	65.04	25.27
0.75	75.72	80.12	82.63	302.71	63.63	24.03
1	73.71	79.05	80.12	297.56	64.10	20.95
2	70.51	68.37	68.10	292.02	52.79	17.25

4.9 Conclusions

This chapter reports the synthesis, characterization, properties, and applications of $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites prepared by a combustion method using L-tartaric acid dihydrazide as a novel fuel. Optimization studies using thermal, structural, and magnetic analyses identified an optimum oxidizer: fuel ratio of 1:0.175, yielding single-phase cubic spinel ferrites with reduced crystallite size and single-domain characteristics. Phase purity, stoichiometry, and oxidation states were confirmed using XRD, ICP-AES, IR, Raman, and XPS techniques. Magnesium substitution resulted in increased lattice parameters, reduced crystallite size, and enhanced surface area, as supported by BET and HR-TEM analyses. Dielectric and magnetic investigations revealed frequency and temperature-dependent behaviour, with Curie temperature decreasing with increasing magnesium content and a transition from single-domain to superparamagnetic nature. Sintering improved crystallinity and particle growth while preserving the spinel structure. Electrochemical studies demonstrated promising supercapacitor performance, with the composition $x = 0.3$ exhibiting the highest specific capacitance.

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Chapter 5

$\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x= 0.0\text{-}0.5$) ferrites: Synthesis, characterization, solid state properties and their applications

5.1 Introduction

The technological importance of the spinel ferrite materials due to their extraordinary properties has made it possible to be used in potential applications like catalysis, high frequency devices, gas sensors, supercapacitors etc. [1-3]. These attractive applications of the ferrite materials motivated various material researchers to develop numerous synthesis methods for preparation of ferrites such as ceramic, combustion, precursor, co-precipitation, precursor-combustion, sol-gel auto combustion method, etc. [4-7]. Synthesis methods play a significant role in carrying out intensive research in the field of nanocrystalline ferrite materials.

One major benefit in choosing the ferrite spinel for required applications is that the tuning of the different properties such as size, shape and distribution of the cations in the octahedral and the tetrahedral sites is possible and this can be governed by their unique sample preparation and doping the metal ions appropriately [8]. In the recent times, a substantial research work has been carried out on the structural, electric and magnetic properties of nanocrystalline Co-Zn ferrites, Ni-Zn ferrites, Ni-Co ferrites for scrutinizing their various properties for various applications [9-11]. They discovered high resistivity and saturation magnetization for Ni-Zn ferrites, high magnetocrystalline anisotropy for the Co-Zn and Ni-Co ferrites [12-13]. Intriguingly, Ni-Co-Zn ferrites also belong to the same category and the research work accessible through literature reports on these materials is restricted to a specific cobalt and/or zinc content. Hence, an extensive investigation of the structural, electric, dielectric, magnetic properties of Ni-Co-Zn ferrites with varying zinc concentrations in nickel cobalt ferrites is necessary for various applications. This chapter thus highlights the synthesis of the Ni_{0.5}Co_{0.5-x}Zn_xFe₂O₄ (x = 0.0-0.5) ferrite series which is prepared by the precursor-combustion synthesis route.

The proposed research work stresses on the comparative study of the structural and magnetic properties of 'as prepared' Ni_{0.5}Co_{0.5-x}Zn_xFe₂O₄ (x = 0.0-0.5) ferrite samples with their 'sintered' analogues via precursor combustion route. Our present research work emphasizes on the synthesis, characterization and study of the solid state properties of the synthesized ferrite using precursor-combustion method. During synthesis, we have successfully incorporated hydrazine ligand in the mixed metal fumarate precursor to obtain mixed metal fumarato-hydrazinate precursors which decompose autocatalytically on ignition at room temperature to form the ferrites. Since hydrazine can coordinate easily

with transition metal ions, it slows down the decomposition of metal carboxylates. Due to its thermodynamic instability and positive heat of formation, it gives high exothermicity during the decomposition of precursors, hence supporting the formation of nanocrystalline material at low temperatures [14-15].

5.2 Synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) precursors

$\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were synthesized using the precursor-combustion technique; for which the detailed method of synthesis has been discussed in chapter 2. During the synthesis of these ferrites first an unstable $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors is formed which is very much reactive as can also readily replace hydrazine after absorbing moisture. In chapter 2, it has been already mentioned that the precursors auto catalytically decompose with a burning fragment thus leading to the ferrite formation. This chapter elaborates the characterization of the precursors and the ‘as prepared’ and ‘sintered’ ferrites in detail.

5.3 Characterization of the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors

5.3.1 Carbon Hydrogen Nitrogen (CHN) analysis and hydrazine estimation of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors

The CHN analysis of all the precursors were carried out using the CHNS analyser wherein the experimental data was found to match closely with the theoretical values as indicated in Table 5.1 thus supporting the formula fixed for the precursors as $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$). Besides, the amount of hydrazine present in the precursors has been assessed using titrimetry by Andrew’s condition and titrating against 0.025 M KIO_3 . The experimental values obtained were found to be in close agreement with the theoretical ones and are mentioned in the Table 5.1.

Table 5.1 The theoretical and experimental percentages of carbon (C), hydrogen (H), nitrogen (N) and hydrazine (N_2H_4) in $Ni_{0.5}Co_{0.5-x}Zn_xFe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x = 0.0-0.5$) precursors.

Element	Compositions (x)						
		x= 0.0	x= 0.1	x= 0.2	x= 0.3	x= 0.4	x= 0.5
C (%)	Theoretical	20.42	20.40	20.38	20.36	20.35	20.33
	Experimental	19.65	20.99	20.35	21.15	20.26	19.78
H (%)	Theoretical	4.255	4.251	4.247	4.243	4.239	4.235
	Experimental	4.06	4.68	3.98	5.06	3.79	4.69
N (%)	Theoretical	23.83	23.80	23.78	23.76	23.74	23.72
	Experimental	23.56	23.75	22.93	23.48	24.53	23.77
N_2H_4 (%)	Theoretical	27.27	27.24	27.30	27.20	27.17	27.15
	Experimental	26.91	27.18	27.71	27.18	27.28	26.93

5.3.2 IR studies of $Ni_{0.5}Co_{0.5-x}Zn_xFe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x=0.0-0.5$) precursors

Since the precursor gets decomposed in air, if kept for longer time, the IR spectra of all the precursors were recorded, soon after their synthesis (Fig. 5.1). The Infrared spectrum of the precursor showed different binding modes of fumarato-hydrazinate ligand to the metal ion. The absorption peaks at a frequency of approximately $3190-3353\text{ cm}^{-1}$ attributes to the N-H stretching frequencies [16]. The band at around 970 cm^{-1} is due to N-N stretching frequency revealing the bridging bidentate nature of hydrazine ligand. The frequency band at approximately 1627 cm^{-1} is due to C=C group in fumarate ion. The asymmetric and symmetric stretching of the carboxylate ion is at the frequencies of around $1550-1587\text{ cm}^{-1}$ and around $1391-1375\text{ cm}^{-1}$, respectively [17].

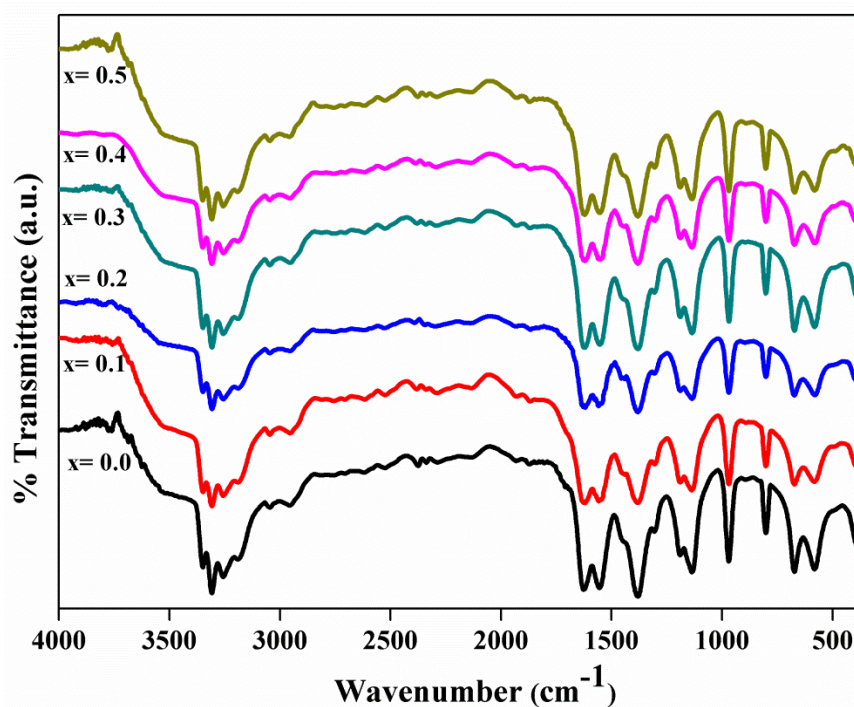


Fig. 5.1 The Infra red spectra of the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x=0.0-0.5$) precursors.

5.3.3 Isothermal mass loss/total mass loss studies of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x=0.0-0.5$) precursors

The isothermal mass loss studies along with the total mass loss for the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x=0.0-0.5$) precursors were carried out at various temperatures. The isothermal mass loss data along with the total mass loss for all the precursors has been shown in Table 5.2. All the precursors were heated for the fixed time for 10 minutes at different intervals of temperature and the mass loss at these temperatures was determined by concurrently estimating the amount of hydrazine at these temperatures. From the Table 5.2, it can be concluded that a stepwise decomposition of the precursors occur with loss of hydrazine at different temperatures. However, all the precursors decomposed beyond 175 °C since with decrease in the hydrazine content, the precursors do not possibly undergo complete auto-combustion due to lack of exothermicity of combustion reaction as the hydrazine concentration decreased with each isothermal step.

Furthermore, to investigate the total mass loss, the known quantity of precursor was weighed and kept in the muffle furnace at 500 °C for 5 h. The total mass loss studies

depict that the theoretical mass losses match closely with the experimental ones (Table 5.2).

Table 5.2 The isothermal mass loss (%) along with hydrazine estimation (%), theoretical and experimental hydrazine and total mass loss (%) of $Ni_{0.5}Co_{0.5-x}Zn_xFe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x=0.0-0.5$) precursors.

Composition (x)	Isothermal mass loss (%) / Hydrazine estimation (%)						Total mass loss (%)	
Temp.	RT-70 °C	70 °C-95 °C	95 °C-125 °C	125 °C-150 °C	150 °C-175 °C	>175 °C	Theo	Exp
0.0	3.31/ 25.95	2.22/ 15.79	6.23/ 12.96	5.38/ 9.53	7.96/ 6.97	Precursor decomposed	66.74	66.34
0.1	4.36/ 26.00	2.25/ 16.78	4.26/ 11.12	6.98/ 10.79	5.54/ 8.69	Precursor decomposed	66.68	66.23
0.2	3.22/ 25.00	2.62/ 15.08	5.80/ 13.89	9.05/ 10.67	7.66/ 6.38	Precursor decomposed	66.62	66.01
0.3	5.12/ 25.87	3.77/ 14.98	8.63/ 11.61	4.36/ 9.23	6.33/ 8.54	Precursor decomposed	66.56	67.32
0.4	5.25/ 25.09	1.36/ 20.03	7.35/ 16.75	4.89/ 14.22	9.68/ 11.87	Precursor decomposed	66.60	65.83
0.5	1.98/ 24.67	3.27/ 18.93	4.68/ 13.21	3.45/ 11.54	6.73/ 9.63	Precursor decomposed	66.44	66.97

5.3.3.1 IR studies of $Ni_{0.5}Co_{0.5-x}Zn_xFe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x=0.0-0.5$) precursors at different temperatures.

To compliment the decomposition pattern of the fumarato-hydrazinate precursors, the IR spectra of all the $Ni_{0.5}Co_{0.5-x}Zn_xFe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x=0.0-0.5$) precursors were carried out during the isothermal process at different temperatures and the IR plots are shown in Fig. 5.2a to Fig. 5.2f. From the IR plots it was observed that the intensity of the peaks approximately at $3190-3353\text{ cm}^{-1}$ which corresponds to N-H stretching frequencies decreased as the temperature increases from 30 °C to 175 °C which is suggestive of stepwise hydrazine loss. Besides, the peak $\sim 970\text{ cm}^{-1}$ which is due to N-N stretching frequency (bridging bidentate ligand) also vanish when the temperature reaches almost

200 °C thus implying complete loss of hydrazine from all the precursors (Table 5.2). It can be seen from the Fig. 5.2a to Fig. 5.2f the most of the absorption bands from the fumarate group disappear at 300 °C confirming the formation of the ferrite sample. However, small quantity of carbonaceous impurity present is burnt when the sample is heated further till 500 °C thus forming the ‘as prepared’ ferrite samples as seen from the IR plots where two distinct characteristic peaks are observed in the frequency range of 400 cm^{-1} and 600 cm^{-1} for tetrahedral and octahedral sites, respectively [18].

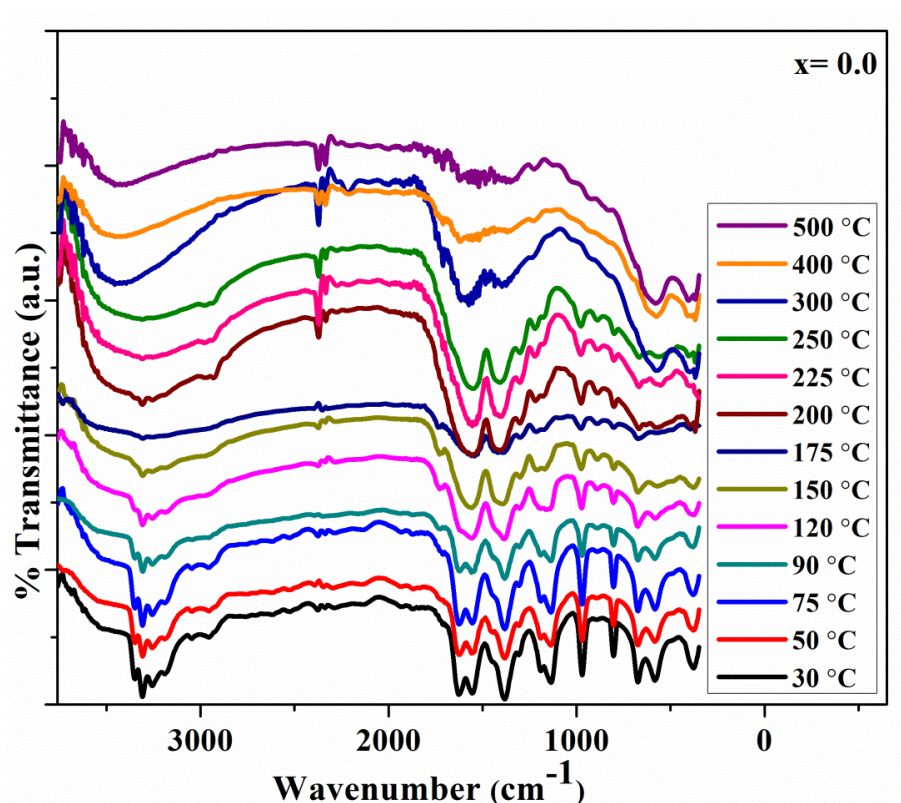


Fig. 5.2a IR spectra depicting the decomposition of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0$) precursors with change in temperature from 30 °C-500 °C.

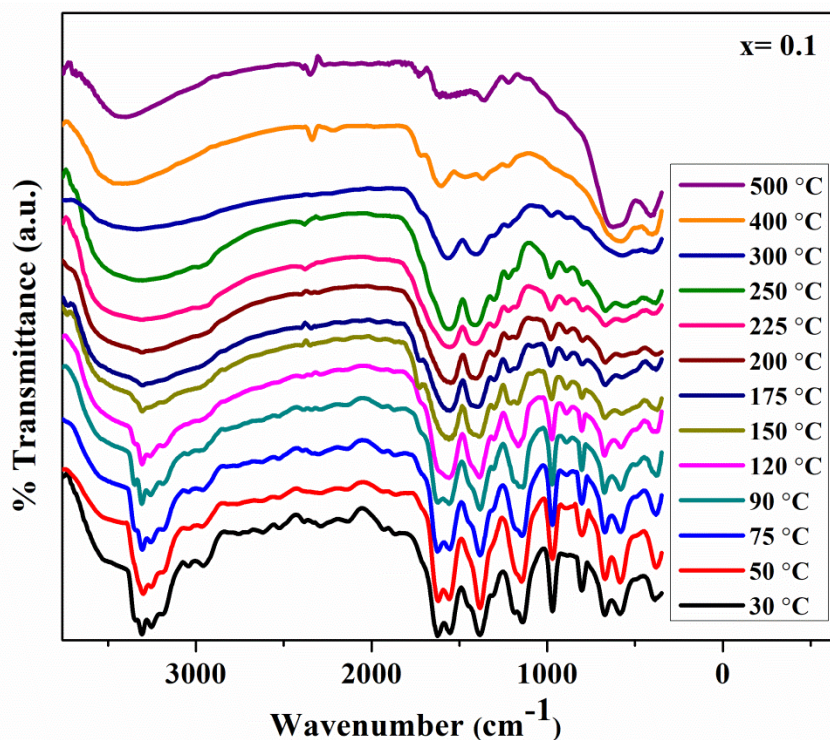


Fig. 5.2b IR spectra depicting the decomposition of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.1$) precursors with change in temperature from 30 °C-500 °C.

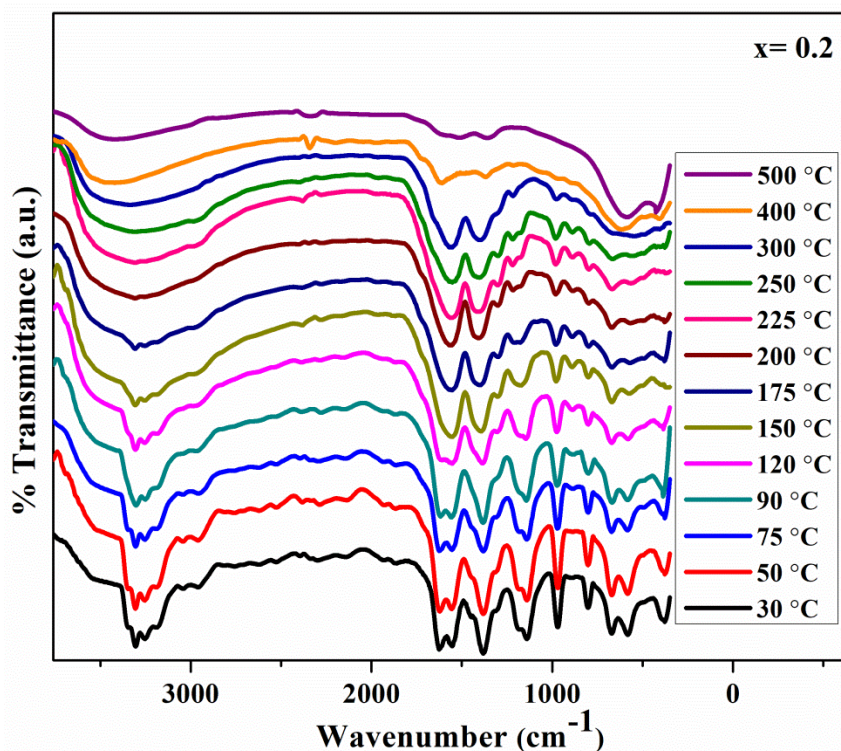


Fig. 5.2c IR spectra depicting the decomposition of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.2$) precursors with change in temperature from 30 °C-500 °C.

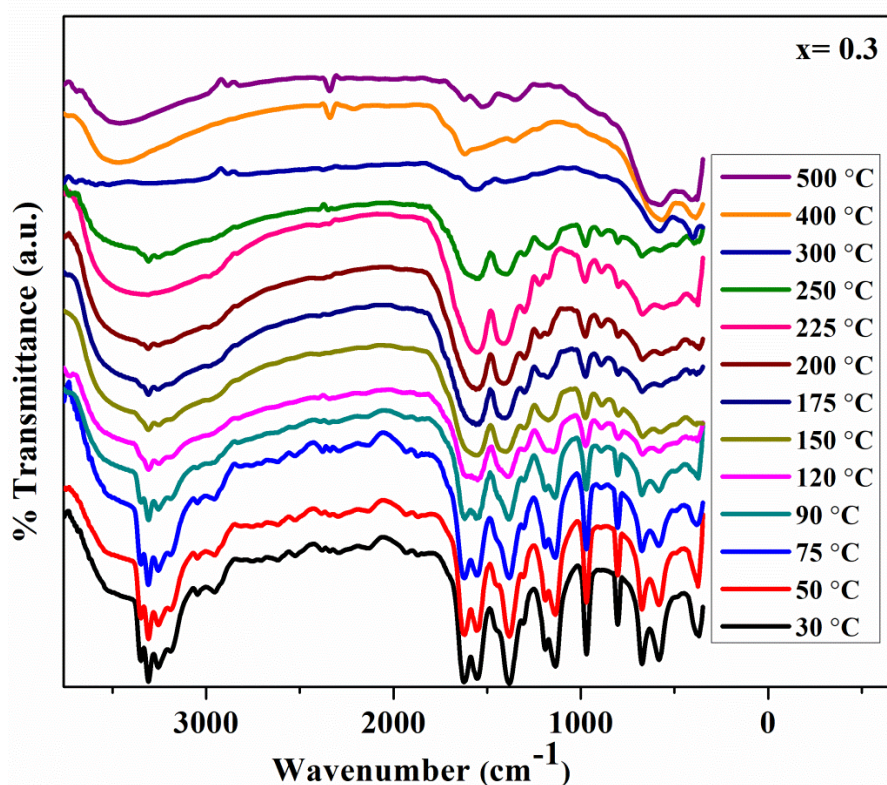


Fig. 5.2d IR spectra depicting the decomposition of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.3$) precursors with change in temperature from 30 °C-500 °C.

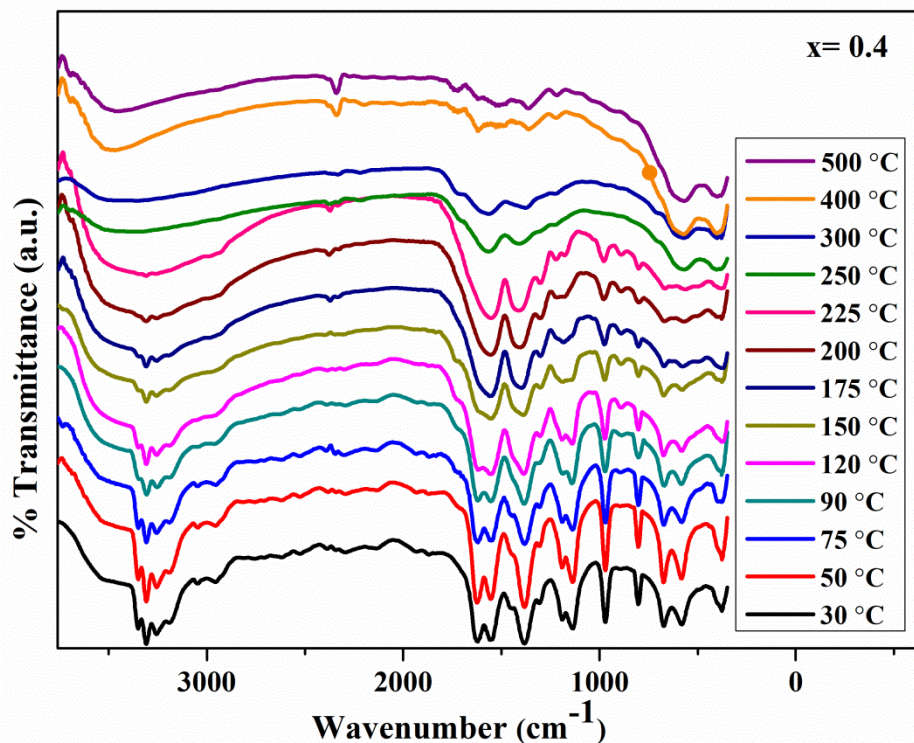


Fig. 5.2e IR spectra depicting the decomposition of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.4$) precursors with change in temperature from 30 °C-500 °C.

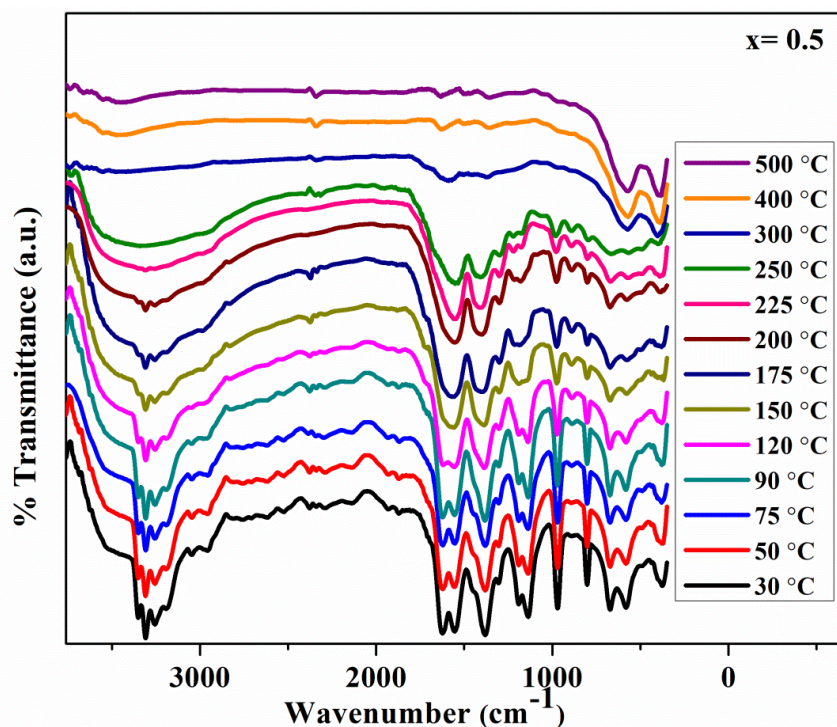


Fig. 5.2f IR spectra depicting the decomposition of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.5$) precursors with change in temperature from 30 °C-500 °C.

5.3.4 TG-DTA-DTG of the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x=0.0-0.5$) precursors

The TG-DTA-DTG plots obtained after carrying out thermal analysis of precursors from room temperature to 800 °C in air atmosphere reveals decomposition pattern of the precursor to form the respective ferrite. The TG-DTA-DTG plots of the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors are shown in Fig. 5.3 which shows first minor step in TG plot at around 100 °C with loss of roughly one molecule of hydrazine while in the second step which is a major step, there is complete dehydrazination with an exotherm shown in DTA. The third step is again a major step of decarboxylation showing corresponding exotherm in DTA, followed by the fourth minor step where any unburnt species is lost leading to formation of the ferrite [2].

The first image in Fig. 5.3 corresponds to the TG-DTA-DTG plot of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0$). In this image, it can be seen that there is initial loss of one hydrazine molecule, from Room temperature (RT) to 93 °C, confirmed by the mass loss of 5.16 % in TG. Thereafter, from 93 °C – 223 °C, total dehydrazination of the precursor takes place with a mass loss of 21.99 % in TG. The corresponding DTA peak (exotherm) is obtained at 138 °C and a peak in DTG is obtained at 130 °C. The total

decarboxylation occurs from 223 °C-389 °C with a mass loss of 38.05 %. A strong exotherm is observed in DTA at 294 °C which is followed immediately with another exo peak. The DTG also shows similar pattern like DTA with major peak at 292 °C. A small mass loss of 1.15 % is seen from 389 °C to 800 °C which corresponds to any unburnt species. The total mass loss observed in TG is 66.35 % which closely matches with the theoretical value of 66.72 %.

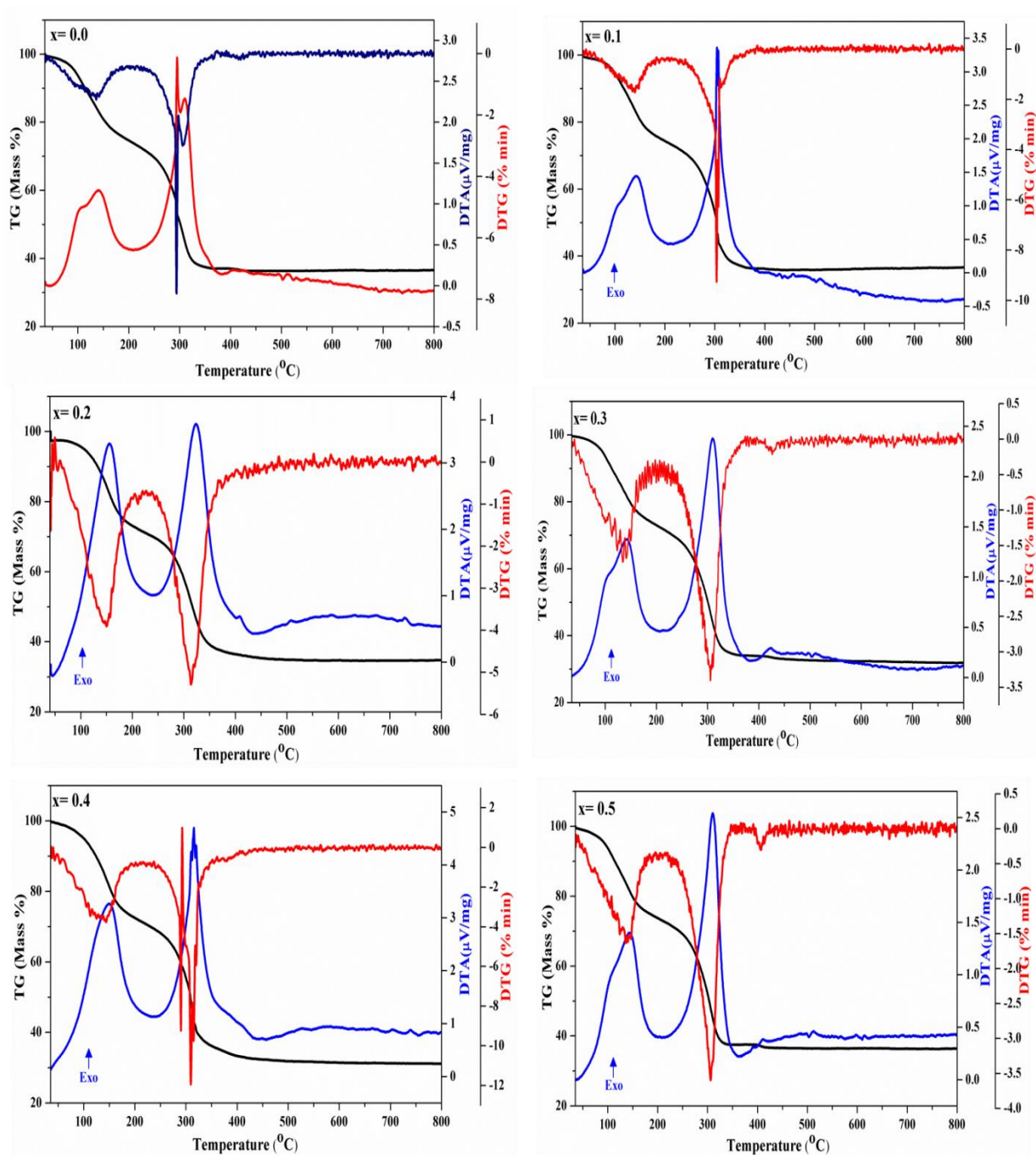


Fig. 5.3 The TG-DTA-DTG curves of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors.

From the TG-DTA-DTG curve of $Ni_{0.5}Co_{0.4}Zn_{0.1}Fe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x = 0.1$), it can be seen that there is a mass loss of 5.92 % from RT-95 °C corresponding to loss of one molecules of hydrazine lost from RT-95°C. The remaining hydrazine molecules are lost at a temperature from 95 °C-239 °C followed by beginning of decarboxylation with a mass loss of 23.8 %. For this step, the corresponding DTA (exotherm) peak occurs at 141 °C and the DTG peak at 135 °C. Total decarboxylation with 35.66 % mass loss in TG is observed from 239 °C-400 °C. For this step, an exothermic peak in DTA is obtained at 306°C and a peak in DTG at 303 °C. Very small mass loss of 0.9 % is observed from 400 °C till 800 °C pertaining to loss of any unburnt species. The total mass loss obtained was 66.28 % which is in near agreement with the theoretical mass loss of 66.67 %.

In case of precursor, $Ni_{0.5}Co_{0.3}Zn_{0.2}Fe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x = 0.2$), (Fig.5.3) one molecule of hydrazine is lost between RT-106 °C with a mass loss of 4.72 %. From 106°C-203°C, there is a mass loss of 22.68 % which implies total dehydrazination followed by initiation of the decarboxylation step. For this step, very sharp exothermic peak is obtained in DTA at 155 °C and a DTG peak at 149 °C. A strong exothermic peak in DTA at 324 °C and a peak in DTG at 311 °C were witnessed, associated with the mass loss of 37.82 % in the temperature range from 203 °C-400 °C due to decarboxylation. Later, little mass loss of 1.14 % is observed from 400 °C-800 °C ascribing to loss of any unburnt species. The formation of ferrite (mixed metal oxide) is confirmed at this temperature where the total residue in TG obtained is 33.64 % that matches closely with the theoretical value of 33.4 %.

The TG-DTA-DTG trace of $Ni_{0.5}Co_{0.2}Zn_{0.3}Fe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$ ($x = 0.3$) depicts the first step with the mass loss of 2.991 % at the temperature ranging from RT-82°C owing to the loss of half hydrazine molecule. The mass loss of 29.46 % at the second step from 82°C to 251 °C attributes to total dehydrazination followed by initiation of decarboxylation. This step has a corresponding exothermic DTA peak at 139 °C and a DTG peak at 135 °C. Later, a strong exotherm in DTA was observed at 312 °C and correspondingly a sharp peak in DTG at 308 °C which ascribes to the total decarboxylation with a mass loss of 32.94 % from 251 °C-400 °C. The mass loss of 1.17 % is observed from 400 °C-800 °C indicating loss of any unburnt species. The total residue of 33.44 % is obtained from the TG studies which are in good agreement with the theoretical value of 33.46 %.

The mass loss of 4.18 % is obtained for the precursor $\text{Ni}_{0.5}\text{Co}_{0.1}\text{Zn}_{0.4}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.4$) (Fig.5.3) from RT-94 °C which accredits to loss of one hydrazine molecule. Further, from 94 °C-275 °C, a mass loss of 31.17 % is observed in TG, to which a corresponding DTA exotherm is observed at 155 °C with a DTG peak at 134 °C. This step depicts total dehydrazination followed by beginning of decarboxylation. Also, there is a sharp exothermic DTA peak at 315 °C to which an analogous DTG peak is obtained at 310 °C from 275 °C-400 °C with the mass loss of 29.71 % which accounts to the total decarboxylation step. The slight mass loss of 1.29 % seen from 400 °C-800 °C demonstrates loss of any unburnt species present. The total mass loss obtained was 66.89 % which is in close agreement with the theoretical mass loss of 66.54 %.

The precursor $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.5$) (Fig.5.3) is showing the mass loss of 4.65 % accounting to the loss of one molecule of hydrazine from RT-92 °C. From 92 °C-260 °C, the mass loss of 27.55 % with respective DTA exotherm at 142 °C and a peak in DTG at 140 °C is observed corresponding to the total dehydrazination. The mass loss of 32.8 % is obtained in TG from 260 °C-400 °C with a sharp exothermic DTA peak at 309 °C and a peak in DTA at 305 °C indicating total decarboxylation of the precursor. In the final step from 400 °C-800 °C there is a small mass loss of 1.3 % which ascribes to the loss of any unburnt species. The total residue obtained was 33.71 % which matches closely with the theoretical residue of 33.56 %. Table 5.3 represents the TG-DTA and DTG data for all the precursors.

Table 5.3 The data pertaining to TG-DTA-DTG of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) precursors.

Composition (x)	TG		DTG Peak (°C)	DTA peak (°C)	Observations
	Temp. (°C)	Mass loss (%)			
0.0	RT-93	5.16	-	-	Loss of 1 N_2H_4 molecule
	93-223	21.99	130	138 (exo)	Total dehydrazination
	223-389	38.05	292	294 (exo)	Total decarboxylation
	389-800	1.15	-	-	Loss of unburnt species (carbon residue)
0.1	RT-95	5.92	-	-	Loss of 1 N_2H_4 molecule
	95-239	23.8	135	141 (exo)	Total dehydrazination accompanied by the starting of decarboxylation
	239-400	35.66	303	306 (exo)	Total decarboxylation
	400-800	0.9	-	-	Loss of unburnt species (carbon residue)
0.2	RT-106	4.72	-	-	Loss of 1 N_2H_4 molecule
	106-203	22.68	149	155 (exo)	Total dehydrazination accompanied by the starting of decarboxylation
	203-400	37.82	311	324 (exo)	Total decarboxylation
	400-800	1.14	-	-	Loss of unburnt species (carbon residue)

0.3	RT-82	2.99	-	-	Loss of 0.5 N ₂ H ₄ molecule
	82-251	29.46	135	139 (exo)	Total dehydrazination accompanied by the starting of decarboxylation
	251-400	32.94	308	312 (exo)	Total decarboxylation
	400-800	1.17	-	-	Loss of unburnt species (carbon residue)
0.4	RT-94	4.18	-	-	Loss of 1 N ₂ H ₄ molecule
	94-275	31.17	134	155 (exo)	Total dehydrazination accompanied by the starting of decarboxylation
	275-400	29.71	310	315 (exo)	Total decarboxylation
	400-800	1.29	-	-	Loss of unburnt species (carbon residue)
0.5	RT-92	4.65	-	-	Loss of 1 N ₂ H ₄ molecule
	92-260	27.55	140	142 (exo)	Total dehydrazination
	260-400	32.8	305	309 (exo)	Total decarboxylation
	400-800	1.3	-	-	Loss of unburnt species (carbon residue)

5.4 Characterization of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites

5.4.1 Chemical analysis of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites

The stoichiometry of the elements present in the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrite samples has been evaluated by performing the chemical analysis of the samples. MP-AES technique was employed to determine the percentages of the elements present in ‘as prepared’ samples and the values are tabulated in Table 5.4. The experimental percentages are found to be closely matching with the theoretical ones hence validating the stoichiometric formation of the ferrites.

Table 5.4 Theoretical and experimental percentages of nickel, cobalt, zinc and iron present in the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites.

Composition	Ni%		Co%		Fe%		Zn%	
	(theor.)	(expt.)	(theor.)	(expt.)	(theor.)	(expt.)	(theor.)	(expt.)
x= 0.0	12.51	12.54	12.56	12.48	47.63	48.00	-	-
x= 0.1	12.47	12.75	10.02	9.50	47.50	46.25	2.78	2.04
x= 0.2	12.44	11.98	7.79	8.60	47.37	47.28	5.54	5.52
x= 0.3	12.40	13.00	4.98	4.06	47.24	48.12	8.29	8.37
x= 0.4	12.37	12.69	2.48	2.52	47.11	46.51	11.03	10.79
x= 0.5	12.34	12.12	-	-	46.98	47.32	13.75	13.25

5.4.2 Structural characterization of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites by powder XRD studies

The powder XRD pattern of all the synthesized ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites is depicted in Fig.5.4 and it confirmed the formation of cubic spinel structure without any impurity peak. All the peaks obtained are found to be broad and the intensity of this peaks was found to be less. The lattice parameters (a), average crystallite sizes (D), measured density (d_m), theoretical density (d_x) and porosity (P) of all the ferrites were calculated and the data is shown in Table 5.5. It can be seen from the table that the lattice constant was found to increase linearly with an increased Zn content and it varies from

8.3502 Å for Ni-Co ferrite to 8.3769 Å for zinc substituted Ni-Co ferrite. The increase in lattice parameter is ascribed to the change in the ionic sizes of the different cations. When Zn^{+2} is substituted, it prefers the A site and an increase in the lattice parameter is expected as the larger Zn^{+2} (0.74 Å) ions replace the Co^{+2} ions (0.65 Å) [19]. The average crystallite sizes (D) was found to be in the range of 36-48 nm and there was no trend as such followed by the crystallite sizes (Table 5.4).

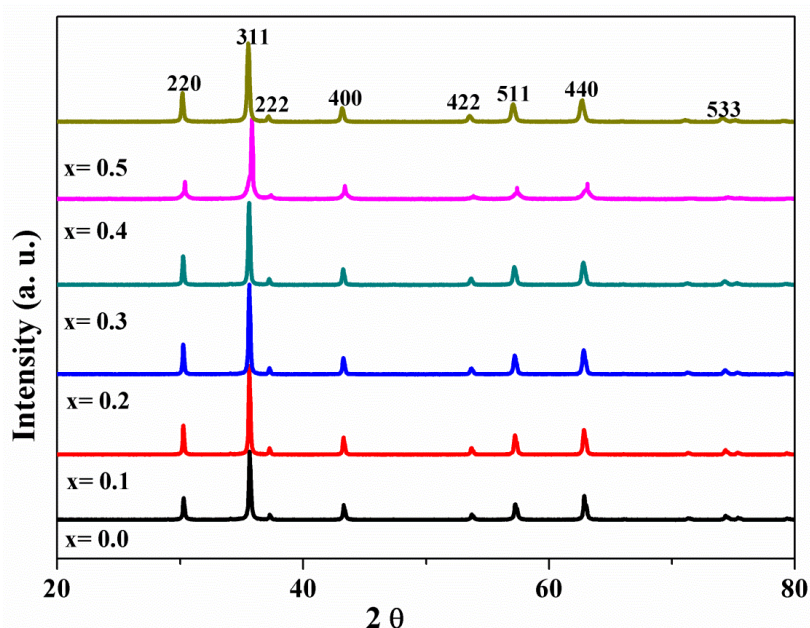


Fig. 5.4 Powder XRD patterns for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

Table 5.5 The lattice parameter (a), measured density (d_m), theoretical density (d_x) porosity (P) and crystallite sizes (D) of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

Composition (x)	Lattice parameter (a) (Å)	Measured density (g/cm^3)	Theoretical density (g/cm^3)	Porosity (%)	Crystallite size (D) (nm)
0.0	8.3502	3.9602	5.3490	25.96	43
0.1	8.3570	3.9044	5.3514	27.03	48
0.2	8.3584	3.8798	5.3636	27.66	45
0.3	8.3622	3.9602	5.3863	26.47	43
0.4	8.3679	4.0655	5.3744	24.35	40
0.5	8.3769	4.6605	5.3715	13.23	36

5.4.3 Infra-red (IR) spectroscopy studies of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites

The characterization of the ‘as prepared’ ferrites was also carried out by employing Infrared studies. The IR spectra of all the $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites, are shown in the Fig. 5.5. The IR spectra of the ‘as prepared’ ferrites were recorded in the range of $4000-350\text{ cm}^{-1}$ and from this Fig.5.5, it can be seen that, it shows two major absorption peaks at around 600 cm^{-1} and around 400 cm^{-1} which are the characteristic feature of all the spinel ferrites. The approximate peak at 600 cm^{-1} i.e. the higher frequency absorption band (ν_1), is because of metal-oxygen stretching vibrations at the tetrahedral sites and the peak at around 400 cm^{-1} i.e. lower frequency band (ν_2), is caused due to metal-oxygen stretching vibrations at the octahedral sites [20-22]. The precise values of both the bands observed in IR spectra are given in Table 5.6.

Table 5.6 The ν_1 and ν_2 values observed in the IR spectra of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites.

	Wavenumbers obtained from IR spectra of ‘as prepared’ ferrites (cm^{-1})	
Composition	ν_1	ν_2
0.0	608	402
0.1	604	405
0.2	601	409
0.3	598	402
0.4	596	409
0.5	593	401

From the IR spectra it is observed that there is a shift in the wavenumber (decrease) from 608 cm^{-1} to 593 cm^{-1} . This is because Ni^{2+} and Co^{2+} are mostly stabilised in octahedral site while Zn^{2+} preferentially occupy the tetrahedral site and the ionic radii of Ni^{2+} and Co^{2+} are smaller than the ionic radii of Zn^{2+} . Thus, there is decrease in wavenumber at the tetrahedral site as the zinc concentration increases [12, 23].

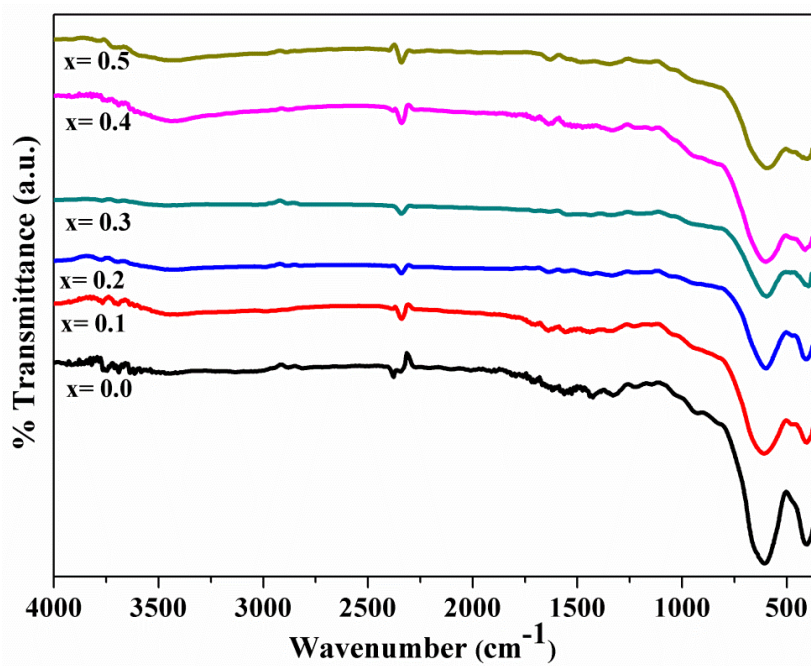


Fig. 5.5 IR spectra of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

5.4.4 Raman spectroscopy of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The characterization of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites was carried out using Raman spectroscopy, since it is sensitive technique towards cation distribution and can reveal the extrinsic iron oxide phase like haematite facilitating in identification of the impurities in the samples. The room temperature Raman spectroscopic analysis of all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites was carried out from 100-800 cm^{-1} and the Raman profiles of the same are depicted in Fig. 5.6 and the corresponding peak values are tabulated in Table 5.7.

According to group theory there are five predicted basic Raman active modes of spinel ferrites viz. ($A_{1g} + E_g + 3 T_{2g}$) that exists in the range from 200-800 cm^{-1} . The symmetrical stretching of metal-oxygen bond at the tetrahedral sites shows the vibrational modes above 600 cm^{-1} while the vibrational modes below 600 cm^{-1} represent the symmetrical and asymmetric bending of metal-oxygen in the octahedral (B) sites [20]. Out of these modes, A_{1g} mode exemplifies the symmetric stretching of oxygen along the M–O bond at the A-site, E_g band is due to symmetric M–O bond bending at the B-site. However, T_{2g} (2) and T_{2g} (3) represent the asymmetric stretching and asymmetric bond bending of M–O bond at

the B-sites, respectively [24]. T_{2g} (1) band represents the translation motion of cations and oxygen tetrahedral.

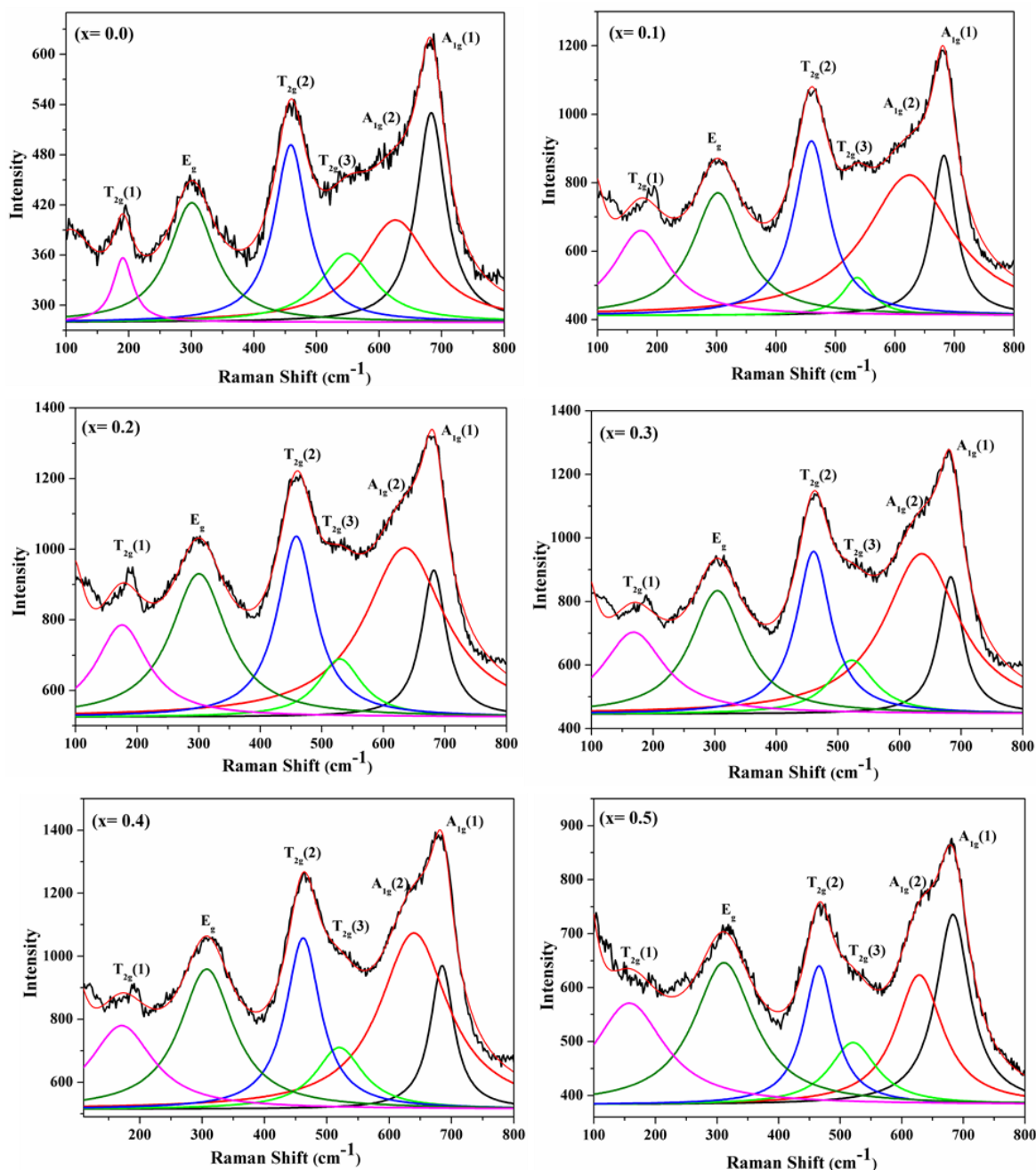


Fig 5.6 The Raman spectra of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

The notable frequency band observed at frequency of around 700 cm^{-1} of A_{1g} is due to symmetric stretching of oxygen atom along metal oxygen bond at the tetrahedral sites. The persistent peaks for all the samples at $\sim 680-730\text{ cm}^{-1}$ belong to the A_{1g} symmetry band. The A_{1g} band of all the ferrite samples has shoulder to its left at around $645-676\text{ cm}^{-1}$ implying the mixed spinel nature of all the ferrites. The respective peaks at approximately

300 cm^{-1} and at around 200 cm^{-1} corresponds to E_g and T_{2g} (3) modes ascribed to symmetric and asymmetric bond bending of metal-oxygen at the octahedral sites [25]. T_{2g} (2) mode appears due to asymmetric metal-oxygen stretching at octahedral site and T_{2g} (1) band is due to translational motion of the cations and oxygen tetrahedral unit.

Besides, there are no sharp spikes at around 240 and 300 cm^{-1} in the Raman spectra which can be due to presence of the impurity phase like $\alpha-Fe_2O_3$. A slight shift in the peaks is seen with increasing zinc concentration. These results validate the formation of monophasic ferrites a non-magnetic and is present in the tetrahedral site of the spinel structure whereas cobalt is the magnetic material and it occupies space in the octahedral site [26]. Also, Fe is present in the octahedral site having magnetic behaviour and which interacts magnetically with cobalt. Because of this, the intermolecular distance between Fe and O atoms increases and the bonding energy between them decreases which results in a shift towards higher side of the Raman frequency [12].

Table 5.7 The Raman shifts observed for the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x= 0.0-0.5$) ferrites.

Composition	A_{1g} (1) cm^{-1}	A_{1g} (2) cm^{-1}	T_{2g} (3) cm^{-1}	T_{2g} (2) cm^{-1}	E_g cm^{-1}	T_{2g} (1) cm^{-1}
x= 0.0	682	645	572	460	304	192
x= 0.1	723	652	574	508	344	240
x= 0.2	724	663	576	512	349	241
x= 0.3	725	667	578	514	354	240
x= 0.4	728	669	579	515	362	243
x= 0.5	730	673	583	521	365	246

5.4.5 X-Ray phototelectron spectroscopy (XPS) studies of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites

The XPS technique was used to validate the oxidation states elements present in ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x= 0.0-0.5$) ferrites. XPS PEAK 41 software was employed to plot the deconvoluted core level XPS spectra for all the elements viz. Ni 2p, Co 2p, Fe 2p, Zn 2p and O 1s for all the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x= 0.0-0.5$) ferrites. The entire spectral range was calibrated for charge correction for C 1s peak at the fixed value of 284.8 eV. The deconvoluted core level spectra of the respective elements

for all the ferrites are shown in Fig. 5.7 ($x = 0.0$), Fig. 5.8 ($x = 0.1$), Fig. 5.9 ($x = 0.2$), Fig. 5.10 ($x = 0.3$), Fig. 5.11 ($x = 0.4$) and Fig. 5.12 ($x = 0.5$). The XPS spectra (full scan) for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites has been shown in Fig. 5.13 and the binding energy values of all the elements are given in the Table 5.8.

In all the ferrite samples, the binding energy peak for cobalt is observed at ~ 795 eV and ~ 780 eV which are allocated for the Co $2p_{1/2}$ and Co $2p_{3/2}$, respectively. Besides, the binding energies at 786 eV and at around 802 eV affirms that cobalt exists in +2 oxidation state [26]. The peak observed at binding energy of approximately 855 eV is corresponding to Ni $2p_{3/2}$ whereas peak at around 872 eV is due to Ni $2p_{1/2}$ [27]. The respective satellite peaks are observed at around 861 eV and 880 eV for Ni $2p_{3/2}$ and Ni $2p_{1/2}$ respectively, confirming that nickel is present in divalent oxidation state [2, 28]. The formation of NiO is ruled out since there is no satellite peak with the main peak which would have been at the value of 1.2 eV from the main peak [29]. The exact values of the binding energies for Ni^{2+} and Co^{2+} have been shown in Table 5.8.

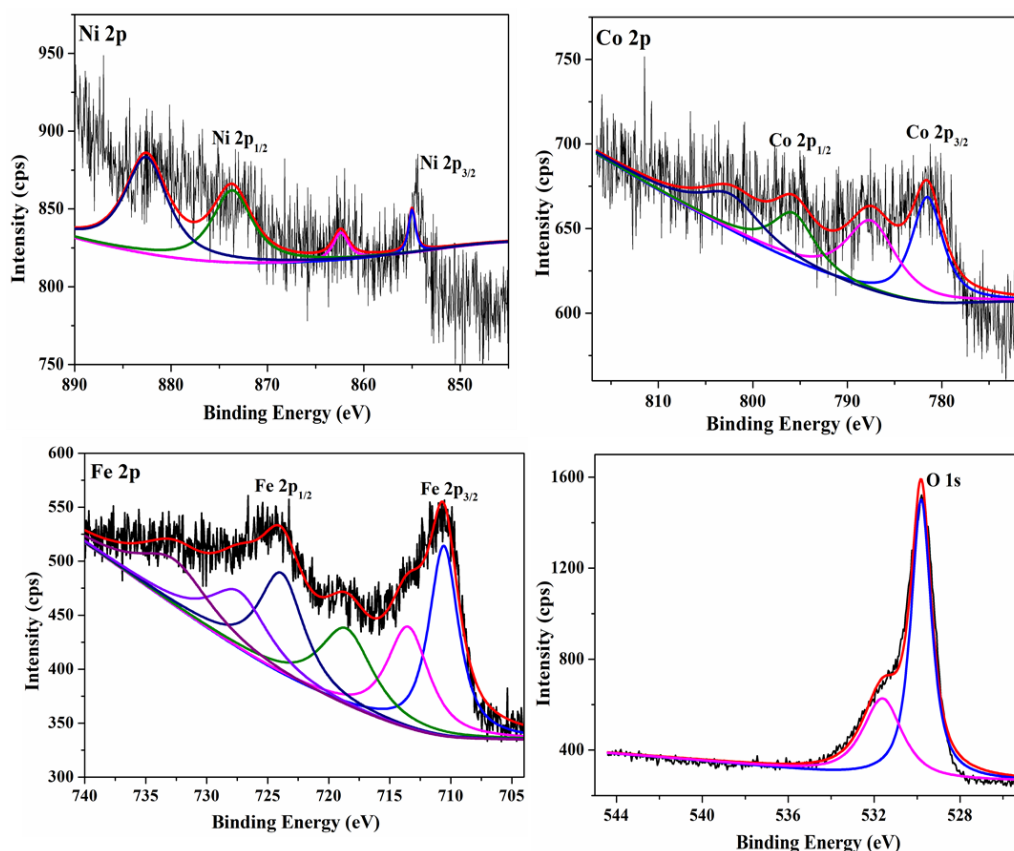


Fig. 5.7 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p and O 1s of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0$) ferrites.

The deconvoluted XPS spectra of Zn shows the binding energies of roughly 1021 eV for $\text{Zn } 2p_{3/2}$ and 1044 eV for $\text{Zn } 2p_{1/2}$ for the ferrite samples thus affirming that zinc is present in the divalent state and which dwells in the tetrahedral sites [30-31]. The binding energy of the oxygen species equivalent to around 529 eV is due to O 1s and is attributed to the contribution of lattice oxygen, while the peak at a little higher energy (~ 531 eV) is due to lower coordinated lattice oxygen suggestive of the structural defects in all the ferrite samples [27, 32-34].

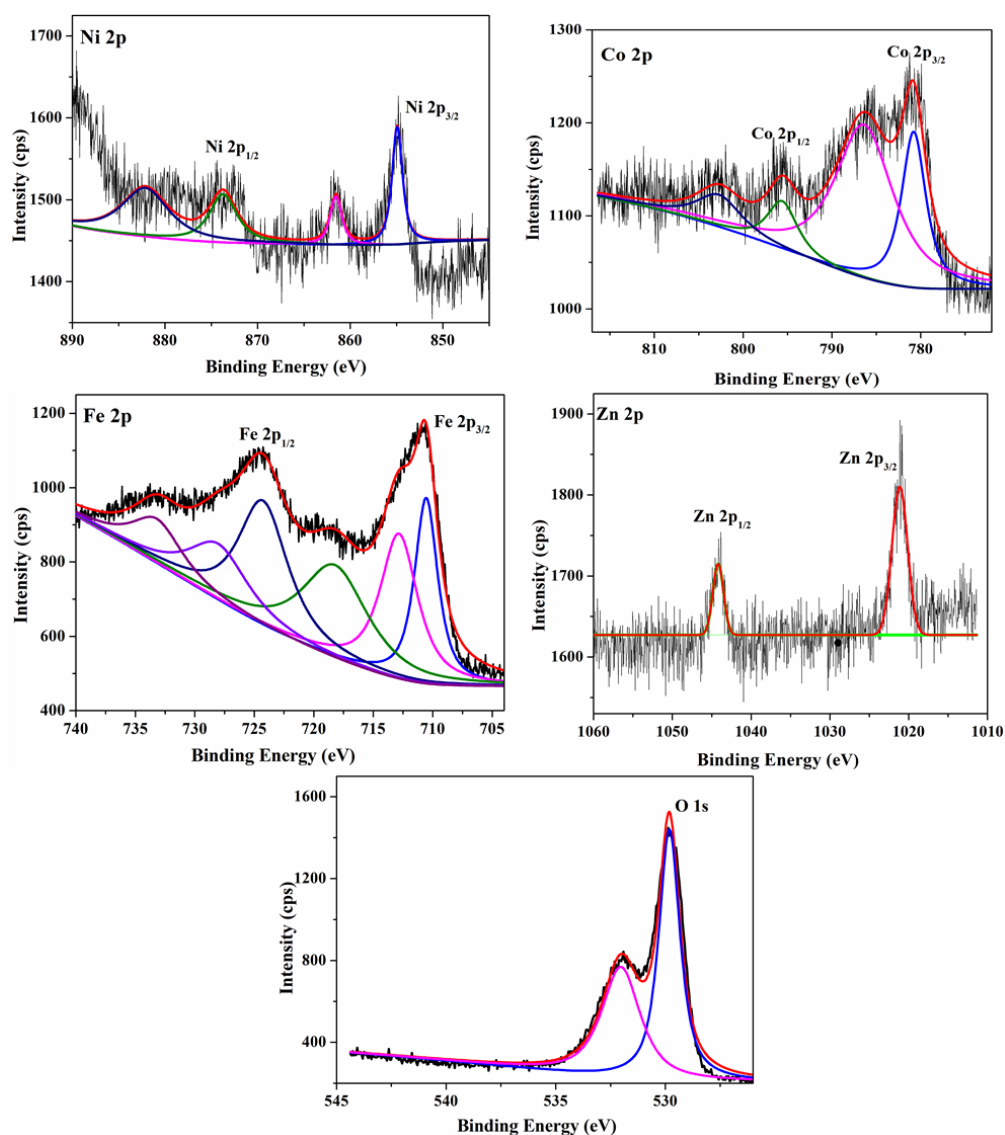


Fig. 5.8 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p, Zn 2p and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.1$) ferrites.

The deconvoluted spectra of Fe 2p spectra has been plotted for all the 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite samples. It can be seen from the figures, that the peak at ~ 724 eV is ascribed to Fe $2p_{1/2}$ and the peak at roughly 710 eV can be attributed to Fe $2p_{3/2}$ [35-37]. The main peak Fe $2p_{1/2}$ is having a satellite peak at around 718 eV which is ~ 8 eV more than the main peak which is a typical for Fe^{3+} thus validating that Fe is in trivalent oxidation state [38-40]. The Fe $2p_{3/2}$ has a split; one at 710 eV which is due to presence of Fe^{3+} in the octahedral sites and the peak roughly at 713 eV corresponding to Fe^{3+} cations at the tetrahedral sites [41]. In the same way, the Fe $2p_{1/2}$ also undergoes splitting; the peak ~ 728 eV is due to Fe^{3+} at the tetrahedral sites and the peak ~ 724 eV corresponds to Fe^{3+} cations at the octahedral sites [42]. The absence of any peak at ~ 716 eV confirms that there is no impurity of Fe^{2+} present in the compounds [43].

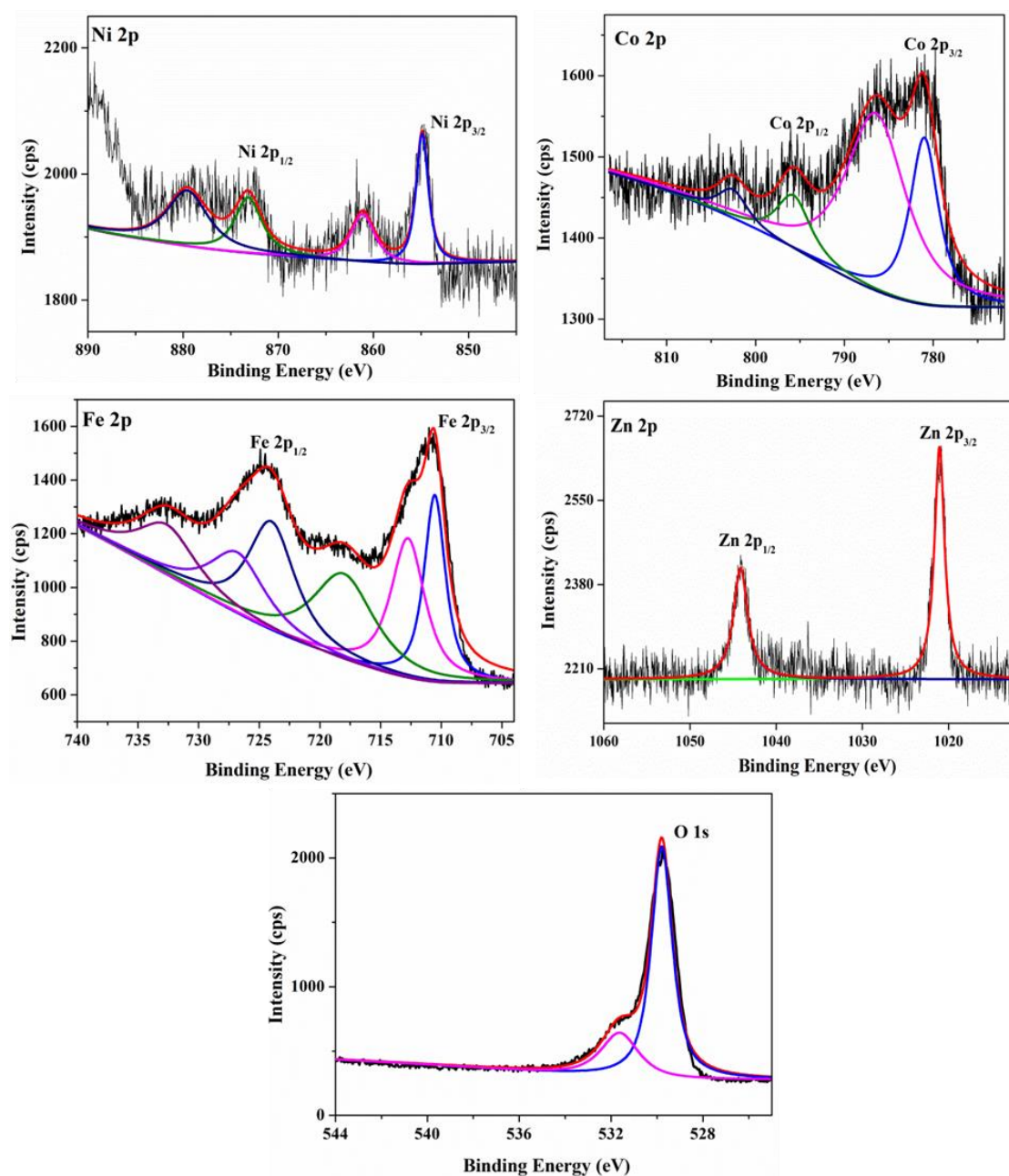


Fig. 5.9 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p, Zn 2p and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.2$) ferrites.

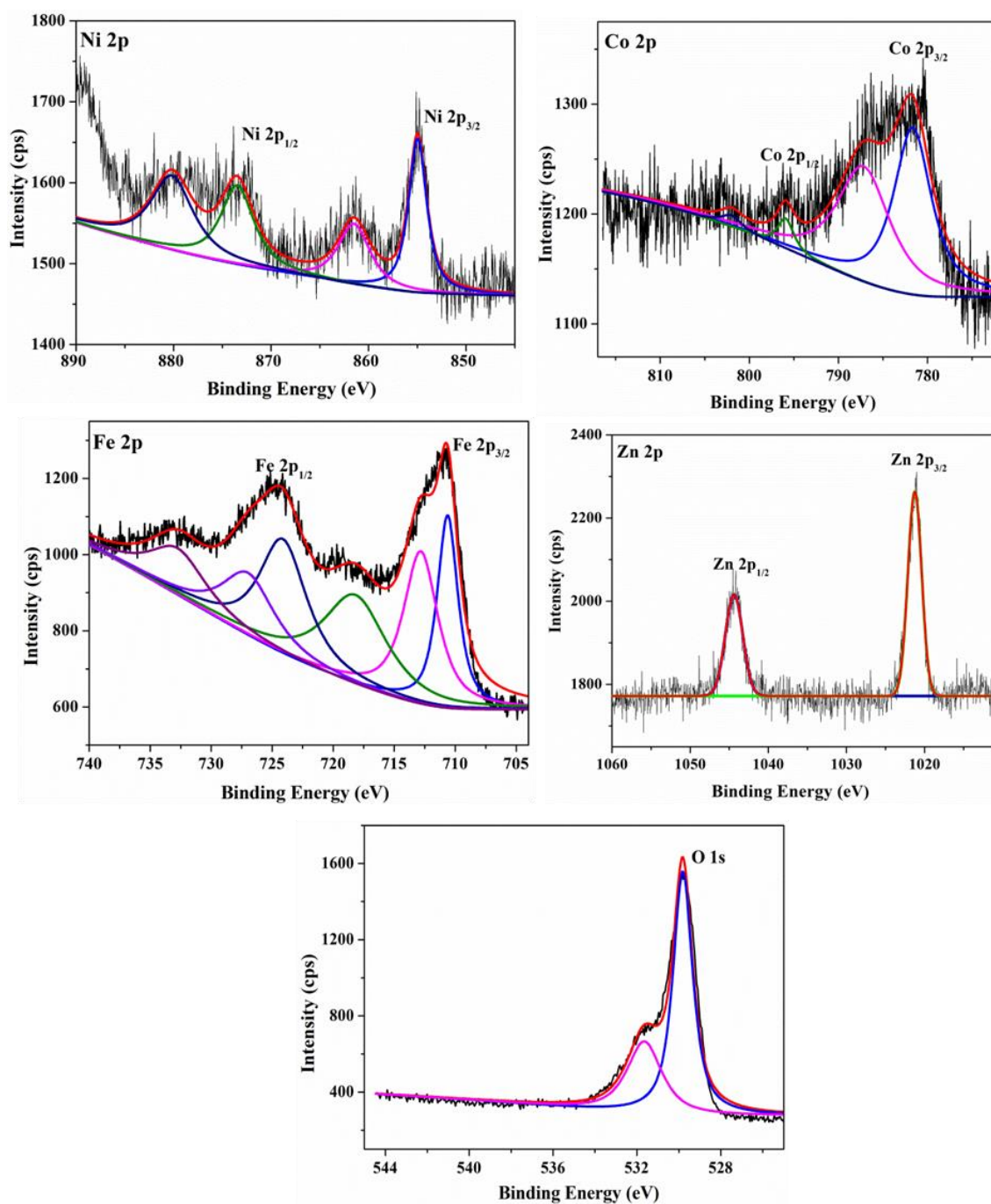


Fig. 5.10 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p, Zn 2p and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3$) ferrites.

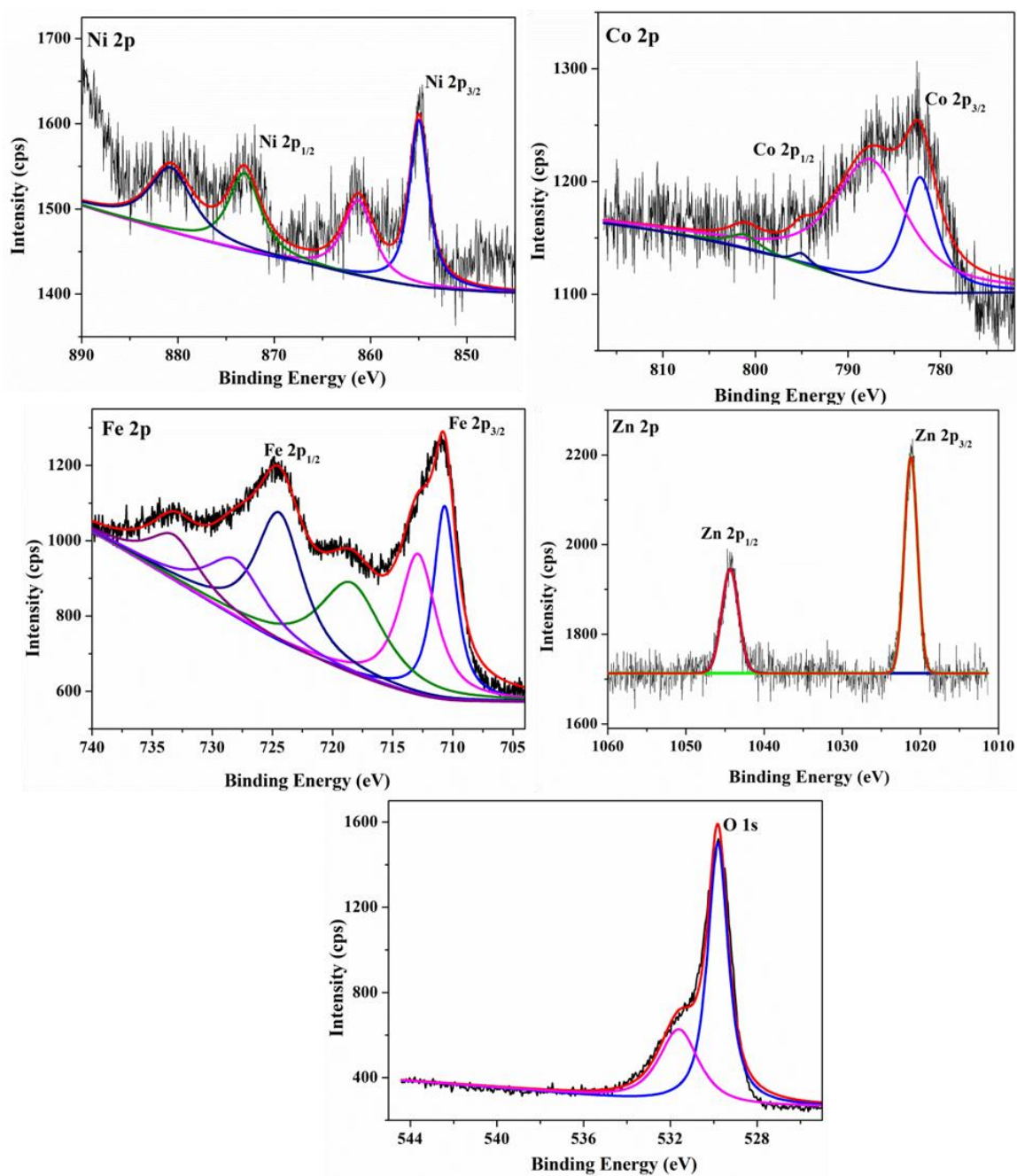


Fig. 5.11 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Co 2p, Fe 2p, Zn 2p and O 1s of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.4$) ferrites.

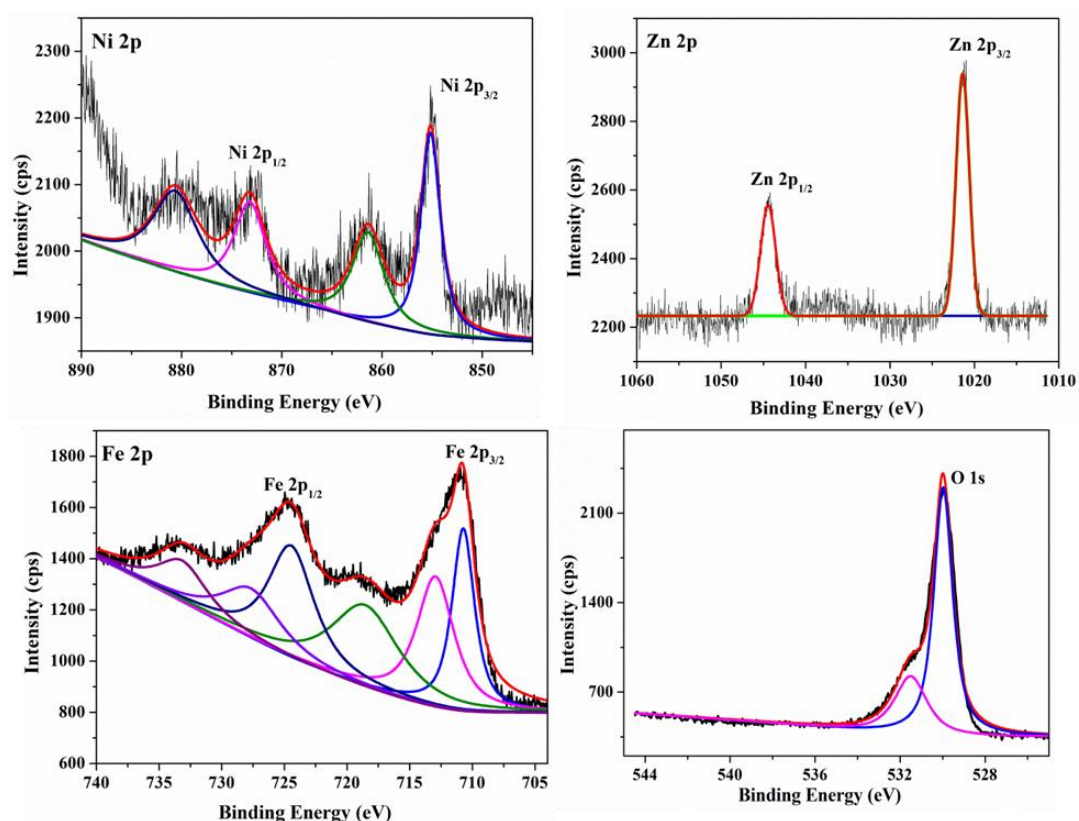


Fig. 5.12 High resolution deconvoluted XPS spectra corresponding to Ni 2p, Fe 2p, Zn 2p and O 1s of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5$) ferrites.

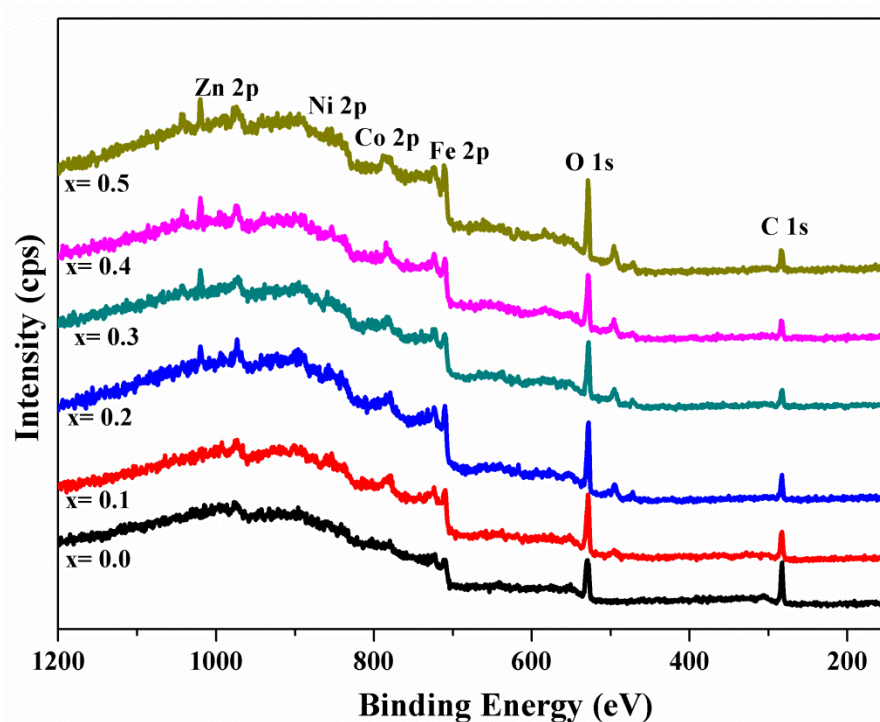


Fig. 5.13 The full scan XPS spectra of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Table 5.8 The binding energies of all the elements determined from deconvolution of XPS peaks of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Compositions (x) (Binding energies)	0.0	0.1	0.2	0.3	0.4	0.5
Ni 2p _{3/2}	855.1	854.8	854.7	855.3	855.2	854.9
Satellite	861.3	861.5	860.9	861.4	861.2	861.1
Ni 2p _{1/2}	872.1	872.3	871.9	872.7	872.6	872.5
Satellite	880.5	880.2	879.9	880.5	879.6	880.0
Co 2p _{3/2}	780.6	780.9	780.3	780.5	780.6	-
Satellite	785.8	786.1	785.9	786.2	786.3	-
Co 2p _{1/2}	795.7	795.9	796.1	795.9	795.7	-
Satellite	803.1	802.8	802.8	802.9	803.3	-
Fe 2p _{3/2} (oct)	710.6	710.5	710.3	710.5	710.4	710.3
Fe 2p _{3/2} (tetra)	713.1	713.0	712.8	713.0	712.7	712.9
Satellite	718.4	718.1	717.9	718.2	718.0	717.9
Fe 2p _{1/2} (oct)	724.4	724.7	724.8	724.6	724.5	724.7
Fe 2p _{1/2} (tetra)	726.8	726.2	726.5	726.9	726.4	726.6
Satellite	732.4	732.6	732.3	732.7	732.6	732.4
O 1s (lattice)	529.7	529.6	529.8	529.8	529.7	529.7
O 1s (surface)	531.3	531.1	531.2	531.4	531.4	531.3
Zn 2p _{3/2}	-	1021.3	1021.2	1021.5	1021.6	1021.4
Zn 2p _{1/2}	-	1044.3	1044.1	1044.2	1044.1	1044.3

5.4.6 Surface area characterization of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites

5.4.6.1 Brunauer-Emmett-Teller (BET) surface area measurements of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

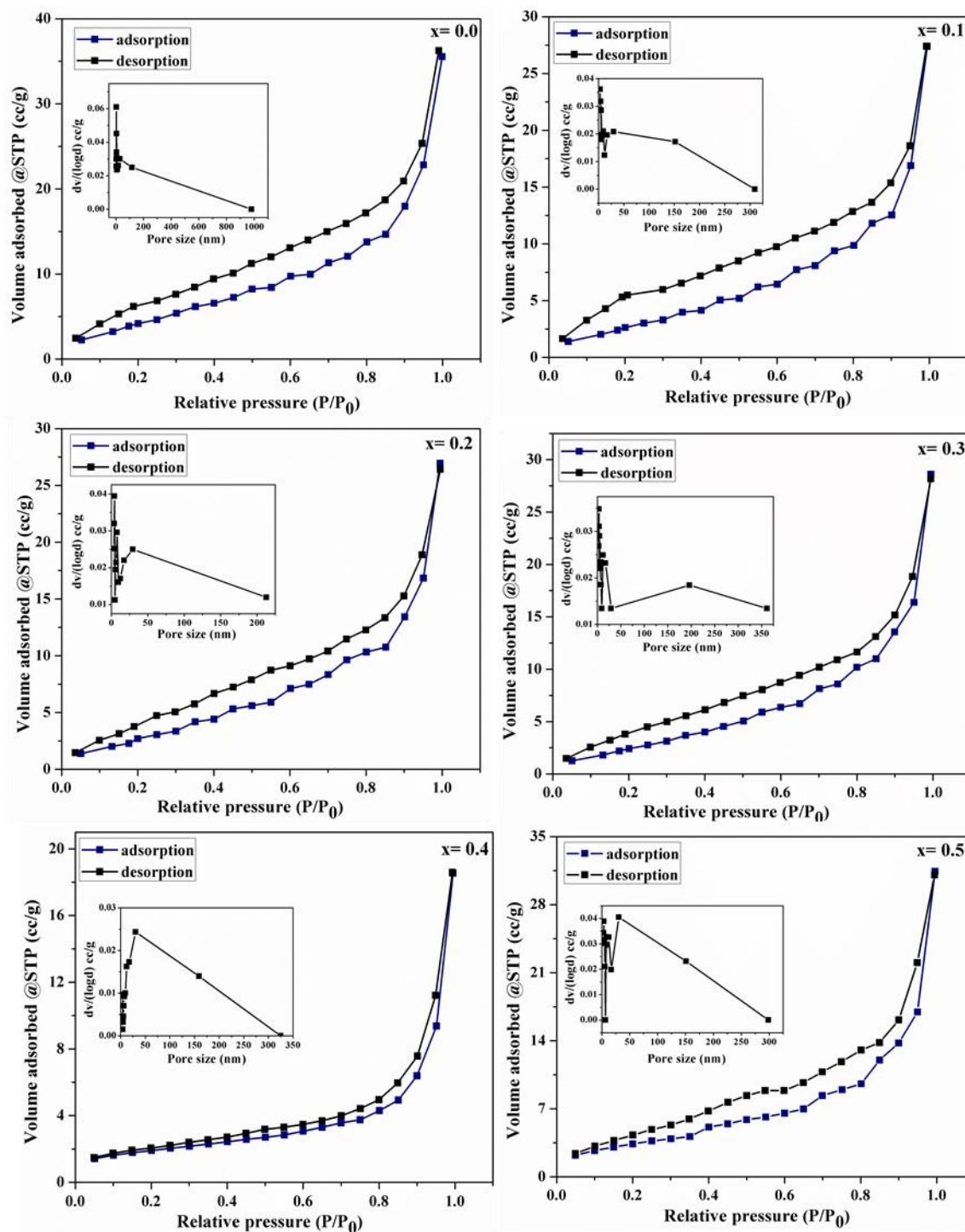


Fig. 5.14 The N₂ adsorption-desorption isotherms of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites [Inset figure: plot of $[dV/d(\log d)]$ cc/g against pore size (nm)].

The ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were also tested for the surface area studies using the 20-point BET measurements. The N_2 -adsorption desorption isotherms for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites are given in Fig. 5.14. From the isotherms the surface area, average pore sizes, total pore volume of all the samples were derived. Larger the surface area more is the surface to volume ratio and thus better is the use of the nanomaterials in various applications. The surface area studies thus help in correlating various applications of the nanomaterials such as gas sensing, catalysis and many more [44]. The precise values of the surface area, total pore volume and average pore sizes are given in Table. 5.9.

Table 5.9 BET surface area, average pore sizes and the pore volumes of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	BET surface area (m^2/g) $\pm 1 \text{ m}^2/\text{g}$	Average pore size (nm)	Total pore volume (cc/g)
0.0	18.32	28.56	0.055
0.1	11.48	20.63	0.042
0.2	11.76	18.77	0.040
0.3	10.98	19.25	0.044
0.4	7.00	13.63	0.028
0.5	12.07	25.69	0.053

Using the IUPAC nomenclature and observing the isotherms, the isotherms obtained for our ferrite samples can be categorized as type IV isotherms having H3 type hysteresis loop confirming mesoporous types of nanoparticles [44-45]. The highest surface area was found to be for the composition $x = 0.0$ ($18.32 \pm 1 \text{ m}^2/\text{g}$). For this series of ferrites, the surface area was found to be in the range of $7.0-18.32 \pm 1 \text{ m}^2/\text{g}$. However, there is no particular trend observed with increase in zinc concentration. The average pore size values were found to be in the range from 13.63 to 28.56 nm.

5.4.6.2 Study of acid base properties by temperature programmed desorption (NH_3 -TPD) and (CO_2 -TPD) of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

NH_3 -temperature programmed desorption studies (NH_3 -TPD) were carried out to determine the surface acidity of all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites and the plots of the same are depicted in Fig. 5.15.

Three distinct peaks are seen in the NH_3 desorption profile indicating the evolution of NH_3 at three different temperature zones. For all ferrite samples, initially a peak is observed at approximately 107-131 °C. This can be attributed to the weakly adsorbed ammonia that needs less energy for desorption from the ferrite surface. The second peak (hump) seen at $\sim 382-425$ °C is ascribed to presence of medium acidic sites in all the samples. The composition $x = 0.1$ and $x = 0.5$ have two small humps for the medium acidic sites at ~ 500 °C and ~ 491 °C, respectively. The final notable peak for all the ferrite samples at high temperatures ranging between ~ 593 °C and ~ 694 °C is due to the presence of strong acidic sites which needs more energy to desorb from the ferrite surface [46-47]. The weak acidic (Bronsted) sites are observed at a lower temperature of NH_3 desorption in contrast to the strong acidic (Lewis) sites which are observed at a higher desorbing temperature [48-50].

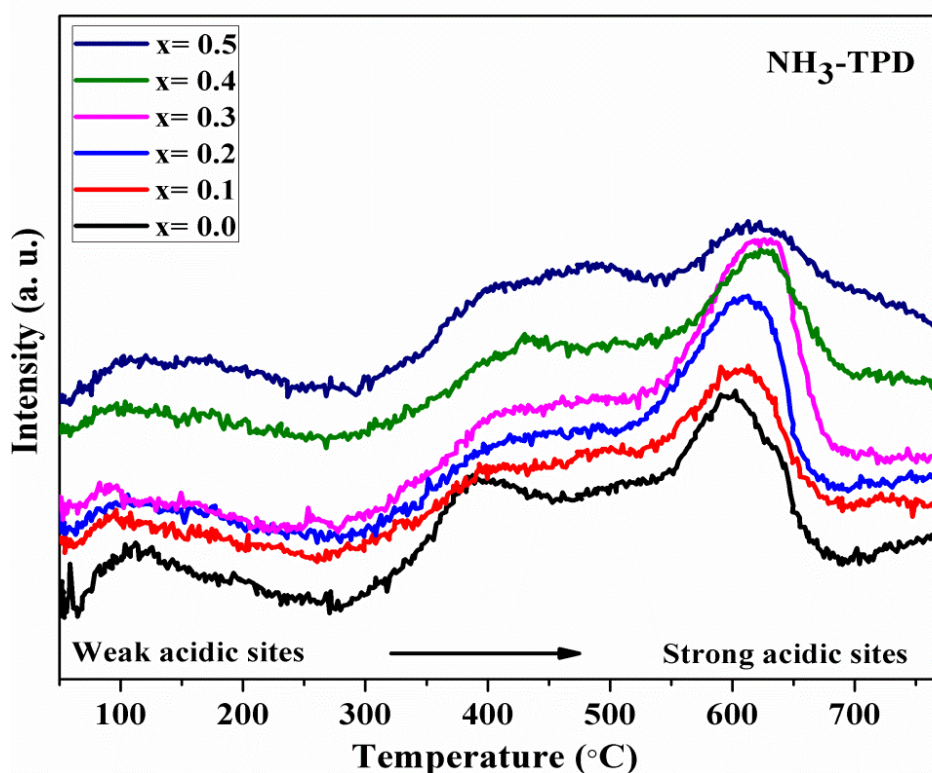


Fig. 5.15 NH_3 -temperature programmed desorption profiles of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

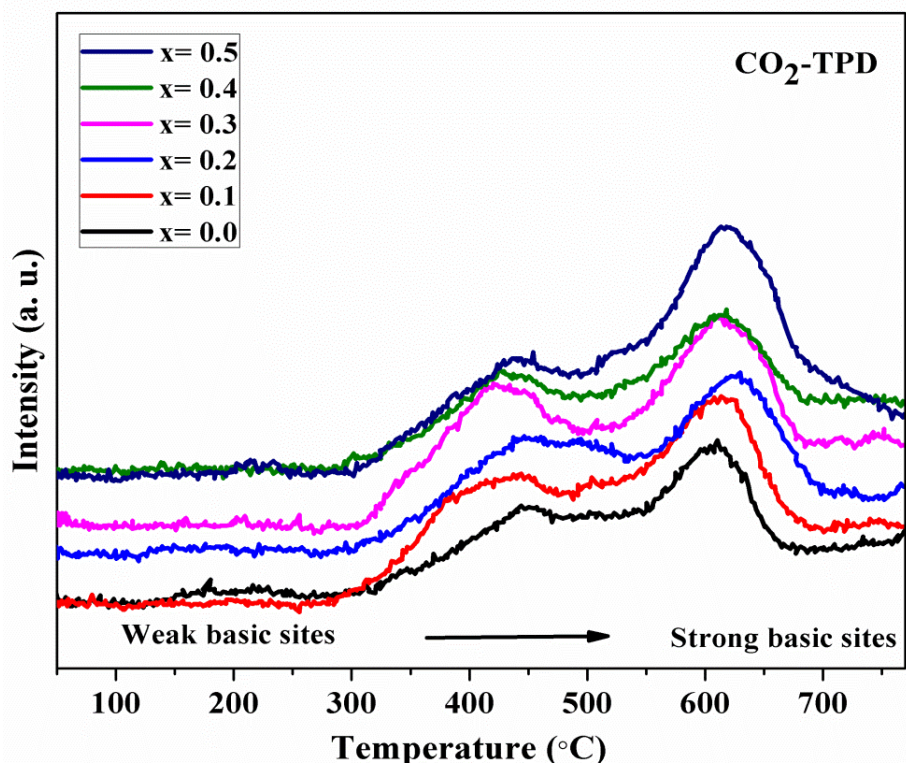


Fig. 5.16 CO_2 -temperature programmed desorption profiles of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

CO_2 temperature programmed desorption (CO_2 -TPD) studies were carried out of all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites to find out the surface basicity and the CO_2 desorption profiles of the same are shown in Fig. 5.16. Two main peaks are observed in this case which attributes to the occurrence of medium and strong basic sites. The first peak in case of all the ferrite samples observed at $\sim 437-447$ °C is attributed to medium basic sites. Besides, the obvious peak at a desorbing higher temperature $\sim 608-620$ °C is as a result of strong basic sites in the ferrite nanoparticles [51-52].

NH_3/CO_2 -TPD studies confirmed that all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites samples have weak, medium and strong acidic sites and medium and strong basic sites.

5.4.7 Morphological studies of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.4.7.1 Scanning Electron microscopy (SEM) studies of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The morphology of the 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites was investigated by SEM analysis. The SEM micrographs of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites have been shown in the Fig. 5.17 and Fig 5.18. The morphology obtained was very similar for all the ferrite samples i.e. the particles are somewhat spherical in shape and nanosized with agglomeration.

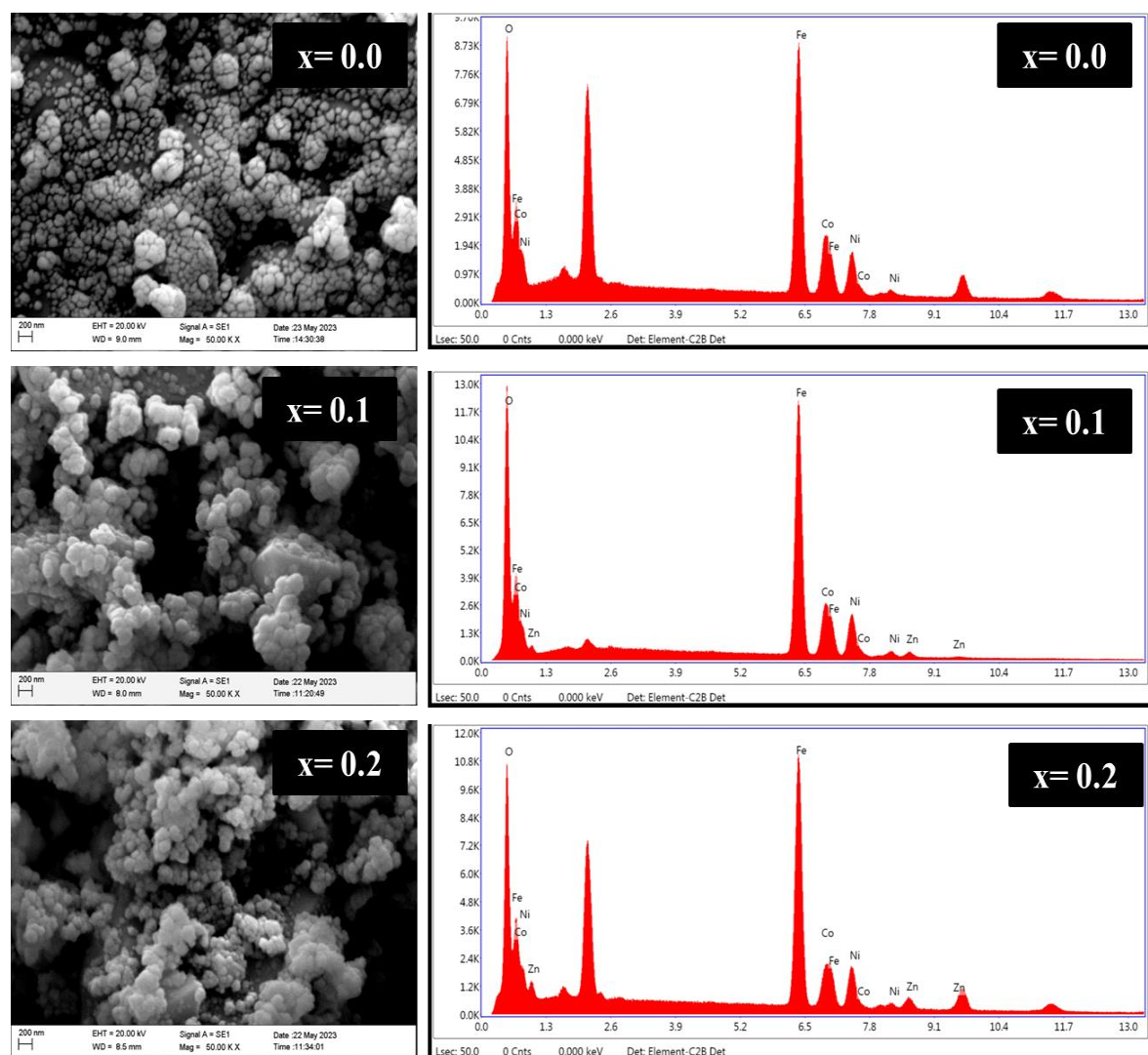


Fig. 5.17 The SEM micrograph and EDAX spectrum of 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.2$) ferrites.

All the nanoparticles were found to be homogenous and uniformly distributed with fine agglomerates of uneven sizes. The agglomeration in these nanomaterials is as a result of strong magnetism in the nanoparticles as well as their high surface area [26]. The EDX images of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites is depicted in Fig. 5.17 and 5.18. The presence of the corresponding metal ions on the surface of the ferrites is also confirmed by the EDX spectra. There is absence of any impurity element peak. The decrease in the intensity of the cobalt peak and an increase in the intensity of the zinc element peak are apparently observed with increasing zinc content. The remaining unmarked peaks in the EDAX spectra are basically due to the sputtering of the noble metal Au during sample preparation.

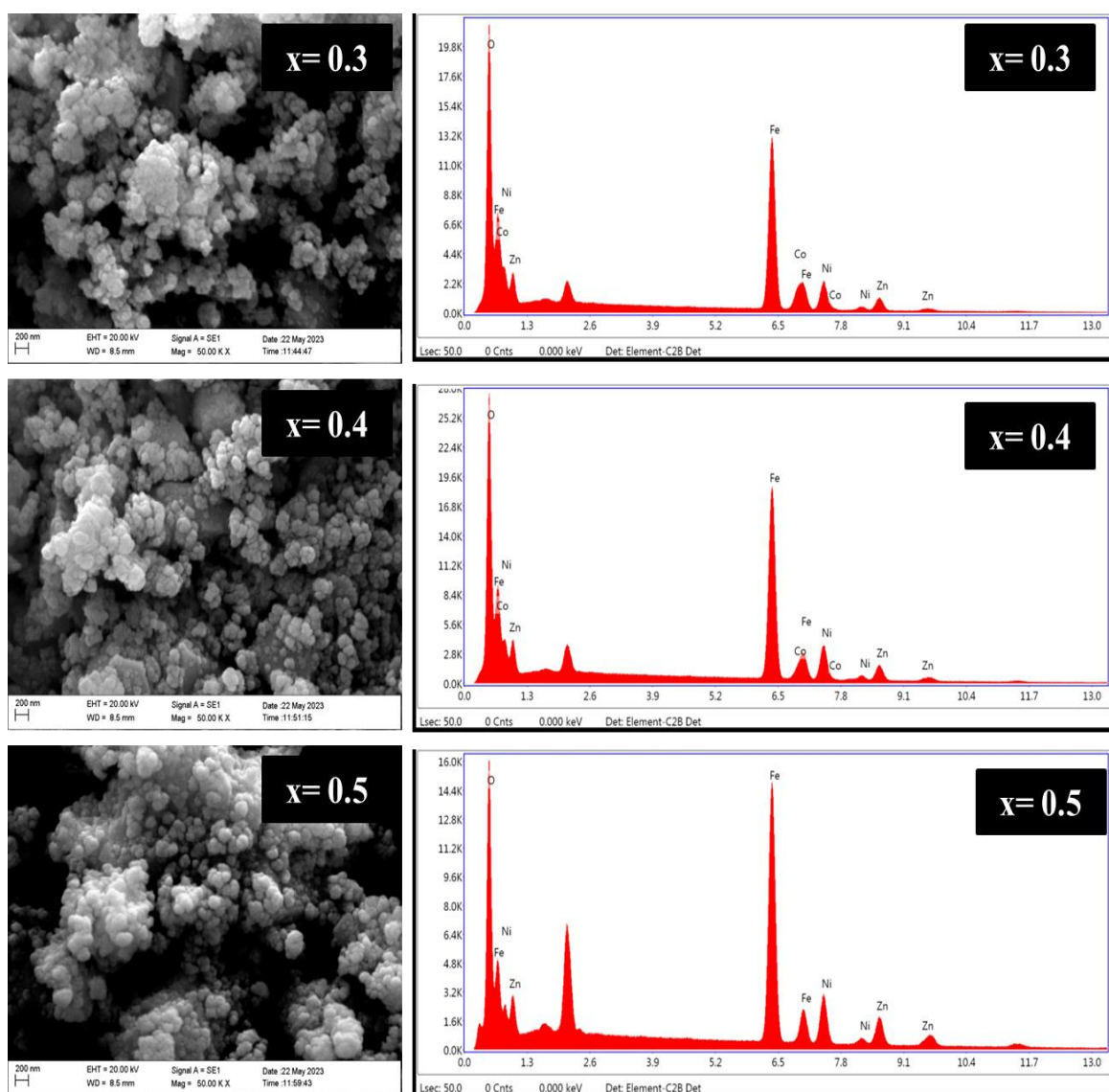


Fig. 5.18 The SEM micrograph and EDAX spectrum of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3-0.5$) ferrites.

5.4.7.2 High Resolution Transmission Electron microscopy (HR-TEM) studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The HR-TEM micrographs reveal nearly cuboidal shaped particles with varying particle sizes ranging roughly from around 30-45 nm which are in good agreement with the powder XRD measurements. The ferrites show relatively uniform size distribution and considerable amount of agglomeration which is arising due to magnetic interactions between the nanoparticles. The HR-TEM images of all the as prepared $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite samples along with their SAED patterns are displayed in the Fig. 5.19. The nanoparticles are larger with irregularity in the shapes and sizes of the particles [53].

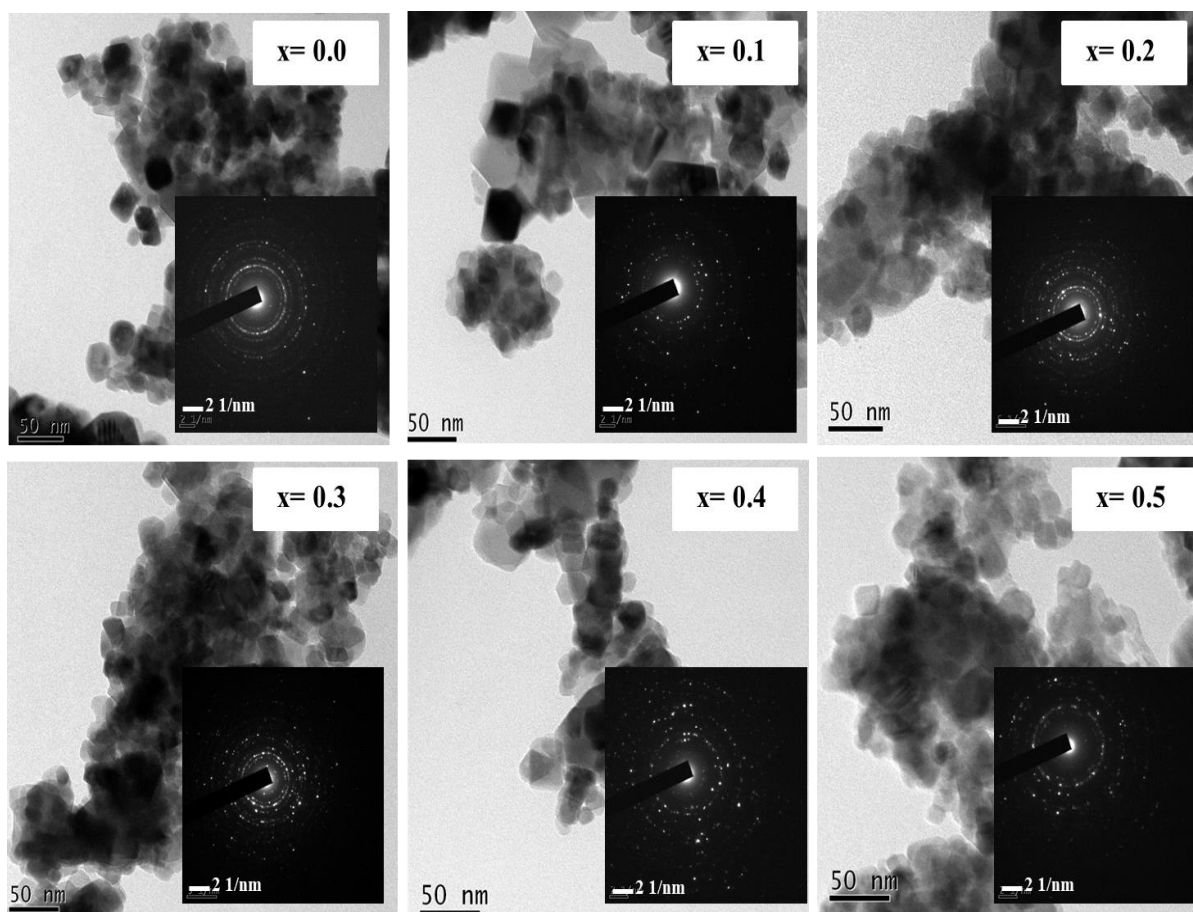


Fig. 5.19 The HR-TEM micrographs and SAED pattern of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Besides, all the ferrite samples display concentric SAED pattern having rings which are indexed for all the peaks mentioned in the powder XRD diffraction patterns. The brightest

spot in the SAED pattern was for the highest intensity (3 1 1) peak, hence proving the nano crystallinity in the nanoparticles [54].

5.5 Solid state studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.5.1 Dielectric properties of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.5.1.1 Dielectric measurements as a function of frequency for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The variation of the dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites as a function of frequency at room temperature is shown in Fig. 5.20a and Fig 5.20b, respectively. The measurements were performed at the frequency range from 20 Hz to 10 MHz. Fig. 5.20c depicts the plot of dielectric properties against compositions.

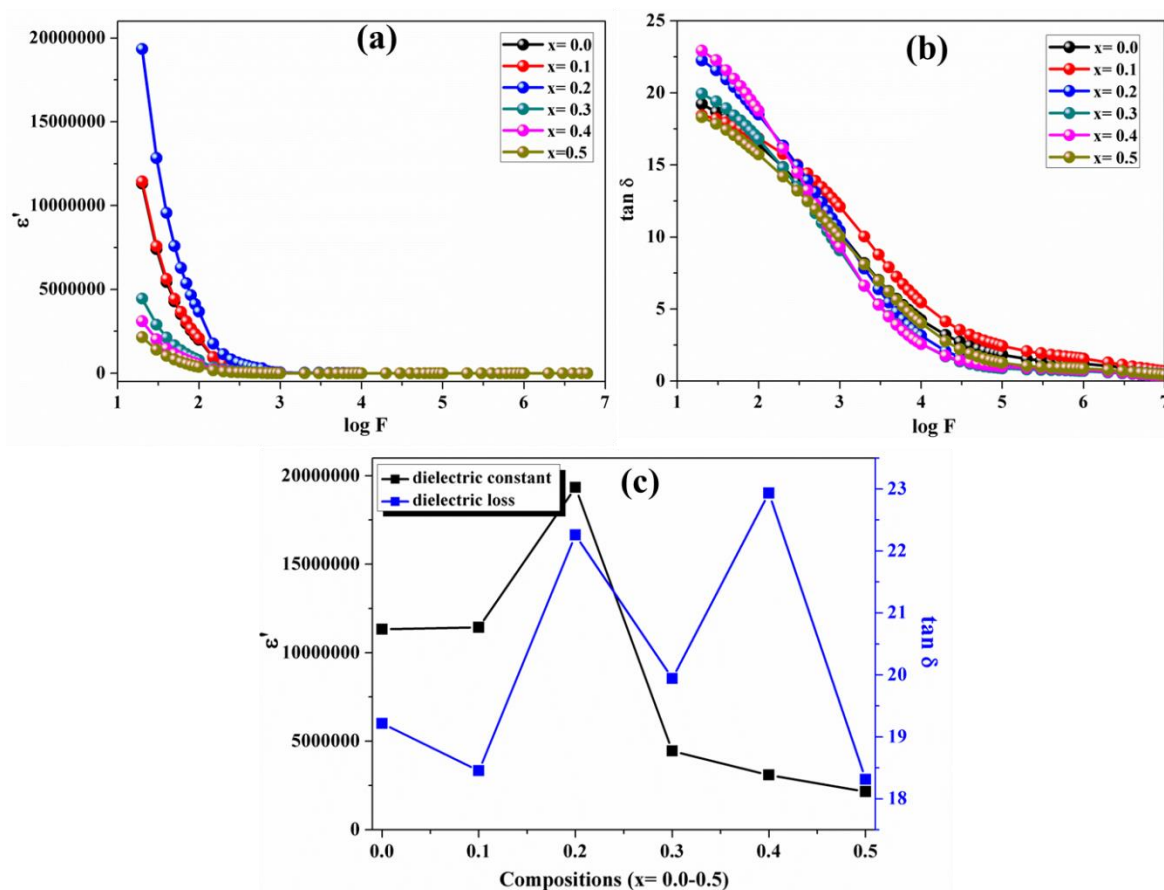


Fig. 5.20 The plots of (a) Dielectric constant against log frequency (b) dielectric loss tangent ($\tan \delta$) against log frequency (c) Plot of dielectric constant and loss tangent as a function of composition at 20 Hz for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

All the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite samples show a substantial decrease in the dielectric constant with increase in frequency. However, this fall in the dielectric constant is quite rapid at lower frequencies till around 1 KHz indicating dispersion in the low frequency regions and later it is constant at higher frequencies. This decrease occurs because the jumping of frequency of the electric charge carriers is unable to chase the variation of applied electric field over a particular frequency. In ferrites specifically, the dielectric dispersion is justified based on the space charge polarization which is due to the presence of grains (higher conductivity phases) in the grain boundaries (insulation of matter or poorly conducting) of a dielectric material which causes a localized accumulation of charges in the applied electric field. All the ferrite samples exhibit dispersion mainly because of the Maxwell Wagner type interfacial polarization which is in agreement with the Koop’s phenomenological theory. At lower frequencies the greater values of the dielectric constant are ascribed to the four types of polarizations effects such as the electronic, ionic, dipolar and space charge [55-56]. The electrons from the ferrites are the main charge carriers and the electron hopping occur between Fe^{2+} and Fe^{3+} ions which are available at the crystallographic equivalent sites, viz. octahedral sites by charge transfer hopping mechanism. But at higher frequencies the hopping of electrons does not follow the fluctuations of the electric field thus leading to a decrease in the dielectric constant as shown in Fig 5.20a [57-58]. The dielectric constant decreased with increase in zinc concentration and the sample $x = 0.0$ shows the highest value of dielectric constant

Fig 5.21b demonstrates the variation of the room temperature dielectric loss tangent ($\tan \delta$) against frequency plots for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite samples. In all the cases, a decrease in the dielectric loss tangent is observed with an increase in frequency. Initially these values decreases promptly and at a later stage at higher frequencies they almost remain constant. Rezlescu and Iwauchi [59-60] have discussed the strong correlation between the resistivity, conduction mechanism and the dielectric properties [58]. They explained an electronic exchange hopping of Fe^{2+} and Fe^{3+} resulting in the local charge displacement that is accountable for polarization and this magnitude of this exchange is strongly dependent on Fe^{2+} and Fe^{3+} ions at the octahedral sites [61]. Kambale et al. [62] also examined nickel substituted cobalt ferrites and explained the variation in the dielectric properties based on $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ (n-type) and existence of $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ type (p-type) conduction mechanism. If the hopping

frequency of the charge carrier is approximately equal to the external applied electric field, maximum values of the loss tangent are observed in all the samples [63]. As observed for the dielectric constant, dielectric loss tangent also decreased with increasing zinc substitution.

5.5.1.2 Dielectric measurements as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The variation of the dielectric constant as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites has been carried out at constant frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C and the plots of the same are represented in Fig. 5.21. When the dielectric measurements are performed as a function of temperature, the increase in the dielectric constant is ascribed to the rise in the charge carrier mobility which is thermally activated [63].

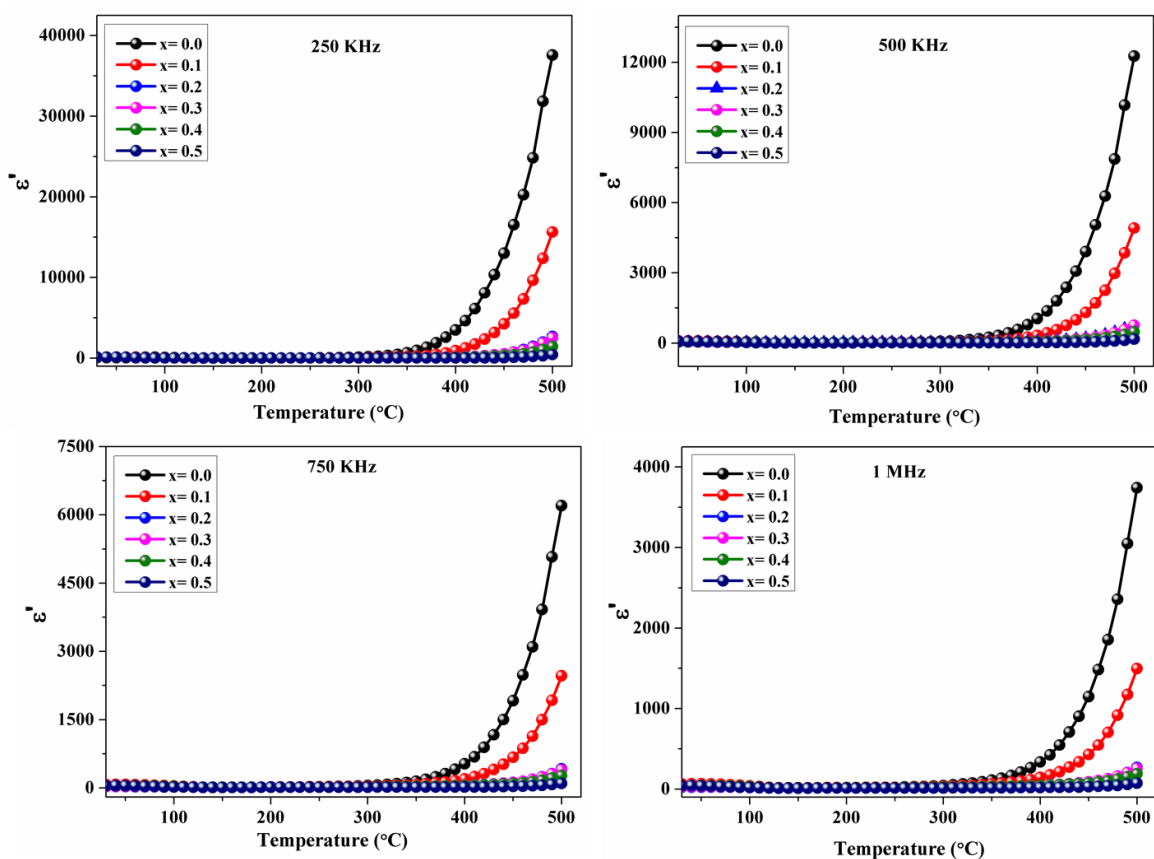


Fig. 5.21 The plots representing variation of dielectric constant as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz).

In this case the increase in the dielectric constant with increasing temperature is attributed to the increase in conductivity by hopping conduction mechanism which occurs due to the thermally activated increase in drift mobility of the charge carriers [64]. Moreover, the dielectric constant almost remains constant up to around 300 °C which further increases with increase in temperature.

For all the ferrite samples it was seen that at lower frequency (250 KHz) the dielectric constant was found to be larger in comparison with the ones at higher frequencies (1MHz) as shown in Fig.5.21. The four types of polarizations are principally responsible (electronic, atomic, dipolar and space charge) for the temperature dependent nature of the dielectric constant [65]. Amongst these, the space charge and dipolar polarizations being strongly temperature dependent play a major role at lower frequencies thus increasing the dielectric constant values with increasing temperature. Contrarily, ionic and electronic polarizations which are both highly temperature and frequency-independent contribute to the lower values of the dielectric constant at higher frequencies [60, 66-67]. The dielectric constant values were found to be highest for the $x = 0.0$ composition as were found to decrease with increase in zinc content. The lowest values for dielectric constant were found to be for $x = 0.5$ composition.

Fig. 5.22 demonstrates the variation of dielectric loss tangent ($\tan \delta$) as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites carried out at constant frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C.

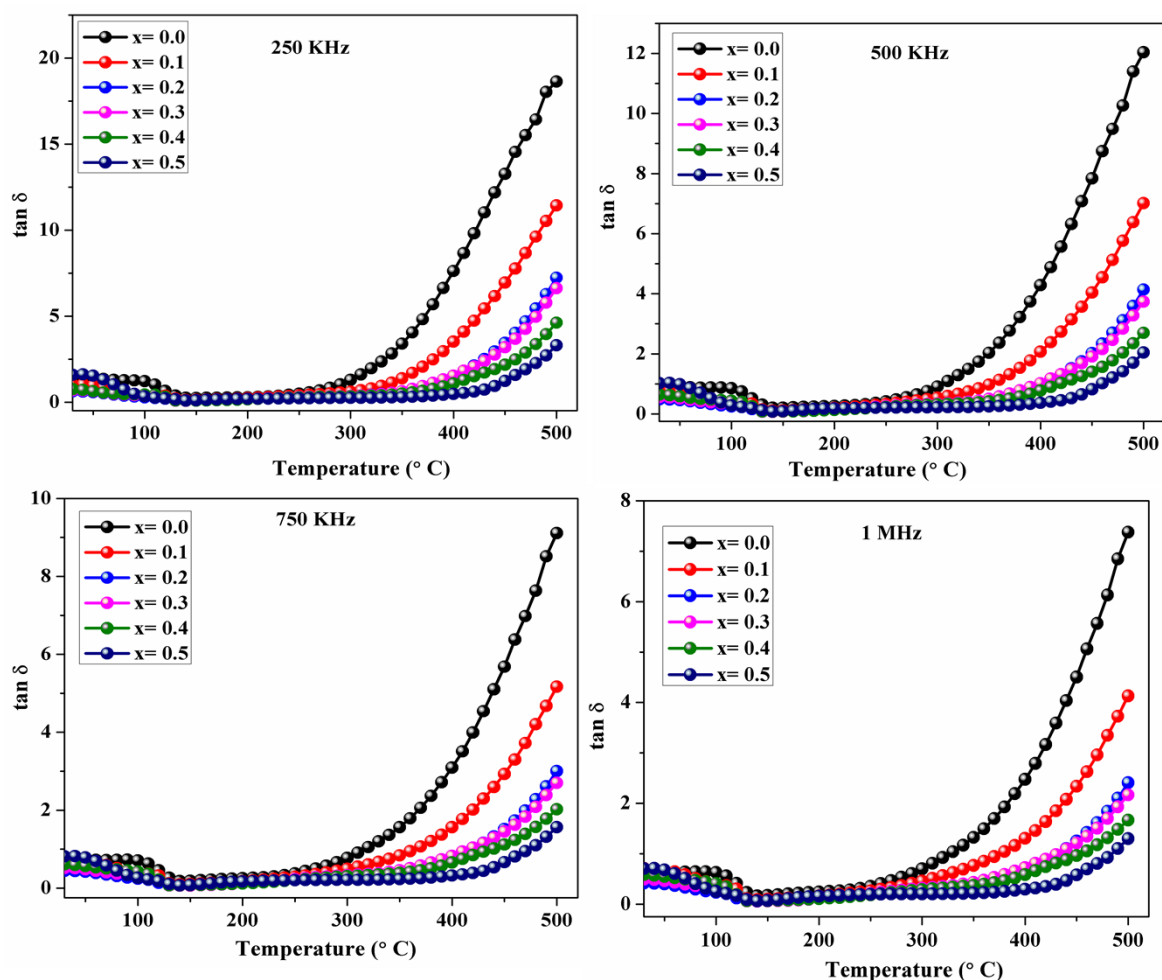


Fig. 5.22 The plots representing variation of dielectric loss tangent as a function of temperature for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz).

A similar phenomenon as that of dielectric constant has been seen in the case of the dielectric loss tangent values with an increase in temperature. The ferrite samples showed greater values of dielectric loss tangent at lower frequency (250 MHz) than at higher frequency (1 MHz). The dielectric loss is very less at higher frequencies because of the conducting behaviour of the grain at high frequency. But, at low frequencies the grain boundaries which have high resistivity indicate that the electrons require more energy and hence the higher dielectric loss [68]. The dielectric loss tangent values were found to be more for the $x = 0.0$ composition and were found to decrease with increase in zinc content ($x = 0.5$).

5.5.2 The magnetization studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.5.2.1 The normalized A.C. susceptibility studies of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

The A.C susceptibility gives knowledge about the different domain states depending upon the nature of the particle size distributions viz. superparamagnetic, single domain and multi domain [69]. Fig. 5.23 depicts the normalized AC susceptibility plots of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite samples and the Curie temperatures of all the ferrite samples obtained are tabulated in Table 5.10.

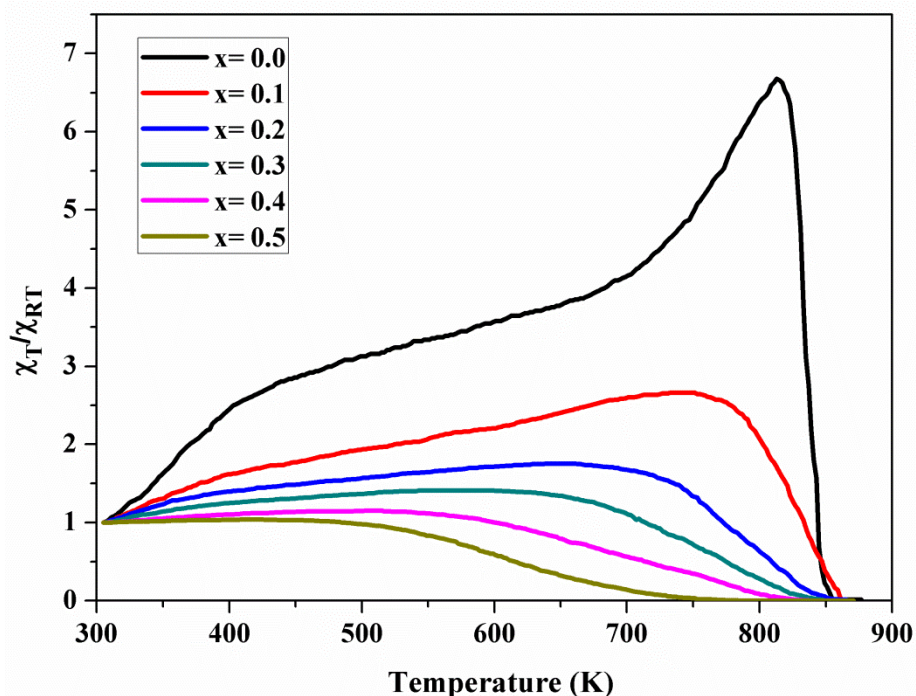


Fig. 5.23 Plots of normalized AC susceptibility against temperature of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) samples.

With increase in zinc concentration, the Curie temperature was found to decrease due to the non-magnetic nature of zinc ions. According to Neel’s theory [70], the Curie temperature depends on super exchange interaction between tetrahedral (A) and octahedral (B) sites metal ions of the ferrimagnetic material [71-72]. The A-B interactions depend on the magnetic ion distribution in octahedral and tetrahedral sites. The magnetic Fe^{3+} ions present in the tetrahedral sites are pushed by non-magnetic Zn^{2+} ions from tetrahedral to octahedral sites hence reducing the A-B interactions thus causing a decrease in the Curie

temperature [73-74]. The broadness in the peaks for all the samples can be attributed to the wide particle size distributions (confirmed by SEM and HR-TEM) and presence of various domain states within the material for different particle sizes [69, 75].

Table 5.10 The Curie temperature of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites determined using AC susceptibility studies.

Composition (x)	Curie Temperature (K)
x= 0.0	859
x= 0.1	856
x= 0.2	841
x= 0.3	829
x= 0.4	813
x= 0.5	809

For composition $x = 0.0$, with the highest cobalt content, the peak in the normalized ac susceptibility plot indicate the single domain type of behavior with a noticeable hump of maximum susceptibility and with further increase there is a sharp fall at the Curie temperature. This hump in the peaks is known as the Hopkinson’s peak. The composition from $x = 0.1$ to 0.4 show a blend of superparamagnetic and single domain particle nature wherein there is a steady increase in the susceptibility observed at lower temperature and a slow fall at the Curie temperature with tailing effect. Moreover, the $x = 0.5$ shows a superparamagnetic behavior indicating a slow decrease in the magnetic susceptibility as the temperature is increased to T_c .

5.5.2.2 Vibrating sample magnetometry (VSM) studies of ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

The vibrating sample magnetometer (VSM) instrument was used in the field strength of -3 Tesla to 3 Tesla for the magnetization measurements as a function of magnetic field (M-H) and as a function of temperature (M-T). Two different temperatures were chosen i.e. room temperature (300 K) and low temperature (60 K) for performing the M-H studies. Additionally, the zero field cooled-field cooled (ZFC-FC) studies were carried out at two different fields at 2000 Oe and at 3000 Oe as a function of temperature. The various magnetization parameters like the saturation magnetization (M_s), remanant magnetization (M_r), coercivity (H_c), and blocking temperatures obtained using this plot are reported in Table 5.11. The hysteresis-loop behaviour and the magnetization data plots with respect to

the magnetic fields (M-H) of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at 300 K and at 60 K are shown in Fig 5.24 and 5.25, respectively.

Both the room temperature (300 K) and 60 K measurements showed a declining trend in the saturation magnetization (M_s) with increase in cobalt and decrease in zinc concentration. This variation of M_s can be explained on the basis of cation distribution between the tetrahedral and the octahedral sites. In case of zinc ferrites, Zn^{2+} preferentially occupy the tetrahedral sites (A-site) whereas Fe^{3+} prefers octahedral sites. However, in the case of CoFe_2O_4 and NiFe_2O_4 , both are inverse spinel and hence Co^{2+} and Ni^{2+} choose to occupy octahedral sites whereas Fe^{3+} tends to distribute itself equally between the tetrahedral and the octahedral sites [76-79].

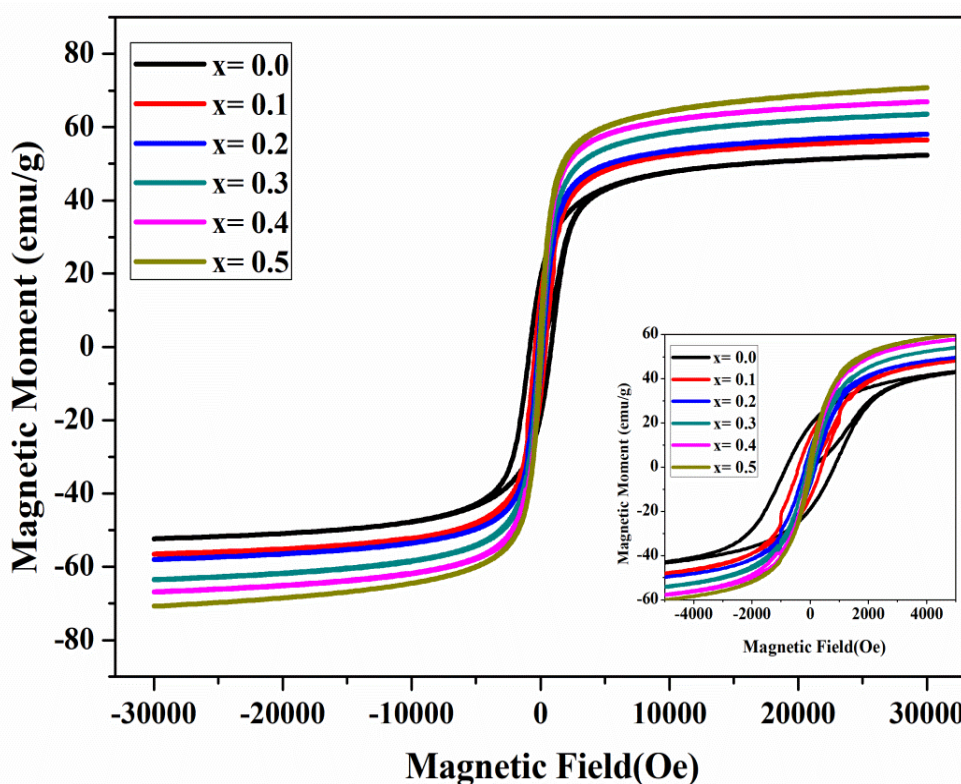


Fig. 5.24 The plot of magnetic moment against magnetic field at 300 K at a field from -3T to 3T of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites [Inset: Magnified region (-0.45 T to +0.45 T) showing coercivity].

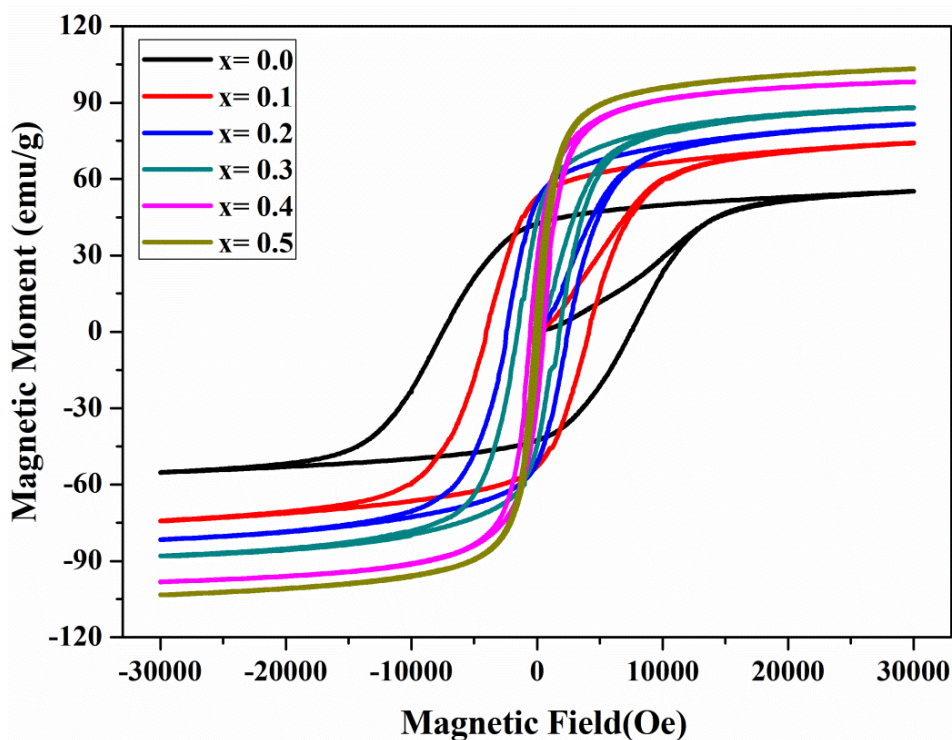


Fig. 5.25 The plot of magnetic moment against magnetic field at 60 K at a field from -3T to 3T of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Thus as discussed before, in the case of inverse spinel, Ni^{+2} (and/or Co^{+2}) ions have a strong preference to occupy the octahedral sites and Fe^{+3} ions strongly prefer to occupy both tetrahedral and octahedral sites. When Zn^{+2} ions are substituted in place of Co^{+2} , these Zn^{+2} ions with a zero magnetic moment have a strong preference to occupy the tetrahedral sites. As a consequence, when zinc is substituted for cobalt in $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, it forces Fe^{+3} ions from the tetrahedral sites to the octahedral sites. This causes an increase in the magnetization of the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite system with increase in the zinc content. Since, higher magnetic moment in Fe^{+3} ($5 \mu_B$) ions in the A site are replaced with the smaller (zero) magnetic moments of Zn^{+2} ($0 \mu_B$) ions, the magnetic moment of the A site decreases and the magnetic moment of the B site increases. Hence, as the Zn^{2+} concentration (x) increases, the magnetization also increases [18]. Additionally, the coercivity values were found to increase with increase in the cobalt content at both the temperature (300 K and at 60 K). This is ascribed to the high values of magnetocrystalline anisotropy energy of the Co^{2+} ions [80]. The strong magnetocrystalline anisotropy of cobalt substituted ferrites is basically due to the Co^{2+} ions in the octahedral sites. Since the crystal field is inefficient to remove the orbital degeneracy of the Co^{2+} ions at the octahedral sites, the orbital magnetic moment doesn’t quench and hence there is

persistent spin-orbit coupling which gives rise to the strong magnetocrystalline anisotropy in cobalt ferrites [19, 81-82].

Table 5.11 Saturation magnetization (M_s), remnant magnetization (M_r), coercivity (H_c), blocking temperature (T_B) at 2000 Oe and 3000 Oe, magnetocrystalline anisotropy (K_{eff}) and squareness ratio of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	Temperature	0.0	0.1	0.2	0.3	0.4	0.5
M_s (emu/g)	60 K	55.37	74.10	81.38	88.55	98.26	103.69
	300 K	52.54	56.44	58.26	63.12	67.03	70.57
M_r (emu/g)	60 K	43.21	52.68	54.71	56.89	61.25	63.78
	300 K	16.25	17.26	18.61	21.27	22.81	24.09
H_c (Oe)	60 K	7965	4399	2803	1818	973	222
	300 K	958	509	251	141	98	63
$K_{\text{eff}} * 10^5 \text{ erg}^{-1}$	60 K	4.47	3.30	2.31	1.6	0.97	0.23
	300 K	0.52	0.29	0.14	0.09	0.06	0.04
η_B	60 K	2.32	3.12	3.43	3.74	4.17	4.41
	300 K	2.20	2.37	2.45	2.67	2.84	3.00
M_r/M_s	60 K	0.78	0.71	0.67	0.64	0.62	0.61
	300 K	0.31	0.30	0.32	0.33	0.34	0.34
T_B (K)	2000 Oe	320	315	265	218	165	120
	3000 Oe	291	260	224	184	118	72

The M-H curves at 60 K for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites show enhanced magnetization values as compared to that in the room temperature measurements [83]. The concentrations of Zn^{+2} and Co^{+2} ions are responsible for the change in magnetic properties of ferrites. The decrease in temperature leads to an increase in the M_s values and an increase in the coercivity values owing to the minimized thermal variation effects at low temperature. As the temperature is decreased to 60 K there is no chaos in the magnetic moments which is present in the magnetic moment of room temperature, thus the spin alignment is in the same direction as that of the magnetic field [82, 84] when the temperature is low.

There is an increase in coercivity and a decrease in saturation magnetization as the cobalt concentration increases. Also increase in zinc concentration increases the M_s value and decreases the coercivity values. The enhancement in the coercivity can be ascribed to the grain size of the materials and the corresponding domain rotation process. The magnetic anisotropy induced by crystal lattice distortion can also influence coercivity [85]. Also, this larger coercivity of the ferrites with increase in cobalt content is attributed to the larger magnetocrystalline anisotropy property of the Co^{+2} ions. The remnant magnetization (M_r) was found to increase with increasing zinc content in all the 'as prepared' ferrites.

The temperature dependent magnetic studies (zero field cooled (ZFC) and field cooled (FC)) for all the 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were performed in the temperature range from 60 K to 350 K in the applied magnetic field of 2000 and 3000 Oe and the magnetization v/s temperature plots are depicted in Fig. 5.26 and Fig. 5.27, respectively. The ZFC plots explain that initially the ferrite nanoparticles were cooled from 350 K to 60 K without applying any magnetic field and later by heating from 60 K to 350 K by simultaneously measuring magnetization (at both the fields i.e. 2000 Oe and 3000 Oe). While when carrying out the FC measurements the ferrite nanoparticles were cooled from room temperature to 60 K (in presence of magnetic field) and then heated from 60 K to 350 K by concomitantly recording the magnetization values at both the fields.

In case of ZFC measurements, both the fields (2000 Oe and 3000 Oe) show an increase in magnetization of ferrite samples with increase in temperature, which then reach the maximum value (called the blocking temperature) of magnetization and then decrease with further increase in temperature for all the ferrite samples except for $x = 0.5$ where it continuously decreases. But in the FC study, the magnetization was found to decrease continuously with increasing temperature. This distinct behaviour in the magnetization of ZFC and FC measurement is justified on the basis of broad particle size distribution which is affirmed by HR-TEM and SEM analysis [86].

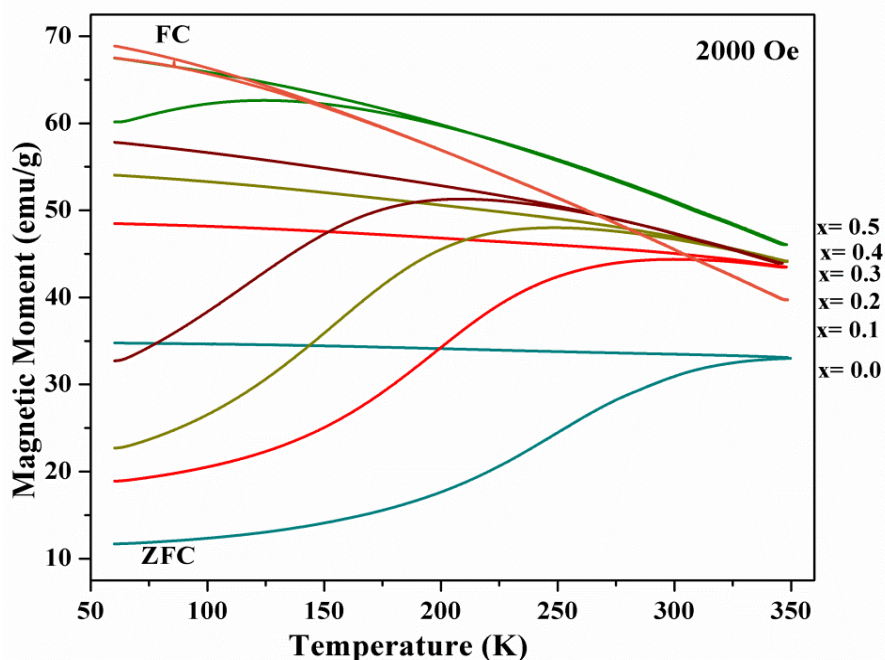


Fig. 5.26 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 2000 Oe and for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

The ferrite samples attain the maximum magnetization values at 60 K as the magnetic anisotropy energy barrier doesn’t allow the magnetic moments to flip. Also, at lower temperatures (60 K) a broad distribution of particle sizes (determined by SEM, TEM) results in the nanoparticles to randomly align along the axis thus leading to highest probable magnetization. With rise in temperature, the magnetic moments tend to thermally trigger and orient themselves along the direction of the externally applied magnetic field. This orientation causes an increased magnetization. Further, beyond the blocking temperature (T_B) the thermal energy overpowers this energy barrier and the magnetic spins fluctuate thus resulting in declining magnetization [87-90].

At both the fields (2000 Oe and 3000 Oe) the blocking temperatures values for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites are found to decrease from 320 K to 120 K for 2000 Oe and from 291 K-72 K incase of 3000 Oe (Table 5.11) with increase in zinc concentration. Since cobalt holds higher magnetic anisotropy than nickel and zinc, all the nanoparticles of the synthesized ferrites fall in ferromagnetic region. Thus, they require higher temperature to orient all magnetic moments to obtain highest magnetization at the blocking temperature [86, 91]. This is justified by the virtue of Néel’s theory which implies the dependence of T_B on the magnetocrystalline anisotropy [82].

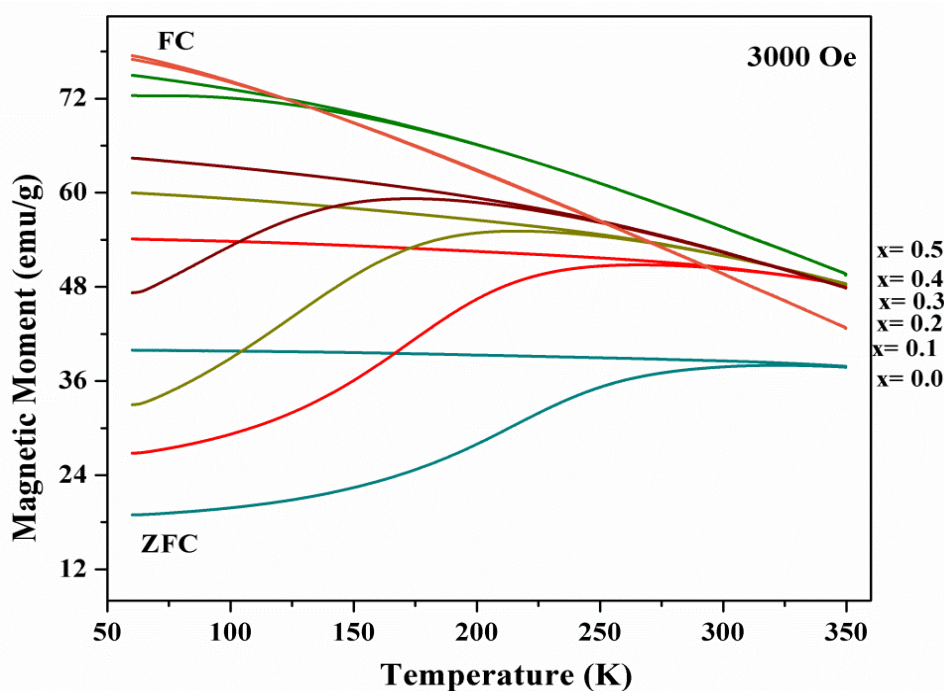


Fig. 5.27 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 3000 Oe for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

With increasing temperature, the ferrites with the compositions $x = 0.0, 0.1, 0.2$ and 0.4 showed an increase in the magnetization values accompanied by a decrease at higher temperature thus depicting the blocking temperature. The broad maxima in the T_B in these samples indicate broad particle size distribution as obtained by the SEM and TEM analysis. However the compositions $x = 0.4$ and 0.5 show a persistent decreasing trend from 60 K to 400 K in ZFC-FC plots [86, 92-93].

The irreversibility temperature (T_{irr}) is the temperature at which both magnetization at FC and ZFC meet. At both the fields the T_{irr} was found to decrease with increase in zinc concentration. This decrease can be explained due to the fact that there is a lowering in the magnetocrystalline anisotropy as the energy needed to flip the spins and orient along the applied magnetic field is reduced with increase in zinc concentration [74, 92]. However, increase in applied field (from 2000 Oe to 3000 Oe) increases the T_{irr} . At low field, the applied magnetic field shows large bifurcation in ZFC and FC plots which suggests magnetically non-homogeneous system [93].

5.6 Characterisation of the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

5.6.1 Structural characterization of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites by powder XRD studies

The powder XRD patterns of all the sintered $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites are depicted in Fig. 5.28 to check for their phase purity. The powder XRD diffraction patterns of each composition matches closely with the standard ferrite patterns as shown in JCPDS cards i.e. 52-0278 for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and 22-1086 for $Co_{0.5}Zn_{0.5}Fe_2O_4$ [94]. Various parameters like the lattice parameter (a), crystallite sizes (D), measured density (d_m), theoretical density (d_x), porosity (P) for all the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrite samples are tabulated in Table 5.12.

Table 5.12 The lattice parameter (a), measured density (d_m), theoretical density (d_x) porosity (P) and crystallite sizes (D) of the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites.

Composition (x)	Lattice parameter (a) (Å)	Measured density (g/cm ³)	Theoretical density (g/cm ³)	Porosity (%)	Crystallite size (D) (nm)
0.0	8.3888	4.2462	5.2759	19.51	50
0.1	8.3837	4.5036	5.3004	15.03	52
0.2	8.3741	4.0532	5.3334	24.00	52
0.3	8.3725	4.5495	5.3509	14.97	50
0.4	8.3686	4.5964	5.3787	14.54	52
0.5	8.3565	5.1841	5.4087	04.15	51

It is observed from Table 5.12 that there is an increase in the average crystallite size (D) upon sintering which can be further confirmed by the increasing particle size by SEM analysis of sintered samples (section 5.6.4.1). The increasing crystallite sizes can be attributed to various factors like surface stress, surface pressure etc. [90, 95]. The lattice parameter values are found to decrease with increase in zinc concentration. Furthermore, upon sintering the lattice parameter is found to show increased values. Similar trend had been reported by P. Mathur et al. [95] in which they reported increase in the lattice parameter values upon sintering. One of the reasons for this increase can be the decrease in the surface tension of the nanomaterial with increased particle size [91]. The intensities

of all the peaks were found to increase upon sintering which is opposite for their ‘as prepared’ analogues, also the broadness of the peaks was found to decrease upon sintering.

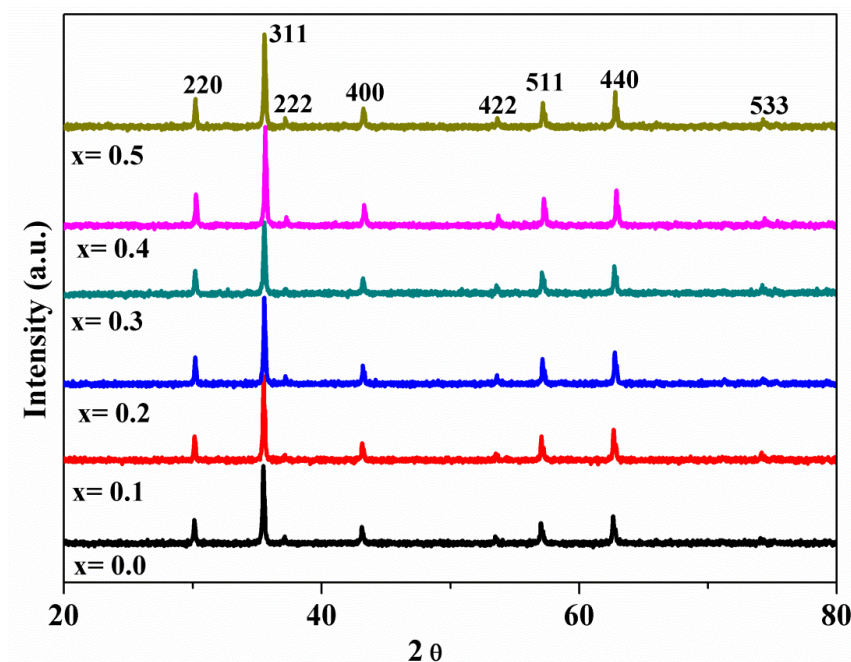


Fig. 5.28 The powder XRD patterns for the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites.

5.6.2 Infra-red (IR) spectroscopy of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites

The room temperature IR spectra of all the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrites recorded between $350-4000\text{ cm}^{-1}$ are shown in the Fig. 5.29. Two characteristic peaks are observed in all the ferrites samples; one at $\sim 400\text{ cm}^{-1}$ which corresponds to the stretching band of the metal-oxygen bond at the octahedral sites whereas the band position at $\sim 600\text{ cm}^{-1}$ is due to metal vibrations of the metal oxygen bonds at the tetrahedral sites of the ferrite samples [22-23]. The exact values of wavenumber obtained from the IR spectra of these samples are reported in Table 5.13.

Table 5.13 The ν_1 and ν_2 values observed in the IR spectra of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Composition	Wavenumbers obtained from IR spectra of ‘as prepared’ ferrites (cm^{-1})	
	ν_1	ν_2
0.0	622	412
0.1	620	401
0.2	619	401
0.3	619	418
0.4	618	401
0.5	617	406

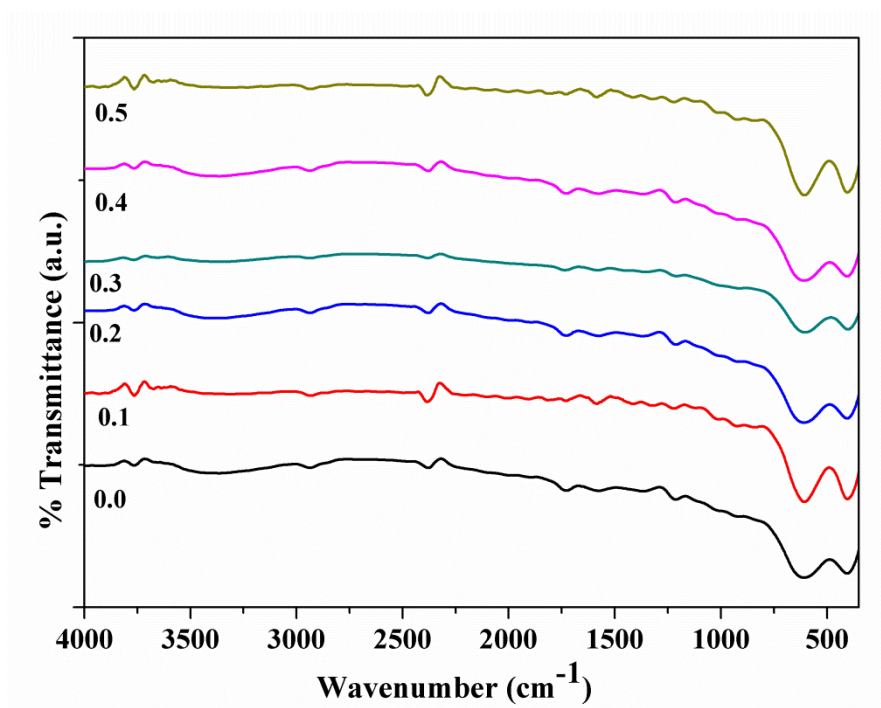


Fig. 5.29 IR spectra of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

5.6.3 Raman spectroscopy studies of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

Since Raman spectroscopy is sensitive for structure elucidation hence it can be easily used to investigate the short-range disorder which is induced by different types of interactions and surface distortions. Fig. 5.30 demonstrates the room temperature Raman spectra for all the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites recorded in the range from 100-800 cm^{-1} . Table 5.14 depicts the exact Raman shift obtained for all the ‘sintered’ ferrites.

All the Raman spectra pertain to characteristic spinel structure indicating Raman active bands (A_{1g} , E_g and T_{2g}) [86, 96]. In all the samples the bands above 600 cm^{-1} (A_{1g}) is due to the symmetrical stretching of oxygen atom for M–O bond at the tetrahedral sites. The lower frequency peaks observed below 600 cm^{-1} belong to symmetric bending, asymmetric stretching and asymmetric bending for M–O bond at the octahedral sites which are represented as E_g , $T_{2g}(2)$ and $T_{2g}(3)$ respectively. Besides, absence of any peak ($\alpha\text{-Fe}_2\text{O}_3$) at $\sim 240\text{ cm}^{-1}$ affirmed the formation of monophasic cubic spinel structure for all the ‘sintered’ samples [24, 53].

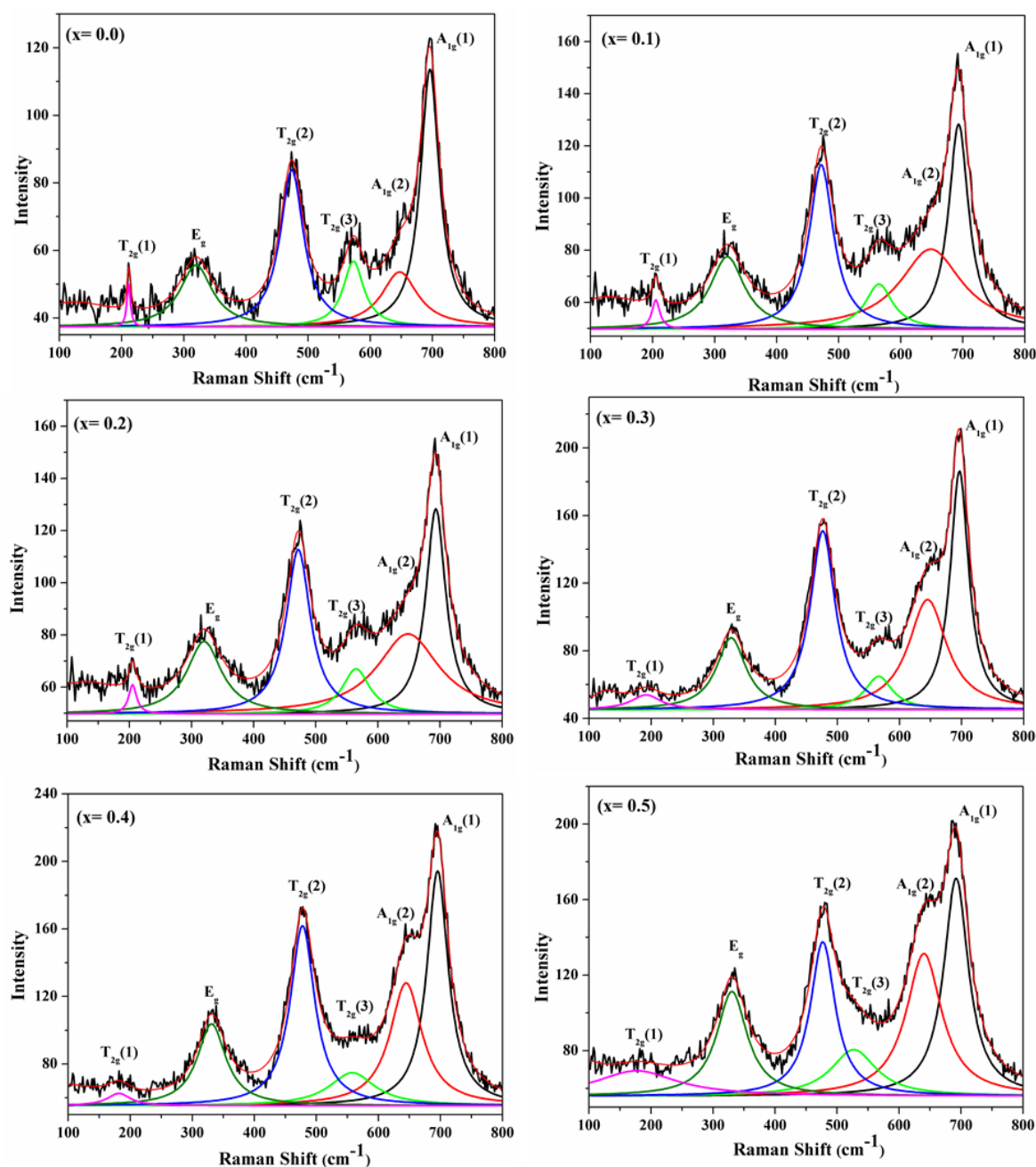


Fig. 5.30 The Raman spectra of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

The intensity of A_{1g} peak is influenced by the cobalt ions in the tetrahedral sites and thus some obvious changes correlated to the peak position and peak intensity has been observed in the ferrites for higher concentration of cobalt ions. It is observed that in the ferrite sample having higher concentration of cobalt, there is peak widening for the A_{1g} peak and the intensity of the peak is lesser [86]. Moreover, a small shift is also observed in the ferrite samples with increasing zinc content in the ferrite samples.

Table 5.14 The Raman shift observed for the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	A_{1g} (1) cm^{-1}	$A_{1g}(2)$ cm^{-1}	$T_{2g}(3)$ cm^{-1}	$T_{2g}(2)$ cm^{-1}	E_g cm^{-1}	$T_{2g}(1)$ cm^{-1}
0.0	690	647	565	473	313	190
0.1	691	648	564	472	318	199
0.2	692	649	562	473	321	202
0.3	692	650	567	477	331	199
0.4	694	651	568	479	333	174
0.5	695	652	569	479	334	184

5.6.4 Morphological studies of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

5.6.4.1 Scanning Electron microscopy (SEM) studies of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

The SEM micrographs along with the EDAX spectra of the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites are shown in Fig. 5.31 and Fig. 5.32. The SEM images revealed that there is an increase in the particle sizes on sintering since the nanoparticles merge together and as a result the agglomerated lumps are formed which are having larger particle sizes. The SEM micrographs do not possess any obvious difference between all the synthesized ferrites [97]. Upon sintering, however the particles are also irregularly shaped which were nearly spherical in the ‘as prepared’ analogues. The agglomeration of the particles can also be ascribed to strong magnetism of the nanoparticles [26, 98]. The agglomeration was found to decrease with increase in zinc content in the samples.

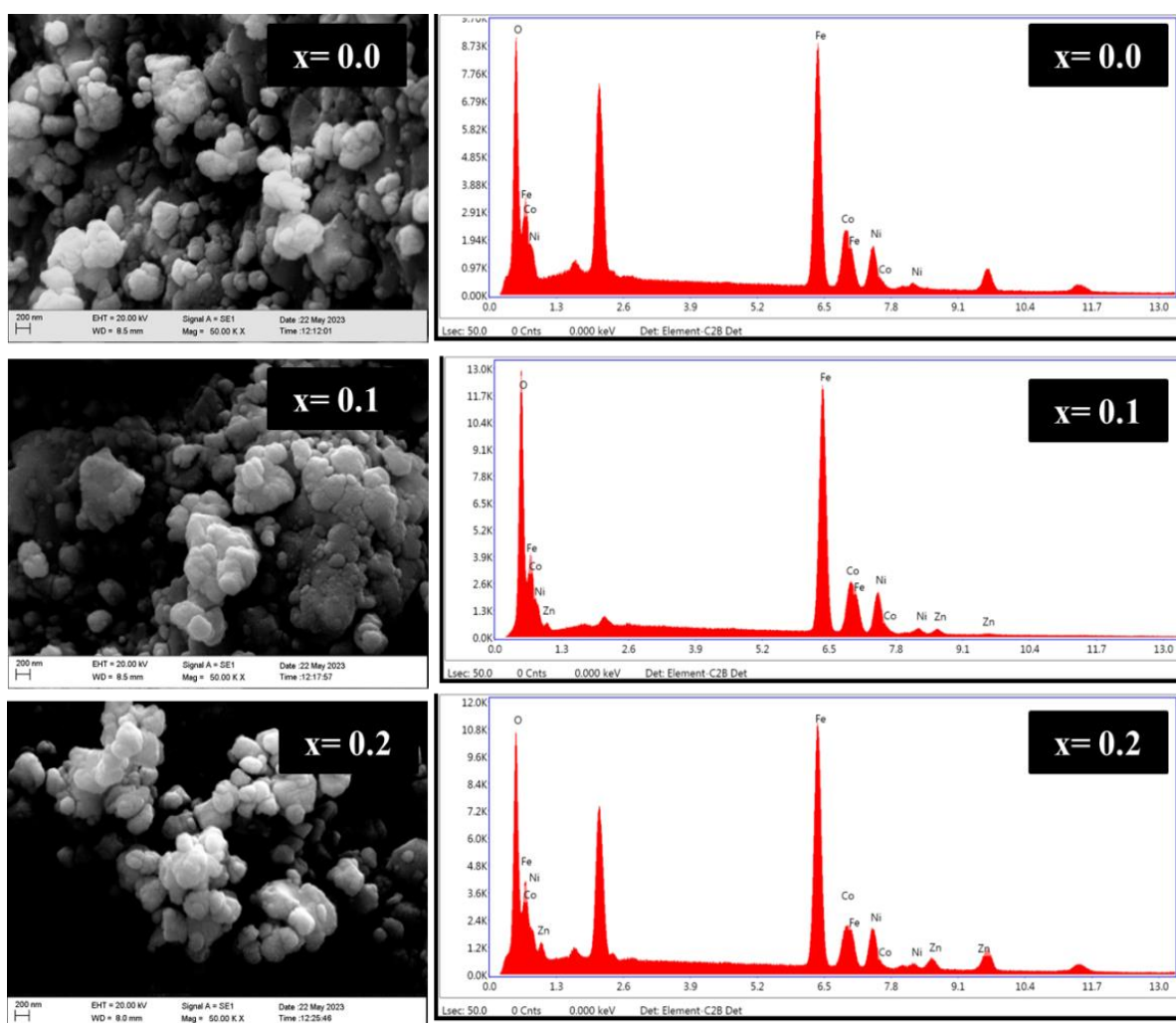


Fig. 5.31 The SEM micrograph and EDAX spectrum of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.2$) ferrites.

The EDAX analysis confirmed the presence of corresponding metal ions in the ferrite samples without any impurity element peaks observed. With increase in zinc concentration, the decrease in the intensity of the cobalt peak is observed.

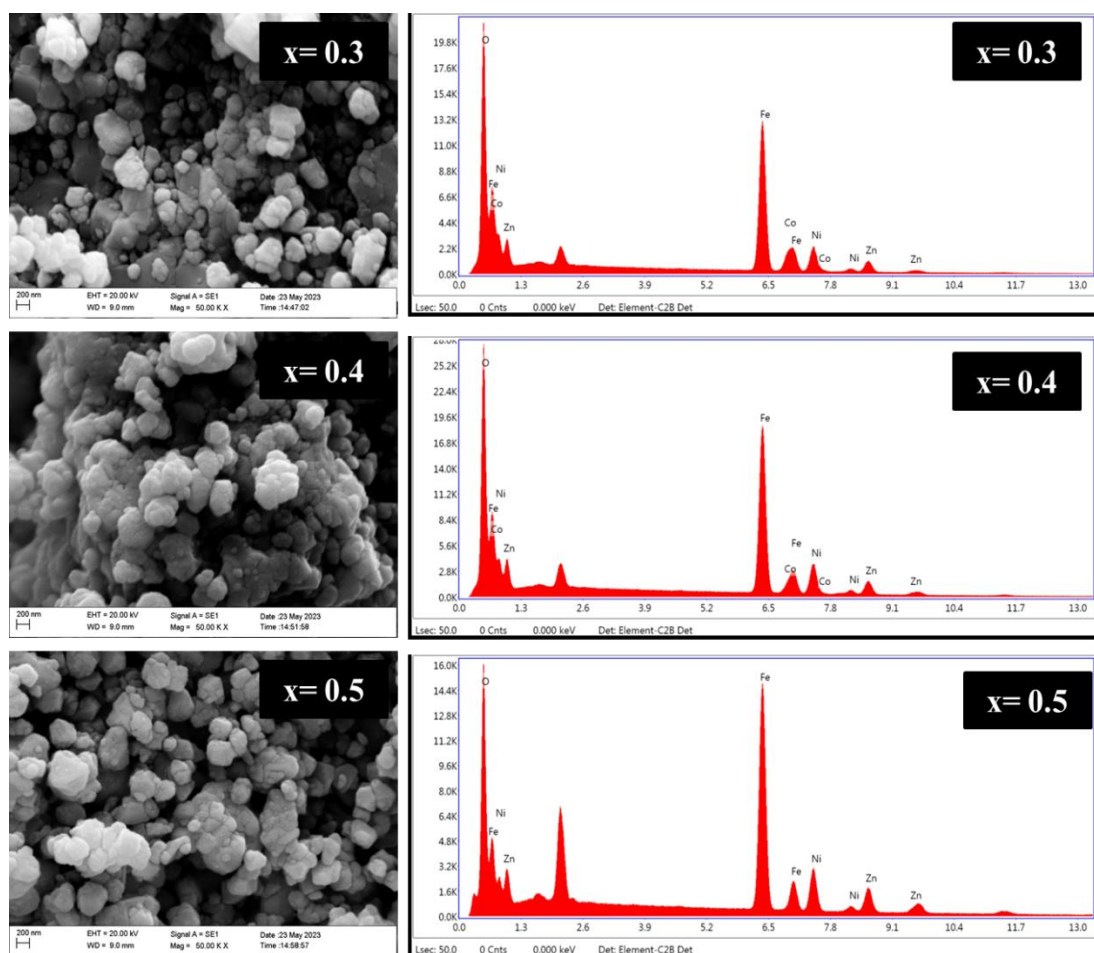


Fig. 5.32 The SEM micrograph and EDAX spectrum of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3-0.5$) ferrites

5.7 Solid state studies of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.7.1 Dielectric properties of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.7.1.1 Dielectric measurements as a function of frequency for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

In view of the fact that all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites samples show a large dependency of dielectric properties, hence the dielectric properties for their ‘sintered’ analogues were also recorded in order to see the variation in their dielectric properties upon sintering. The dielectric constant for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were measured against frequency in the frequency range from 20 Hz to 10 MHz and the plots of the same are depicted in Fig. 5.33a. In all the cases, it was observed that the dielectric constant values were found to be highest at lower

frequencies up to around 1 KHz and as the frequency increases the values were found to decrease and later remain almost constant.

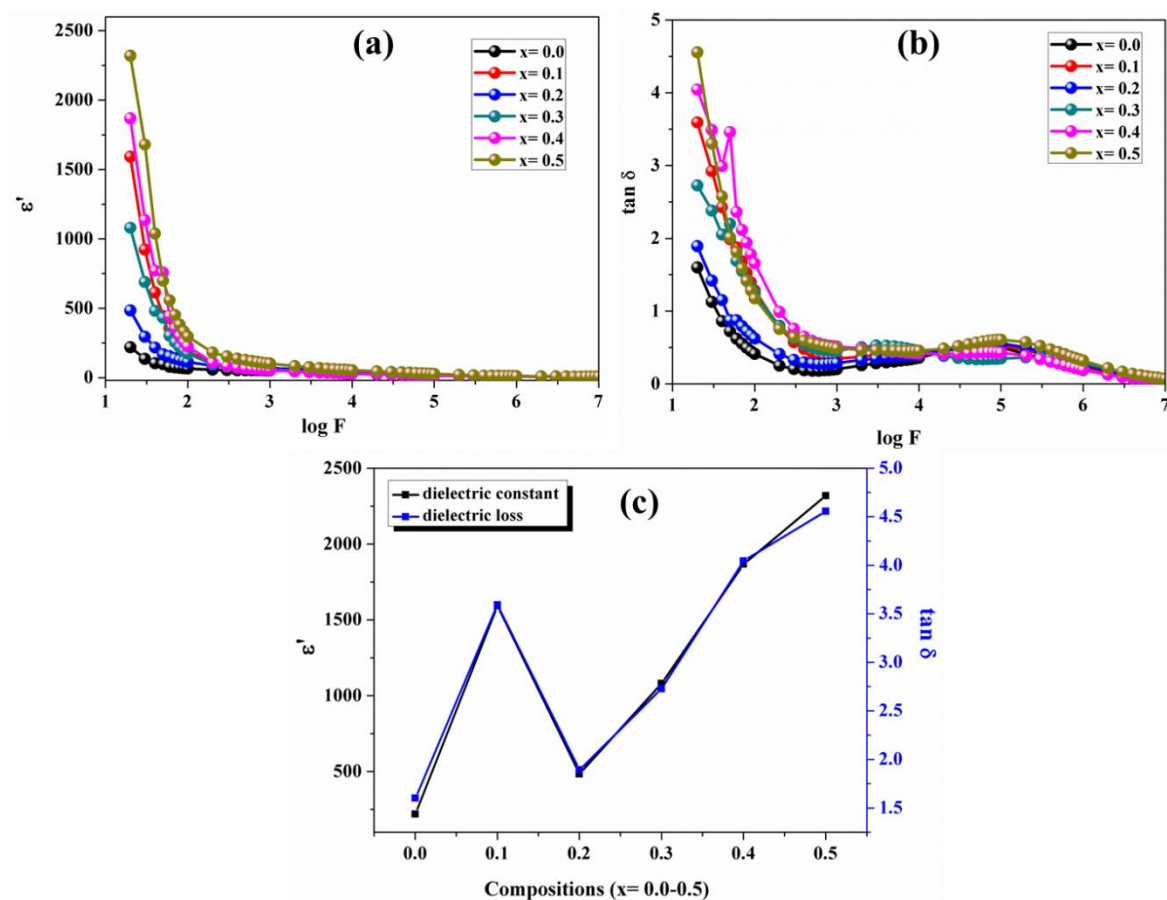


Fig. 5.33 The plots of (a) Dielectric constant against log frequency (b) dielectric loss tangent ($\tan \delta$) against log frequency (c) Plot of dielectric constant and loss tangent as a function of composition at 20 Hz for ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

All the compositions show a normal dielectric behaviour with increasing frequency (same as shown for all the ‘as prepared’ analogues) and this is found to be in conformity with the Maxwell-Wagner interfacial polarizations along with Koop’s theory of dielectric materials [56, 99-100,]. As per the Maxwell Wagner theory, electrons reach the grain boundaries through hopping and they accumulate at the grain boundary thus causing charge build-up and leading to interfacial polarizations [56, 100]. But, with increase in frequency, the hopping of electrons cannot follow the change in applied electric field and hence the direction of the charge carriers is reversed. Hence, the probability of electrons reaching the grain boundaries decreases. G. R. Mohan et al. [101] explained the electronic exchange between $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Ni^{2+} and Ni^{3+} hopping do not follow the applied electric field up to a specified frequency thus explaining that dielectric constant is independent of frequency.

The dielectric constant does not have any specific trend with increasing zinc substitution and the composition with $x = 0.4$ shows the highest value of dielectric constant.

The dielectric loss tangent against frequency plots for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites are demonstrated in Fig. 5.33b. All the loss tangent plots show the normal nature of ferrites i.e. the dielectric loss tangent decreases with increase in frequency. The dielectric loss tangent values are very high at lower frequency and later the values tend to decrease with increase in frequency (up to 1 KHz) and then remaining almost constant at higher frequencies. The dielectric loss tangent also did not have any specific trend with increasing zinc content. The plot of dielectric properties against compositions for the ‘sintered’ samples has been depicted in Fig. 5.33 c

5.7.1.2 Dielectric measurements as a function of temperature for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

Fig 5.34 depicts the variation of the dielectric constant as a function of temperature for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites carried out at constant frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C. The temperature profiles show that first the dielectric constant remains constant followed by an increase in the dielectric constant with temperature.

This increasing dielectric constant is accredited to the increasing polarizations by increase in the thermal energy at high temperatures [63]. Nevertheless, the increase in the dielectric constant is prominent at lower frequencies (250 Kz) while at higher frequencies it tends to be lesser (1 MHz). The values of dielectric constant remain constant upto at 380 °C and later the values have a drastic increase. As already discussed in the ‘as prepared’ section four types of polarizations (electronic, ionic, dipolar and space charge) affect the dielectric behaviour of any ferrite sample.

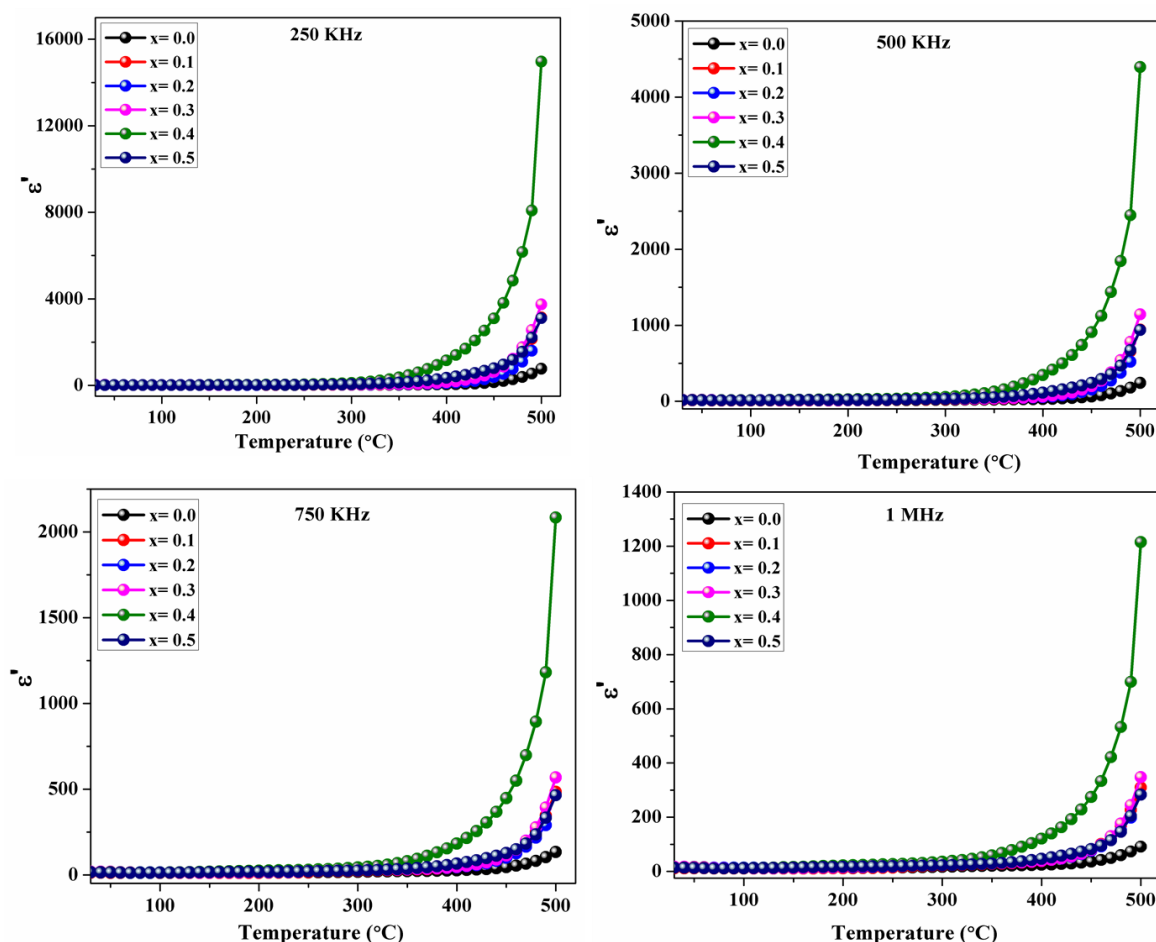


Fig. 5.34 The plots representing variation of dielectric constant as a function of temperature for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz).

Dipolar and space charge polarizations are significantly temperature dependent and hence these are accountable for high dielectric constant at lower frequency of 250 KHz. On the contrary, electronic and ionic polarizations are responsible for dielectric constant at higher frequency (1 MHz) and both the polarizations are temperature and frequency independent. From the temperature profiles for dielectric constant against temperature, it is seen that there is no specific trend as such in the values, however the composition $x = 0.4$ showed the highest value of dielectric constant.

The dielectric loss tangent follows the similar trend as that of ‘as prepared’ samples for all the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites for all the four frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz) wherein the dielectric loss was found to remain constant at lower temperatures and as the temperature increased the values were found to increase (Fig 5.35). This increase can be justified based upon the similar reasons as

explained for the dielectric constant. Amongst all the compositions, the highest dielectric loss was found to be for the ferrite sample having $x = 0.4$ composition and with increase in zinc concentration, the nickel substituted cobalt ferrites did not show any particular trend in the values.

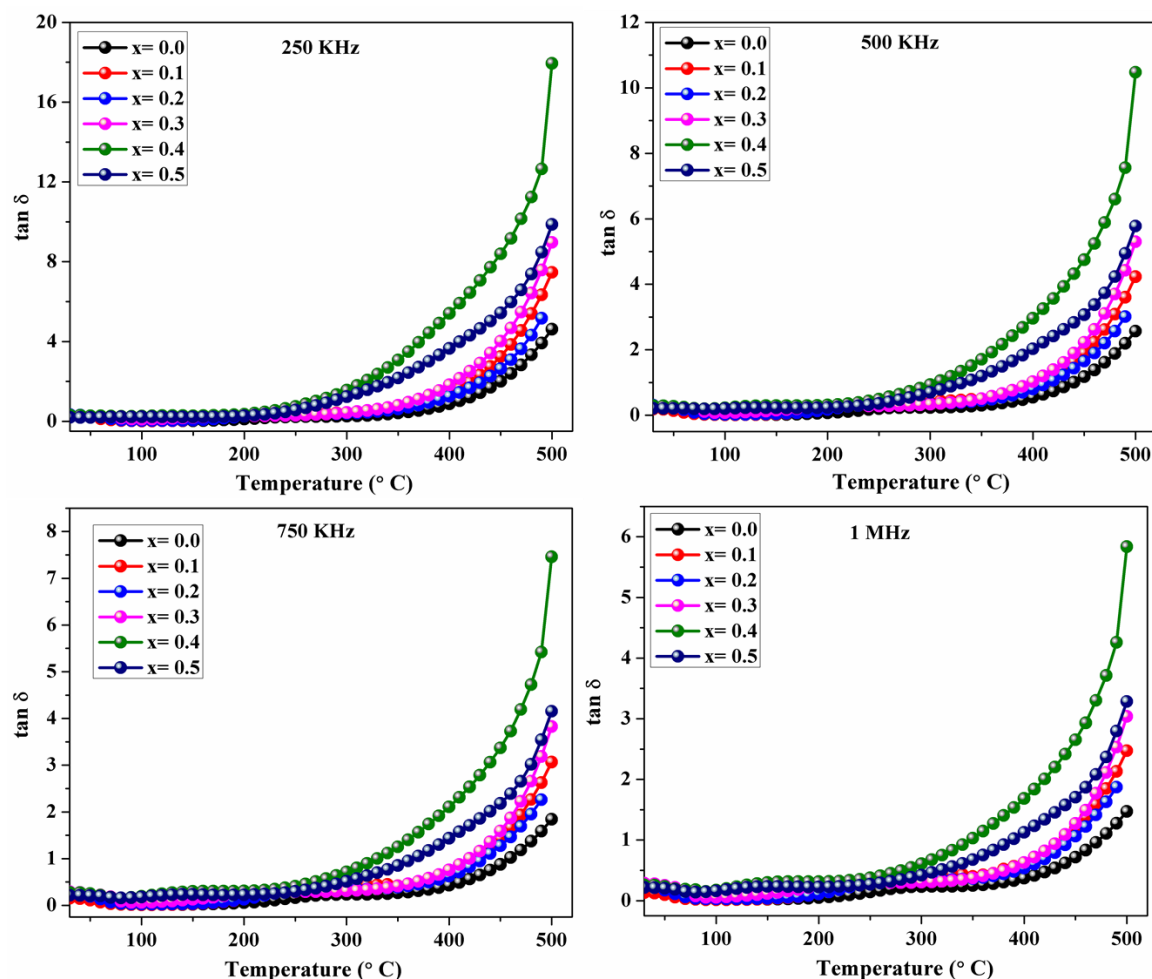


Fig. 5.35 The plots representing variation of dielectric loss tangent as a function of temperature for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at four different frequencies (250 KHz, 500 KHz, 750 KHz and 1 MHz).

5.7.2. The magnetization studies of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

5.7.2.1 The normalized A.C. susceptibility studies of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites

Fig. 5.36 demonstrates the normalized AC Susceptibility plots of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) samples. It was observed from the Fig. 5.36 that the ferrite sample with compositions $x = 0.0-0.4$ indicate an eventual rise in the magnetization values followed by a slow increase at a little higher temperature constituting a Hopkinson’s peak

just before the Curie temperature and later succeeded by an abrupt fall at the T_c which is suggestive of the multi domain nature of the nanoparticles. Whereas ferrite sample with the composition $x = 0.5$, initially showed a gradual increase accompanied by a decrease with tailing effect at the Curie temperature exhibiting a mixture of single domain-multi domain nature of particles. The exact values of the Curie temperatures obtained for all the ‘sintered’ ferrite samples are reported in Table 5.15.

The ‘sintered’ samples also follow the similar trend as the ‘as prepared’ samples i.e. the Curie temperature decreases with an increase in the non-magnetic zinc concentration and is found to be lowest for the composition $x = 0.5$ ($\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$). As already mentioned earlier, the T_c is dependent on A-B interaction strength and as per the Neel’s theory since the A-B interactions are strongest (than A-A and B-B), the non-magnetic Zn^{2+} ions from A-sites forces magnetic Fe^{3+} ions to the B-sites, hence causing reduction in the A-B interactions [74]. Besides, from the powder XRD measurements it was observed that the lattice parameter increases with increase in zinc concentration which is having an inversely proportionate relationship with the T_c .

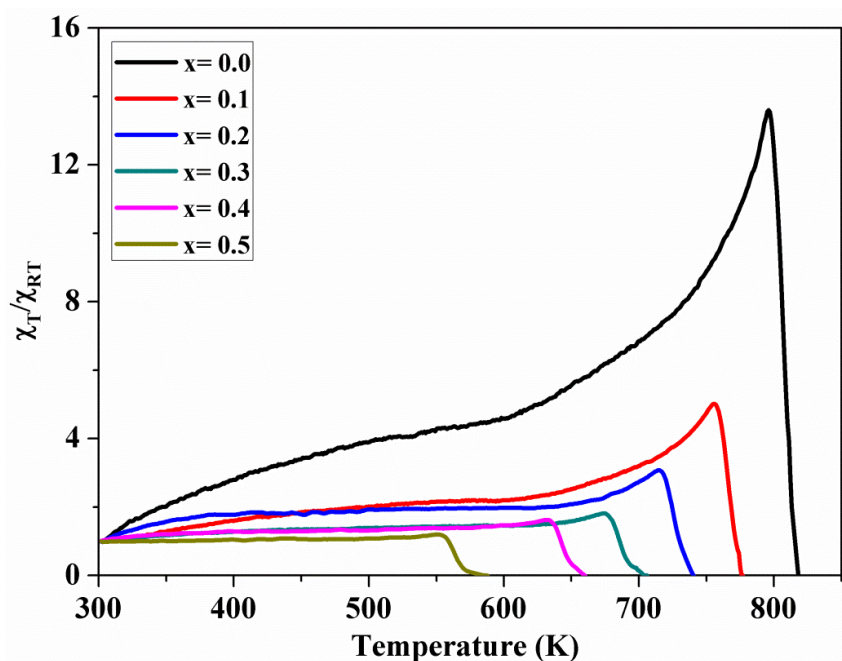


Fig. 5.36 Plots of normalized AC susceptibility against temperature of the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) samples.

The Curie temperature was found to decrease upon sintering and this decrease in the Curie temperature can be justified based on the transformations in the cation distributions of the lattice in octahedral and tetrahedral sites with increase in particle sizes (observed in the SEM images on sintering) [102].

Table 5.15 The Curie temperature of the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites determined using AC susceptibility studies.

Composition (x)	Curie Temperature (K)
x= 0.0	817
x= 0.1	776
x= 0.2	737
x= 0.3	703
x= 0.4	658
x= 0.5	586

5.7.2.2 Vibrating sample magnetometry (VSM) studies of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites VSM) studies

All the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrite samples were investigated for their magnetic properties as a function of applied magnetic field using vibrating sample magnetometer (VSM) till an applied field of 3 Tesla at room temperature (300 K) and at 60 K. The room temperature M-H curves of all the ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ (where $x = 0.0-0.5$) ferrite samples indicate ferrimagnetic nature and the alteration in the magnetic properties is ascribed to the concentrations of Ni^{+2} , Co^{+2} and Zn^{+2} ions. The hysteresis loops of the sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites samples are shown in Fig. 5.37 and Fig. 5.38 for 300 K and 60 K, respectively. The exact values of saturation magnetization (M_s), remnant magnetization (M_r) and coercivity (H_c) at 300 K and at 60 K of ‘sintered’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites are given in Table 5.15.

From the Fig. 5.37 and 5.38 and Table 5.16 it can be seen that the M_s values were found to decrease with increased cobalt content and decreasing zinc concentration for all the ‘sintered’ samples at both the temperatures (300 K and 60 K). The same trend has been observed in the ‘as prepared’ analogues of the same ferrite samples as discussed in section 5.5.2.2. In the case of inverse spinel, Ni^{2+} and Co^{2+} choose to reside in the octahedral sites and Fe^{3+} prefer to occupy the octahedral and tetrahedral sites [76].

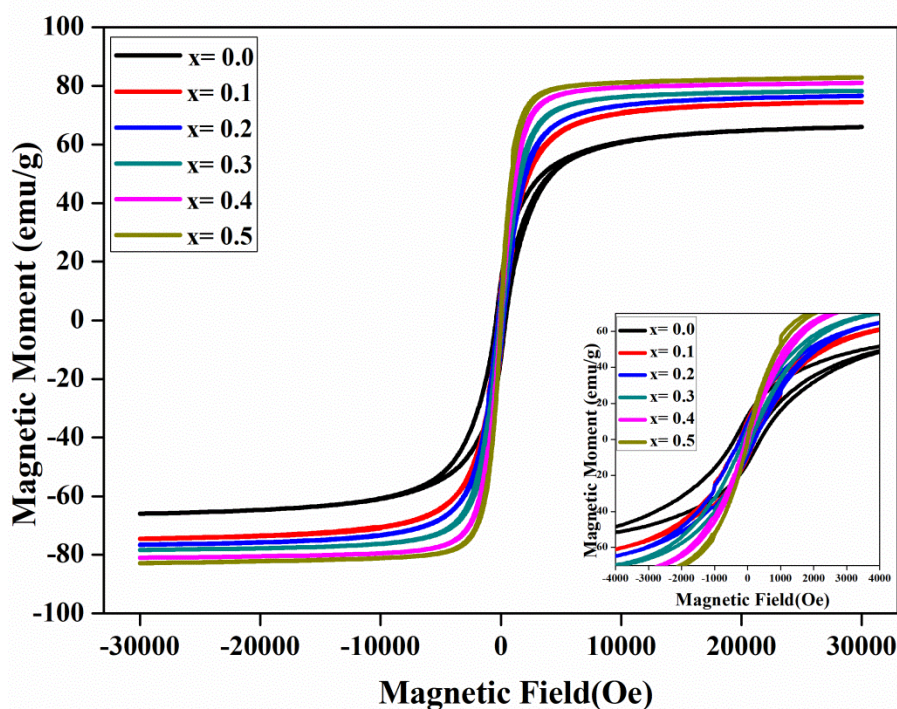


Fig. 5.37 The plot of magnetic moment against magnetic field at 300 K at a field from -3T to 3T of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites [Inset: Magnified region (-0.4 T to +0.4 T) showing coercivity].

Since Zn^{2+} ions are non-magnetic, when Zn^{2+} is substituted in Co^{2+} position it occupies the tetrahedral sites. Hence, it pushes Fe^{3+} ions from tetrahedral sites to the octahedral sites in all the ‘sintered’ samples, thus causing an increment in the magnetization with increasing zinc concentration. As Fe^{3+} ions have a higher magnetic moment of $5 \mu_B$ in the A-site, it is replaced by Zn^{2+} ions with zero magnetic moment thus the A-site magnetic moment has a decrease and that of the B-site show an increase with moving of Fe^{3+} ions at the B-sites, hence leading to increasing magnetization with Zn^{2+} ions [80].

The coercivity values in all the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites for both the temperatures (300 K and 60 K) were found to increase with increase in cobalt concentration which is attributed to the higher magnetocrystalline anisotropy values of the Co^{2+} ions [8, 80,98]. Generally, Co^{2+} ions are present in the octahedral sites, however as the crystal field is not as effective for removing the degeneracy of orbital of cobalt ions at the octahedral sites, the orbital magnetic moment doesn’t quench and thus the prominent spin-orbit coupling causes strong anisotropy effect in the cobalt ferrites [19, 81-82]. Also remnant magnetization (M_r) was found to increase with increasing zinc content in all the ‘sintered’ ferrite samples. The low temperature (60 K) curves for all the ‘sintered’

$\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites also show ferrimagnetic nature. There is an increase in M_s , H_c at such lower temperatures which is accredited to the minimum thermal variation effects at lower temperature [103].

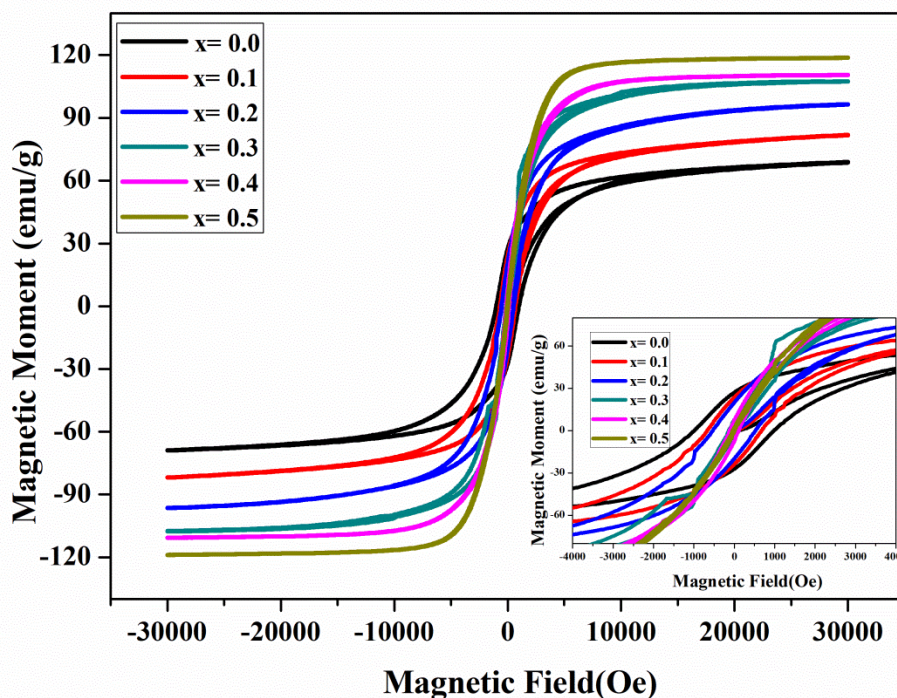


Fig. 5.38 The plot of magnetic moment against magnetic field at 60 K from at a field from -3T to 3T of ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites [Inset: Magnified region (-0.4 T to +0.4 T) showing coercivity].

The magnetization values for the ‘sintered’ samples were observed to be higher than their ‘as prepared’ analogues (Table 5.16). These higher values for the ‘sintered’ samples are attributed to the greater particle sizes of the samples and the transformation of their magnetic domain from single domain to multidomain upon sintering the ferrites, which is confirmed by the A.C susceptibility studies of the ‘sintered ferrites’ (Fig. 5.36). However, sintering also causes decreased canted spins which are prominent in the ‘as prepared’ analogues due to their greater surface to volume ratio [104].

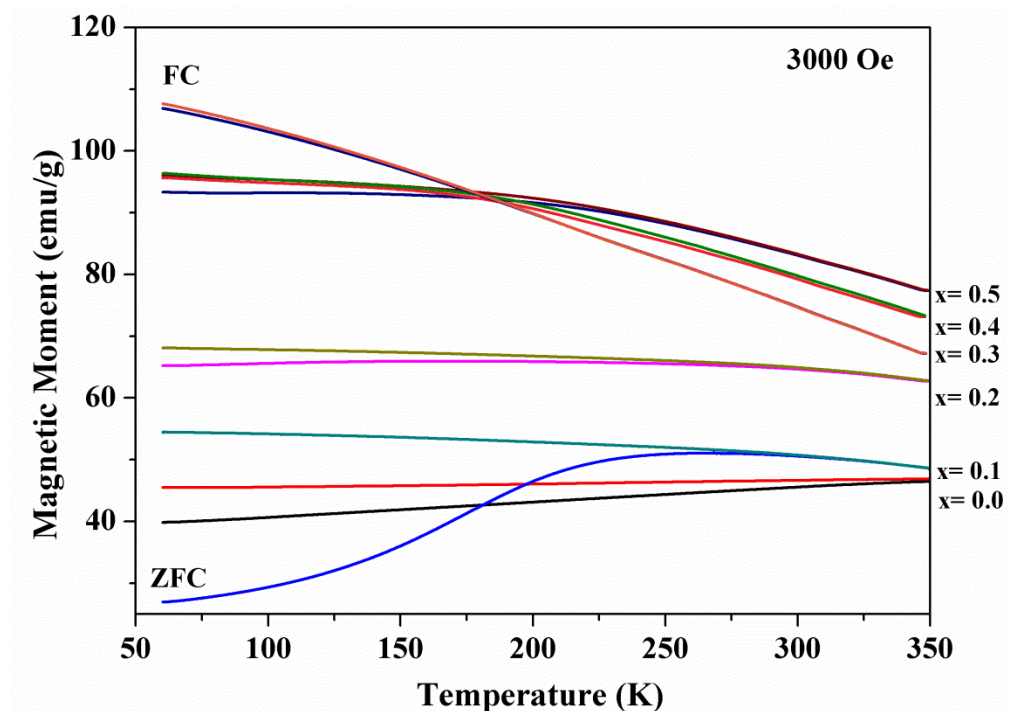


Fig. 5.39 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 3000 Oe and for 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

Further, the ZFC-FC studies for the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were carried out as a function of temperature (M-T) in the temperature range from 60 K to 350 K. The zero-field cooled and the field cooled curves are shown at the two different applied magnetic fields of 3000 Oe and 5000 Oe for all the samples in Fig. 5.39 and Fig. 5.40, respectively. The ZFC-FC magnetizations show bifurcation over the whole temperature range suggesting a magnetically non-homogeneous system [85, 105].

Table 5.16 demonstrates the blocking temperature values for all the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites and the values were found to decrease from 340 K to 256 K at 3000 Oe and from 300 K to 195 K at 5000 Oe with increase in zinc content. The parameters such as broad particle size distribution (confirmed by SEM and HR-TEM), magnetic anisotropy and corresponding particles with respect to their particle sizes of domains in superparamagnetic region are responsible for the variation in blocking temperature.

Table 5.16 Saturation magnetization (M_s), remnant magnetization (M_r), coercivity (H_c), blocking temperature (T_B) at 3000 Oe and 5000 Oe, magnetocrystalline anisotropy (K_{eff}) and squareness ratio of 'sintered' $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites.

Composition (x)	Temperature	0.0	0.1	0.2	0.3	0.4	0.5
M_s (emu/g)	60 K	69.32	81.73	96.03	107.09	111.13	119.36
	300 K	65.70	74.27	76.30	78.32	81.31	83.13
M_r (emu/g)	60 K	22.56	24.87	25.89	26.87	27.12	29.00
	300 K	18.35	19.65	21.56	24.86	25.66	27.45
H_c (Oe)	60 K	1132	858	360	256	207	146
	300 K	501	356	248	182	59	30
$K_{eff} * 10^5$ erg ⁻¹	60 K	0.79	0.71	0.35	0.27	0.23	0.17
	300 K	0.33	0.26	0.19	0.14	0.048	0.025
η_B	60 K	2.91	3.40	4.05	4.53	4.71	5.08
	300 K	2.75	3.14	3.22	3.31	3.45	3.53
M_r/M_s	60 K	0.32	0.30	0.26	0.25	0.21	0.24
	300 K	0.27	0.26	0.28	0.31	0.31	0.33
T_B (K)	3000 Oe	340	318	307	286	274	256
	5000 Oe	300	284	255	238	206	195

Since Co^{2+} ions have high magnetocrystalline anisotropy than Ni^{2+} [106-107] thus it requires higher temperature to align magnetic moments in the direction of field so as to obtain greatest magnetization at T_B . However, the A.C. susceptibility data proves that with increase in cobalt content, the single domain region gets improved thus assisting the reason for the increase in T_B .

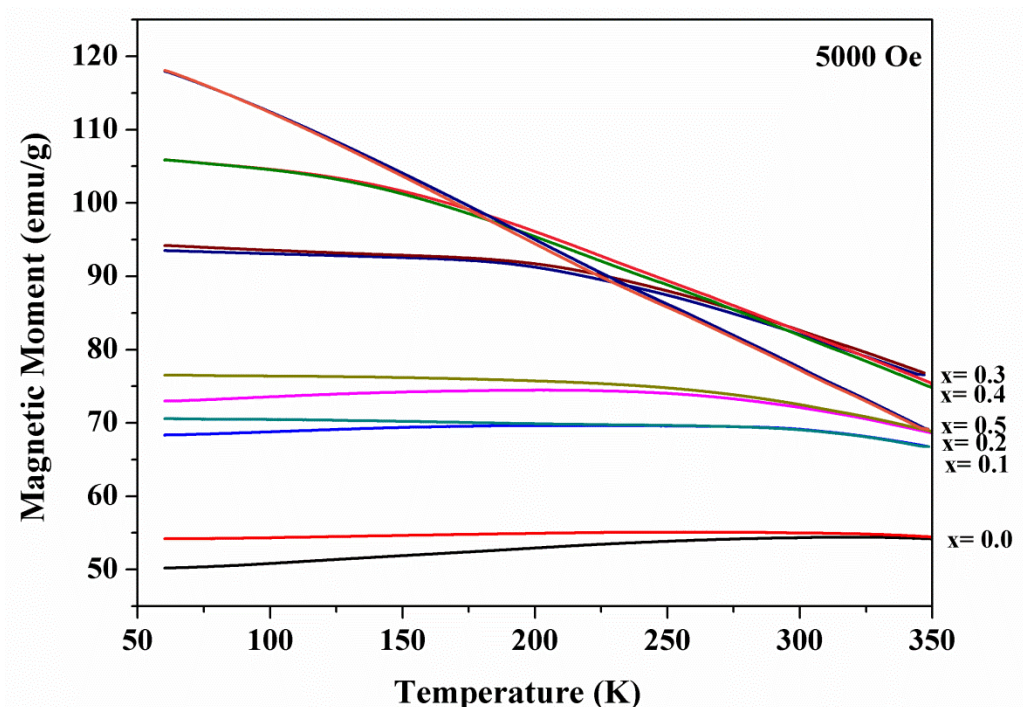


Fig. 5.40 Temperature-dependent (M-T) field cooled and zero field cooled (ZFC-FC) magnetization curves at the field of 5000 Oe for ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites.

The ‘sintered’ ferrite with all the compositions showed a decrease in the magnetization in FC measurements from 60 K to 350 K. However, certain samples showed continuous increase in the magnetization. The increase in the magnetization at lower temperature for FC measurements is due to the presence of non-interactive particles in this region and due to higher zinc concentration, a certain degree of magnetic frustration takes place in the glass spin state below T_B [108]. The T_{irr} was seen to decrease with increase in the zinc content for both the fields as observed for the ‘as prepared’ samples. The ZFC/FC plots show bifurcation at a higher field for the ‘sintered’ samples in comparison with their ‘as prepared’ analogues (increase in T_B and T_{irr}).

5.8 Applications of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites

5.8.1 Electrochemical Properties of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites

The investigation of the electrochemical properties of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites has been carried out by using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The ferrite sample working electrode fabrication has been already discussed in chapter 2 in detail.

The Fig. 5.41 demonstrates the CV curves for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites at varying scan rates between the potential window of 0.0-0.6 V and Fig. 5.42 depicts the plot of specific capacitance against scan rate for all the ferrite samples. Fig. 5.41 depicts nearly a duck-shaped (rectangular) curve with a pair of humps which implies pseudocapacitive behaviour of the ferrite material [109-110]. All the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrite samples have reduction peak in the positive area at around 0.2 V for reduction processes and the peak for the oxidation processes are seen nearly at 0.4 V [8, 111]. This is due to of faradaic nature, indicating pseudocapacitive behaviour of ferrites [109, 112] It was observed that the CV plots were more symmetrical and rectangular at a greater scan rates indicating highly reversible oxidation-reduction processes at the electrode interfaces [3]. Moreover, the redox peaks show a little shift towards higher potential with increasing scan rates which can be explained due to the predominant charge transfer process in the diffusion controlled charge-transfer system [113].

The specific capacitance (C_{sp}) at varying scan rates has been calculated and the values of the same are been tabulated in Table 5.17. From this Table it is obvious that the C_{sp} values were found to decrease with increasing scan rates. This can be explained due to the occurrence of inner active sites that do not participate in the redox process totally perhaps due to diffusion of proton within the electrode [3, 114]. This decrease in the C_{sp} values indicates that all the part of the working electrode is unattainable at higher charging-discharging rates, thus the C_{sp} gained at slower rates is considered to be close to the entire utilization of the working electrode [3]. However, the electrolytes do not have enough time to completely diffuse at a higher scan rate through the electrodes surface [115].

The C_{sp} values were calculated for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites and it was seen that even though all the ferrites have good specific capacitance

ranging from 28.81-56.98 F/g but the sample with the composition $x = 0.3$ has the highest value of C_{sp} at 10 mV/s scan rate, indicating a good pseudocapacitive behaviour.

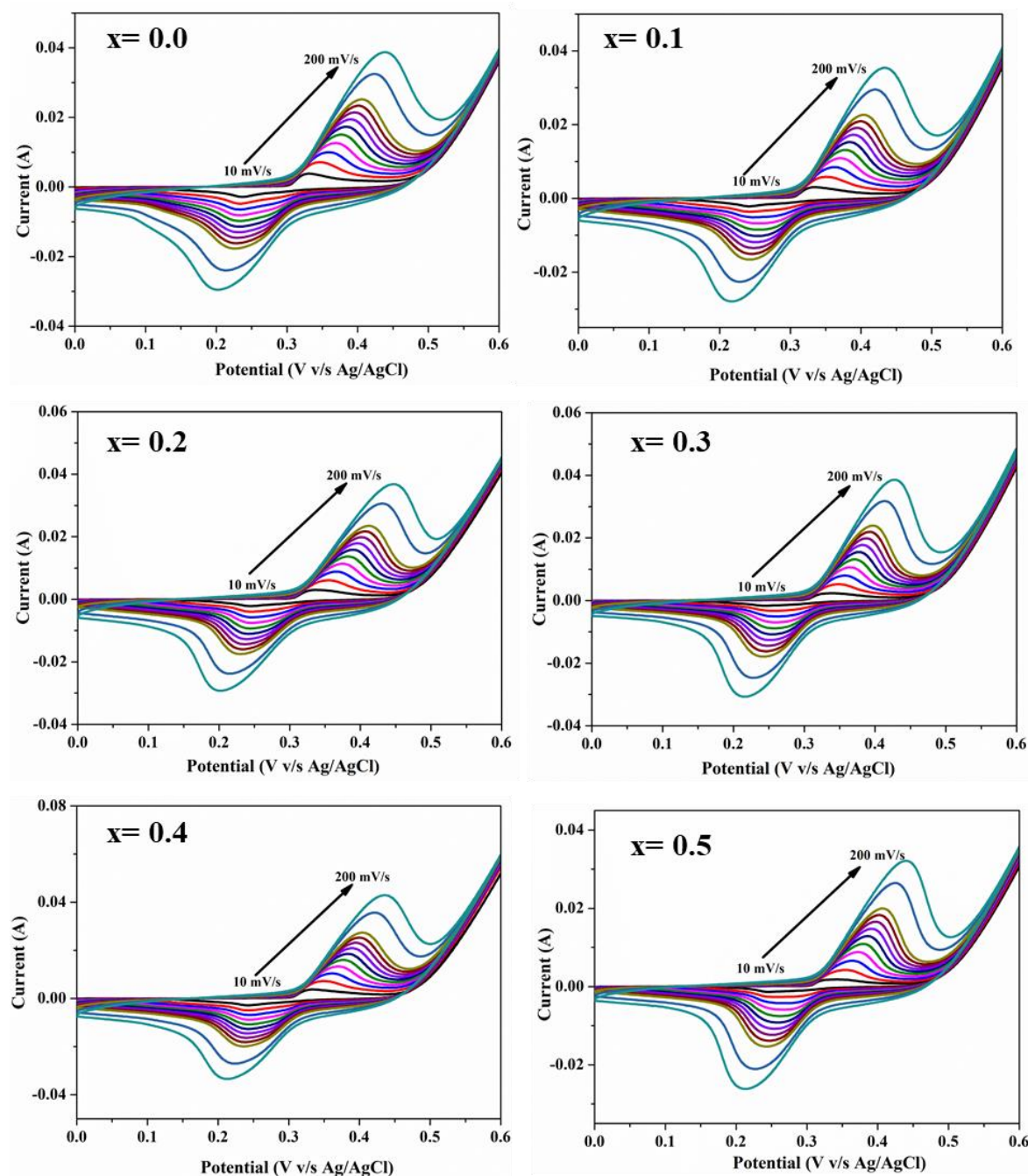


Fig. 5.41 Cyclic voltammograms of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites at varying scan rates ranging from 10 to 200 mV/s, with the potential window between 0.0-0.6 V.

CV studies imply that the zinc substituted nickel cobalt ferrites have favourable electrochemical properties with a properly developed CV curve and good specific capacitance. Hence, these findings suggest that these ferrite nanoparticles can be used to store energy.

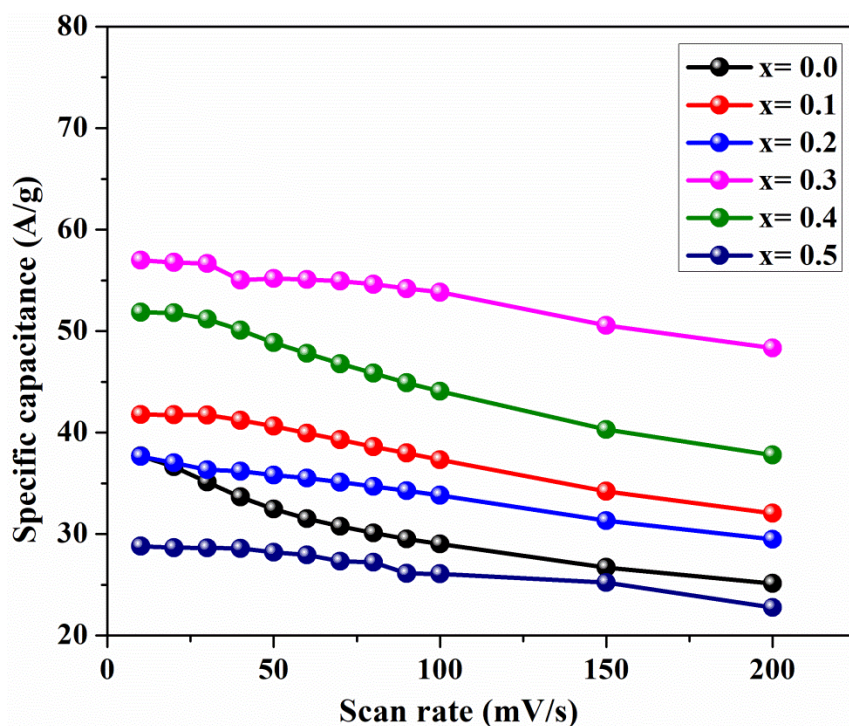


Fig. 5.42 The plot of specific capacitance against the scan rates plots for the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites.

The galvanostatic charge-discharge (GCD) technique is also a useful tool for accurately determining the electrochemical performance of the supercapacitors if the material has pseudocapacitive properties [116]. The evaluation of the pseudocapacitive nature of all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites samples was performed by GCD studies at varying current densities from 0.1 to 2.0 A/g (0.1 A/g, 0.25 A/g, 0.5 A/g, 0.75 A/g, 1 A/g and 2 A/g) as demonstrated in Fig. 5.43a and Fig. 5.43b. The GCD curves were found to show a distinct plateau having non-linear behaviour confirming pseudocapacitive nature of all the ferrite samples [117-118]. It was found that with increase in the current density the specific capacitance (C_{sp}) decreases as can be seen from the GCD plots. This can be interpreted as due to the diffusion effect of a proton inside the electrode, the presence of the inner active sites cannot fully sustain the redox transitions at a higher current density [62, 118]. The GCD curves for all the samples show non-linear nature and this can be linked to the electrochemical adsorption desorption (Quasi-reversible) redox reactions at the electrode/electrolyte interface [119-120]. Specific capacitance of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites samples at different current densities (Galvanostatic charge-discharge) has been given in Table 5.18

Table 5.17: Specific capacitance of the 'as prepared' $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x= 0.0-0.5$) ferrites samples at different scanning rates (cyclic voltammetry).

Scan rate (mVs^{-1})	Specific capacitance (C_{sp}) (in Fg^{-1}) for 'as prepared' $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x= 0.0-0.5$) ferrites					
(x)	0.0	0.1	0.2	0.3	0.4	0.5
10	37.72	41.77	37.66	56.98	51.85	28.81
20	36.63	41.76	37.02	56.77	51.81	28.65
30	35.13	41.73	36.33	56.65	51.19	28.64
40	33.66	41.21	36.19	55.03	50.09	28.59
50	32.47	40.64	35.81	55.18	48.87	28.21
60	31.51	39.94	35.51	55.08	47.80	27.94
70	30.76	39.30	35.11	54.93	46.78	27.32
80	30.10	38.61	34.70	54.61	45.85	27.23
90	29.52	37.99	34.27	54.19	44.90	26.12
100	29.03	37.32	33.82	53.83	44.07	26.09
150	26.71	34.22	31.32	50.56	40.30	25.23
200	25.14	32.05	29.48	48.34	37.79	22.77

It is observed that from all the 'as prepared' $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x=0.0-0.5$) ferrite compositions, the working electrode having $x= 0.3$ composition has a longer charge-discharge time displaying a good charge storage capacity.

Electrochemical impedance spectroscopy (EIS) technique was used to gain information about the electrical characteristic of all the ferrite samples in the frequency range of 100 kHz to 0.1 Hz. The Nyquist plot (Fig. 5.44) for all the ferrite samples show the impedance (Z') and the imaginary (Z'') part. EIS technique is useful in knowing the electrode/electrolyte interface as supercapacitors by investigating the equivalent series resistance and frequency behaviour.

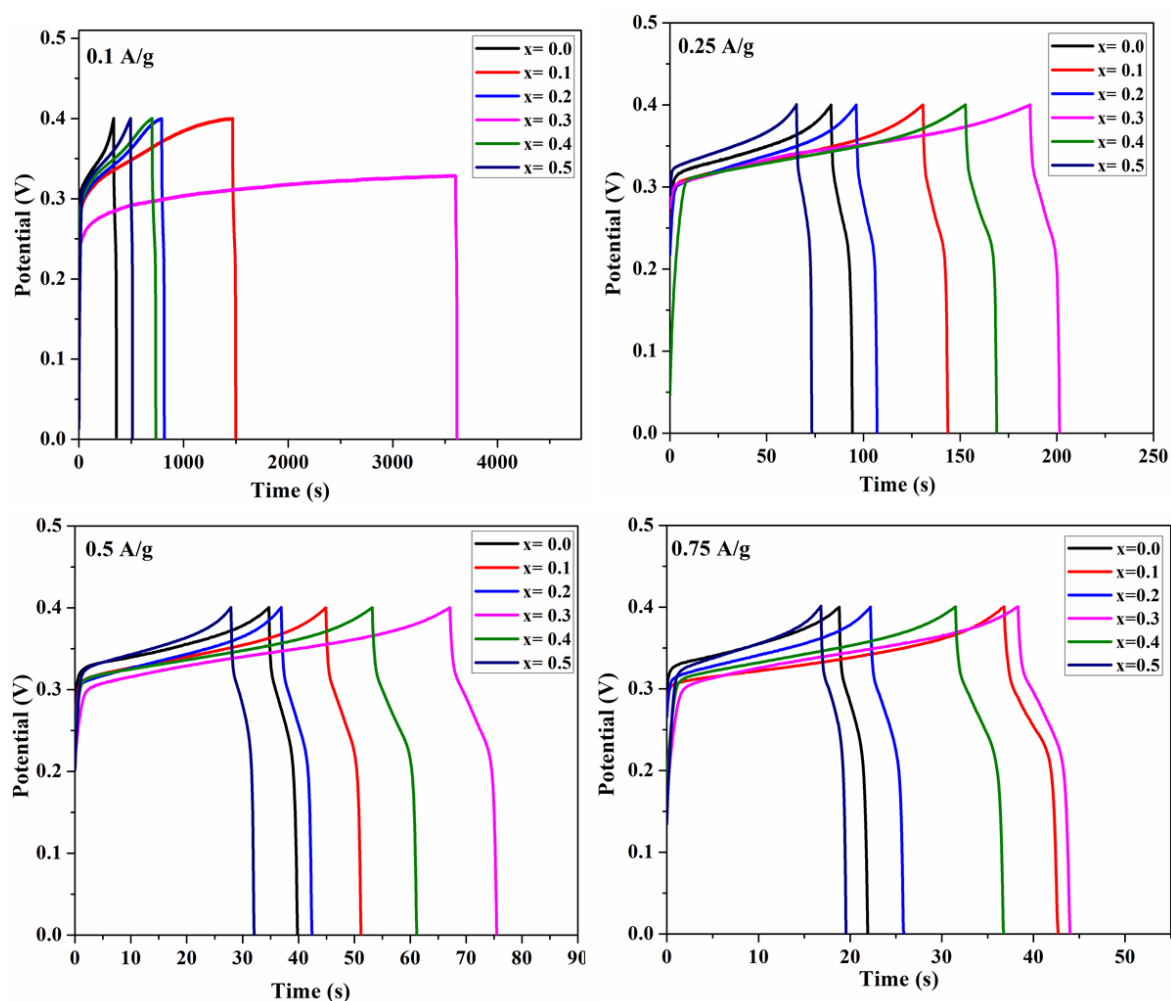


Fig. 5.43a Galvanostatic charge-discharge plots of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at charge-discharge current densities for 0.1, 0.25, 0.5 and 0.75 A/g

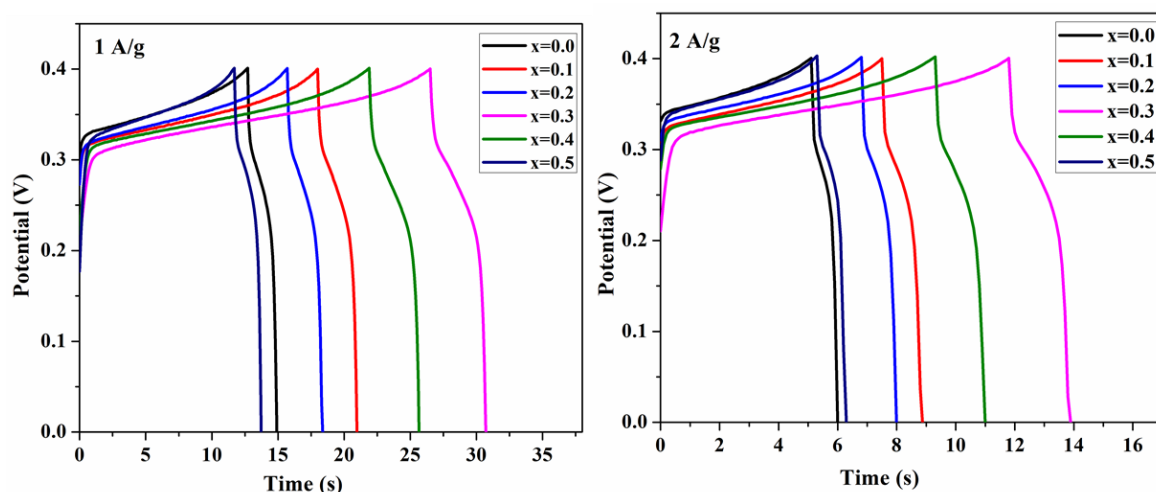


Fig. 5.43b Galvanostatic charge-discharge plots of ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites at charge-discharge current densities for 1.0 and 2.0 A/g.

Generally, a Nyquist plot has a semi-circular form; and the charge transfer resistance at the electrode/electrolyte interface illustrates the diameter of this semi-circle. However, the

obstacle to the charge-flow is decreased and hence the charge transfer process favours a smaller diameter (as seen in the Fig.5.44).

With rise in frequencies, the impedance values also increases indicating conductivity-loss in the ferrite nanoparticles. This behaviour can be anticipated due to restricted charge carrier mobility at a higher frequency [118, 121].

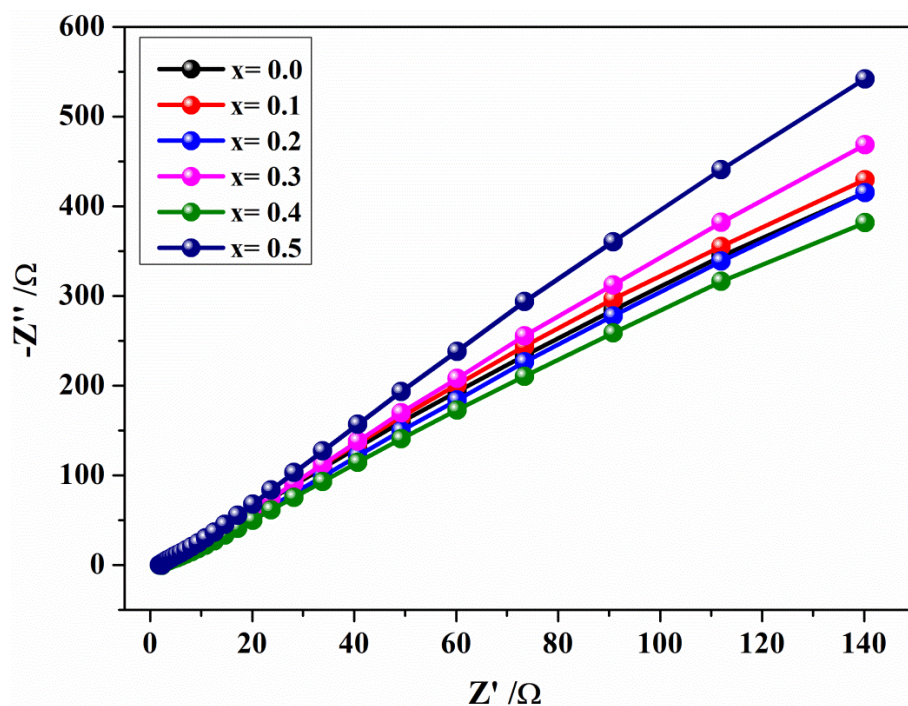


Fig. 5.44 Nyquist plots for ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites samples.

From the Nyquist plot it is observed that the EIS spectra intercepts nearly at 1.36-2.95 Ω of the real part of impedance (Z') illustrating the combined resistance of the solution (R_s) at higher frequencies [122-124]. Nevertheless, at lower frequencies the straight line nearly inclines at an angle of 45° with Z' axis called a Warburg impedance (W) which is associated to the diffusion and transportation of the counter ions in the electrode/electrolyte interface [117, 123, 162].

Table 5.18 Specific capacitance of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites samples at different current densities (Galvanostatic charge-discharge)

Current densities (x)	Specific capacitance (C_{sp}) (in Fg^{-1}) for ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites					
	0.0	0.1	0.2	0.3	0.4	0.5
0.1	34.51	72.64	47.43	118.58	76.12	36.69
0.25	33.28	61.87	46.07	115.51	73.00	35.42
0.5	31.43	57.87	44.87	114.85	72.11	33.90
0.75	29.58	54.35	44.47	113.95	71.22	33.65
1	28.35	53.41	43.26	113.69	64.63	32.58
2	22.18	49.85	38.46	112.18	60.54	32.00

5.8.2 Gas sensing properties of ‘as prepared’ $Ni_{0.5}Co_{1-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites

The ferrite gas sensing properties of ‘as prepared’ $Ni_{0.5}Co_{1-x}Zn_xFe_2O_4$ ($x = 0.0-0.5$) ferrites were examined with three different oxidizing and reducing gases like Cl_2 , NO_2 , NH_3 and LPG by investigating their response-recovery time. The thick films of the ferrites were prepared by following the procedure as mentioned in chapter 2 section 2.6.1.1. The optimum temperature is the temperature at which the ferrite thick film shows the highest response. The ferrite thick film with composition $x = 0.2$ was chosen as a representative sample to carry out the temperature optimization studies of the ‘as prepared’ $Ni_{0.5}Co_{1-x}Zn_{0.5x}Fe_2O_4$ ($x = 0.0-0.5$) ferrite samples. A standard gas concentration of 100 ppm was used for the temperature range from 50 °C to 150 °C.

Fig. 5.45 displays the representation of gas sensing response by $x = 0.2$ ferrite thick film for varying temperatures towards Cl_2 , NO_2 , NH_3 and LPG. From the figure it is observed that the response of the thick film increased till 50 °C after which it was found to decrease. As the temperature increases the thermal energy helps to overcome the activation energy barrier and thus the response increases; however with further increase in temperature the decrease in response can be due to surface adsorbed species on the thick film at a particular temperature and its interaction with the exposed gas. On the basis of these

observations, 50 °C was fixed as the optimum temperature for further studies by using the concentration of 100 ppm.

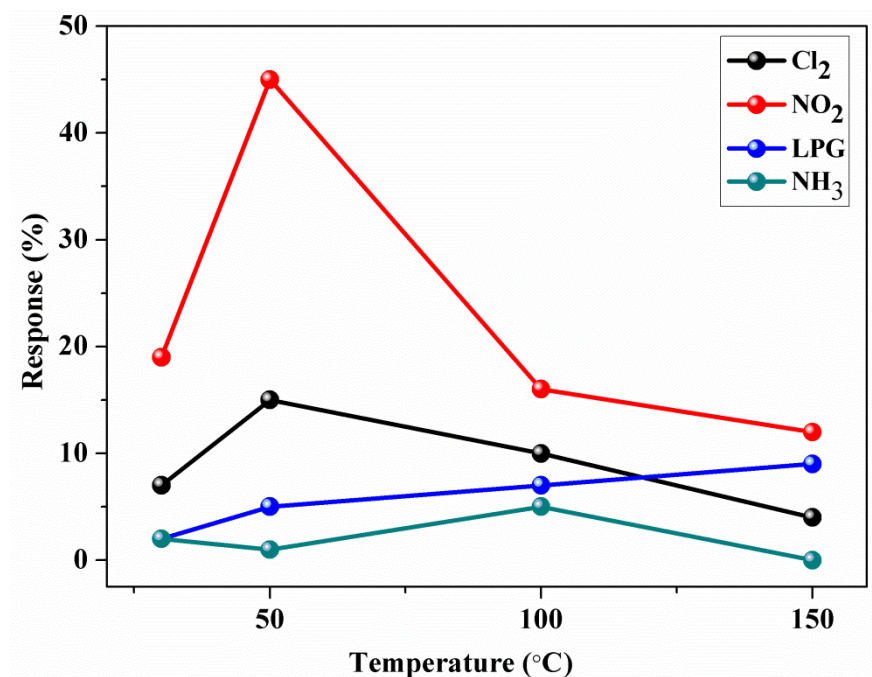


Fig. 5.45 Gas sensing response against temperature for $\text{Ni}_{0.5}\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.2$) ferrite thick film for various gases at different temperatures.

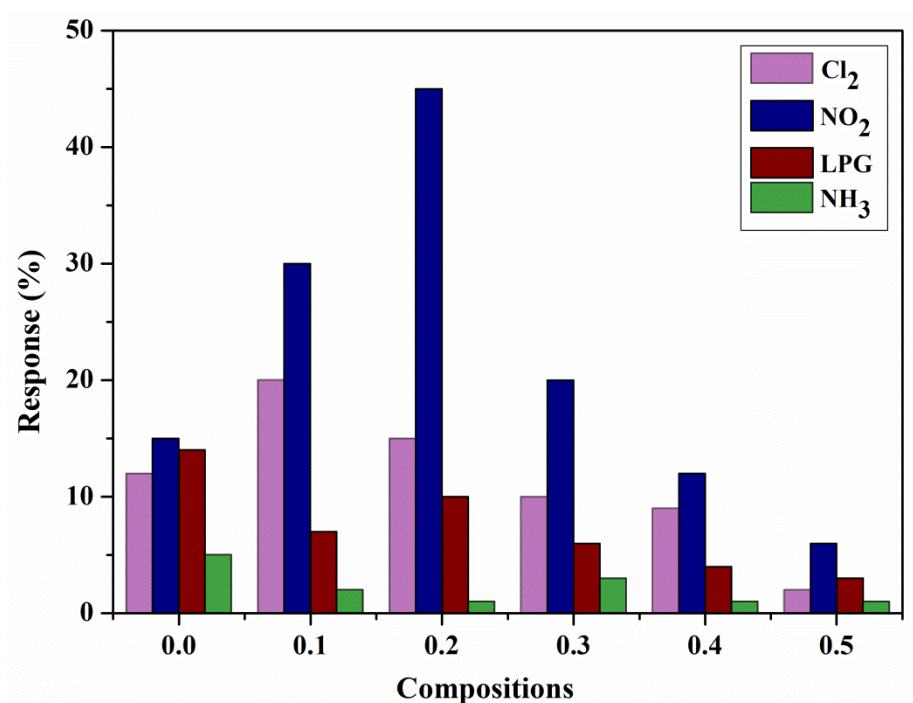


Fig. 5.46 Gas sensing response of $\text{Ni}_{0.5}\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites towards Cl_2 , NO_2 , NH_3 and LPG for 100 ppm of gases at 50 °C.

Fig. 5.46 shows the response carried out at 50 °C for all the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites compositions for all the gases at 100 ppm gas concentrations. The figure clearly shows that highest response was observed for NO_2 gas for all the compositions followed by Cl_2 and then LPG. However, almost negligible response was observed for NH_3 gas. The response for $x = 0.2$ thick film towards NO_2 gas was found to be highest i.e. almost 45 % at 50 °C. Besides Cl_2 also showed a good response of approximately 20 % for composition $x = 0.1$ but also an appreciable response towards NO_2 gas for the thick film which makes it less selective. The ferrite thick films also did not show any trend in the sensing responses with increase in zinc concentration.

The ferrite thick film $x = 0.2$ showed the highest response of 45 % for NO_2 gas with response time of 2 secs and recovery time of 4 seconds which is found to be the fastest response-recovery amongst all the compositions. Besides the composition $x = 0.1$ also shows a better response of almost 30 % however it also shows response for Cl_2 gas (20 %) making it less selective gas sensor. The reproducibility plot of $x = 0.2$ composition for 100 ppm gas concentration at 50 °C has been shown in the Fig. 5.47.

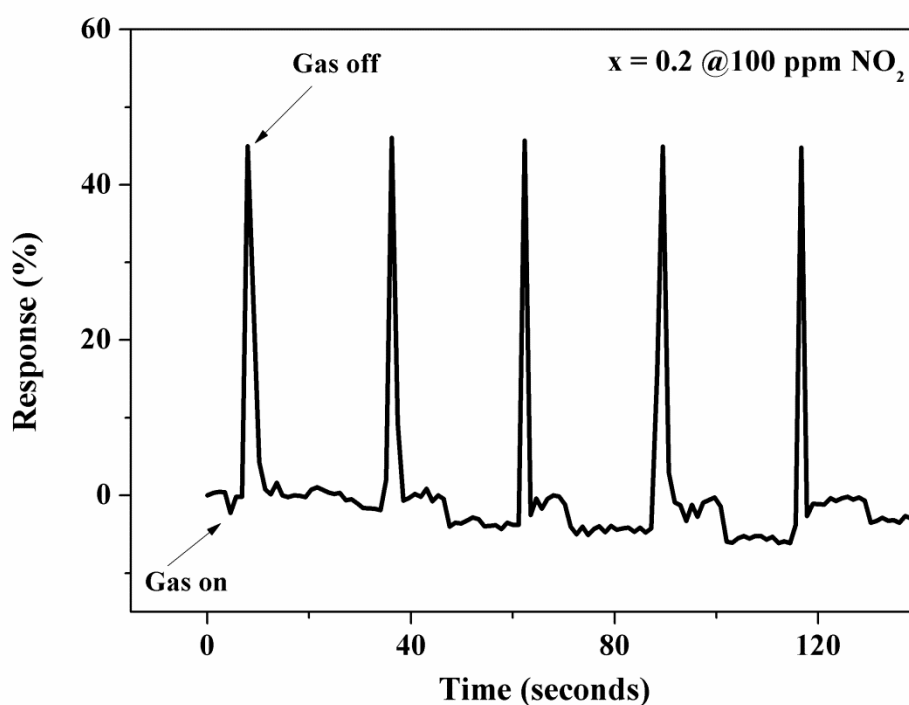


Fig. 5.47 The reproducibility plots of response-recovery against time for $\text{Ni}_{0.5}\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.2$) ferrite thick film towards NO_2 gas at 100 ppm at an operating temperature of 50 °C.

5.9 Conclusion

This chapter presents the synthesis, detailed characterization, properties, and applications of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites prepared via precursor-combustion method. The synthesized precursors were thoroughly characterized to confirm stoichiometry prior to ferrite formation. Phase purity, elemental composition, and oxidation states of the ‘as prepared’ ferrites were confirmed using powder XRD, MP-AES, IR, Raman, and XPS analyses, revealing single-phase cubic spinel structures. Zinc substitution led to an increase in lattice parameter without a definite trend in crystallite size. Morphological and surface analyses confirmed nanoscale particles with moderate surface area and active acidic-basic sites. Dielectric studies showed frequency and temperature-dependent behaviour, with dielectric properties decreasing upon zinc substitution. Magnetic investigations revealed a decrease in Curie temperature and coercivity, accompanied by enhanced magnetization and superparamagnetic behaviour at higher zinc content. Sintering improved crystallinity and particle growth while preserving spinel structure. Finally, the ferrites demonstrated promising electrochemical and gas-sensing performance, with $x = 0.3$ showing optimal specific capacitance.

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Chapter 6

Summary and conclusions

6.1 Summary of the thesis

This chapter deals with the summary of the thesis entitled ‘Synthesis, characterization and solid state properties of pure and substituted nickel-cobalt ferrites and their applications’. We have carried out the synthesis of three different series. The first series comprises of Ni-Co ferrites. Further in the second series, we have substituted Mg in the Ni-Co ferrites and in the third series we have substituted Zn in Ni-Co ferrites. Thus, the studies were carried out to find out the effect of the substitution on the properties of the Ni-Co ferrite samples. Besides this, we have also studied the sintering of all the ‘as prepared’ ferrite analogues.

Chapter 1

This chapter includes a short introduction of the ferrite samples accompanied by the literature survey on Ni-Co ferrites, Ni-Co-Zn ferrites and Ni-Co-Mg ferrites. Besides, we have also incorporated the literature survey of the electrochemical properties of the ferrites along with their gas sensing applications.

Chapter 2

This chapter addresses the methods of synthesis and the characterization techniques used for the characterization of the ferrite samples. Ni-Co ferrites and Mg substituted Ni-Co ferrites were synthesized using combustion method, while Zn substituted Ni-Co ferrites were synthesized using precursor-combustion method. The precursors were characterized using TG-DTA-DTG, CHNS analyzer, isothermal mass loss, IR, hydrazine estimation and chemical analysis have been mentioned. The various techniques used for characterization of the ‘as prepared’ and ‘sintered’ ferrite samples are also discussed in this chapter. Techniques such as powder XRD, Raman, IR, SEM/EDAX, HR-TEM, XPS, BET surface area, NH_3 -TPD and CO_2 -TPD were discussed. The study of solid state properties such as DC electrical resistivity, dielectric studies, AC susceptibility and magnetization studies were discussed. The details about the gas sensing instrument setup, fabrication of the thick film along with the instrumental setup for electrochemical studies and fabrication of the electrode is described in this chapter.

Chapter 3

This chapter deals with synthesis of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites, characterization, solid state properties and their applications. $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were

synthesized by combustion method using tartaric acid as fuel. Initially, optimization of the method was carried out using ten different optimization ratios. The thorough optimization studies were done like TG-DTA of melt, powder XRD before and after calcination, IR, VSM at room temperature and A.C. susceptibility for all these ten oxidizer: fuel ratios (fuel deficit and fuel excess ratios). After proper optimization studies the fuel ratio 1: 0.75 was used for the synthesis of the main series of ferrite compounds as it possessed lesser crystallite sizes with single phase, higher lattice constant values and single domain particle nature. The ‘as prepared’ samples were then sintered at 1000 °C for 10 h.

ICP-AES technique was used to affirm the stoichiometry of the ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites samples. The presence of all elements along with their quantitative detection was done using this technique. Powder XRD pattern of the ‘as prepared’ ferrite samples confirmed the formation of monophasic cubic spinel structures in all the ferrites. Parameters like lattice parameter, measured density, theoretical density, porosity and crystallite sizes were calculated using the data obtained from powder XRD patterns. The lattice parameter and crystallite size was found to decrease with increase in the nickel substitution. The IR and Raman spectra reported for the ‘as prepared’ ferrites affirmed the formation of monophasic ferrites as desired. The XPS spectra of the ‘as prepared’ ferrite samples were carried out and the deconvoluted spectra of few ferrites having compositions $x = 0.0, 0.3, 0.6, 0.8$ and 1.0 have been plotted. The oxidations states of all the corresponding elements were found out by using this technique. Also, the possibility of presence of Fe^{2+} ions in the ferrites is excluded. The specific surface area was found out using the BET measurements. The N_2 -adsorption-desorption isotherms were recorded for the ‘as prepared’ ferrite samples and the surface area was found to be in the range of 24 to $32 \pm 1 \text{ m}^2/\text{g}$. The presence of acidic and basic sites were found using NH_3/CO_2 -TPD and it was observed that the ‘as prepared’ samples exhibit strong, medium, weak acidic sites and medium and strong basic sites.

The morphological investigations were performed using HR-TEM and SEM techniques for the ‘as prepared’ samples. SEM images revealed that the particles are spherically shaped with agglomerations in the particles. Besides this, EDAX technique employed confirmed presence of desired metal ions on the ferrite surface without any impurity peak of any other element. The HR-TEM images revealed the particle sizes and somewhat distorted hexagonal shapes of the nanoparticles. The SAED patterns indicate clear

concentric bright rings which affirmed the nanocrystalline nature of the nanoparticles. The brightest spot having highest intensity was observed for the 311 peak.

The electrical resistivity for the 'as prepared' ferrites confirmed the semiconducting nature of the ferrites as the resistivity was found to decrease with increase in temperature. The resistivity values were found to decrease with increase in cobalt content. The dielectric properties (dielectric constant and dielectric loss tangent) of the 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were measured as a function of frequency at room temperature. The dielectric properties were found to be higher at lower frequencies and decrease with increase in frequencies. No particular trend was observed in the dielectric properties with nickel substitution however the compositions $x = 0.6$ and $x = 0.0$ showed the highest values for dielectric constant and dielectric loss, respectively. The dielectric properties were also investigated as a function of temperature at four different frequencies of 10 KHz, 100 KHz, 500 KHz and 1 MHz from room temperature to 500 °C. The dielectric properties remain constant at lower temperatures until a certain frequency and later at a certain temperature there is a sharp increase in the values of dielectric properties. The compositions 0.1 and $x = 0.4$ showed better values of dielectric constant and dielectric loss tangent for all the frequencies although no trend was seen in the dielectric properties upon nickel substitution.

Further magnetic investigations were done and the Curie temperature (T_c) was determined by A.C. susceptibility measurements. The T_c was found to increase from 773 to 863 K with increase in nickel content. This technique also helped in determining the domain nature of the particles and it was observed that compositions $x = 1.0, 0.9, 0.8, 0.7$ and 0.6 exhibit single domain nature of particles while the compositions $x = 0.5, 0.4, 0.3, 0.2, 0.1$ and 0.0 show single domain nature with Hopkinson's peak. The DC magnetization studies were carried out by VSM technique at two different temperatures 300 K and 60 K. The saturation magnetization (M_s), coercivity (H_c) and remnant magnetization (M_r) were found to decrease with increase in nickel concentration. The magnetocrystalline anisotropy was found to decrease with increase in cobalt content and the values were higher for measurements done at 60 K as compared to that at 300 K. The ZFC-FC measurements were performed at two fields of 5000 Oe and 10000 Oe. The blocking temperature (T_B) values at both the field were found to decrease with increasing nickel content and the values at 5000 Oe were found to be more than at 10000 Oe.

The ‘as prepared’ samples were sintered and characterizations of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x= 0.0-1.0$) ferrites samples were performed. Powder XRD peaks indicated that the peaks are sharper in ‘sintered’ samples as compared to that in the ‘as prepared’ ones. The porosity was found to decrease while crystallite size was found to increase upon sintering. Raman spectroscopy and the IR spectroscopy indicated the formation of the monophasic spinel ferrites. The morphology of the ‘sintered’ ferrite samples was evaluated using the SEM technique and it was revealed that the particles form larger agglomerates and the particle size increases upon sintering.

The DC resistivity of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x= 0.0-1.0$) ferrites was found to decrease with increase in temperature revealing the semiconducting nature of the ferrite samples. The dielectric properties of the ‘sintered’ samples showed a similar trend as shown for the ‘as prepared’ ferrite samples. The dielectric properties (dielectric constant and dielectric loss tangent) as a function of frequency were measured at room temperature and the values were found to decrease rapidly up to a certain frequency and later remained constant. The composition $x= 0.7$ and $x= 0.9$ of the ‘sintered’ ferrite samples were found to show higher values of the dielectric properties. Besides this, the dielectric properties were also determined as a function of temperature for four different frequencies as that of the ‘as prepared’ samples. It also showed the similar behavior as that of the ‘as prepared’ analogues, i.e. the dielectric properties were found to be constant at lower temperatures and later it was found to increase with increasing temperature. The highest values of dielectric constant and dielectric loss tangent was found to be for composition $x= 0.0$.

The Curie temperature of the ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x= 0.0-1.0$) ferrites were evaluated and the T_c were found to increase from 770 K to 850 K. Besides, all the ‘sintered’ samples show multi-domain particle nature. The VSM measurements for the ‘sintered’ samples show similar trend as that of the ‘as prepared’ ferrite samples. The M_r , M_s and H_c values were found to decrease with increase in nickel content. The magnetocrystalline anisotropy (K_{eff}) was also found to decrease with increasing content and the values were found to be more for VSM studies done at 60 K than at 300 K. T_B values were found to be higher for the ‘sintered’ ferrites at both the fields (5000 Oe and 10000 Oe). The M_s values were found to be higher in ‘sintered’ ferrites as compared to that in the ‘as prepared’ ferrites.

The ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites were tested for application as gas sensors and supercapacitors. The ferrites were fabricated as working electrode and three electrode systems was used to investigate the electrochemical performance of the samples. The composition $x = 0.3$ shows the highest C_{sp} values of 84.95 F/g at a scan rate of 10 mV/s using cyclic voltammetry measurements. The gas sensing applications were carried out by preparing the thick film of the ‘as prepared’ ferrite samples and testing gases like Cl_2 , NO_2 , NH_3 and LPG at four different temperatures ie. 30 °C, 50 °C, 100 °C and 150 °C.

Chapter 4

This chapter focusses on the synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites their characterization, solid state properties and their applications. The ferrites samples were synthesized by combustion method using L-tartaric acid dihydrazide as a novel fuel. The optimization studies of the middle composition $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrite were done using five different optimization ratios. The complete optimization studies were done of the fuel deficit ratios using TG-DTA of the melt; powder XRD, IR and A.C. susceptibility measurements set up. After the optimization studies we chose to synthesize the main ferrite $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) series by using the oxidizer to fuel ratio of 1: 0.175 taking into account parameters like single domain particle nature, lower crystalline sizes, higher lattice constant and single phase formation in XRD without impurity in this fuel ratio.

The elemental composition and the stoichiometry of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites was confirmed using the ICP-AES technique. The percentages of nickel, cobalt, magnesium and iron were determined and the experimental percentages were found to match closely with the theoretical ones. The single phasic nature of all the ferrite samples has been affirmed by powder XRD studies. The lattice constant was found to increase with increasing magnesium substitution. The crystallite size was calculated using Scherrer’s formula and the values show that the crystallite size was decreasing with increasing magnesium content. The IR spectra determined the presence of two characteristic peaks in at 400 cm^{-1} and 600 cm^{-1} , respectively for octahedral and tetrahedral sites which are characteristic of a spinel structure. Moreover, Raman spectroscopy also confirmed the formation of single phase spinel ferrite without any impurity peak.

The oxidation states of all the ‘as prepared’ ferrite samples ($x = 0.0-0.5$) were determined using XPS technique and the deconvoluted spectra was plotted for all the elements after removing the binding energy values for C 1s for peak corrections. The N_2 -adsorption-desorption isotherms were reported for all the ‘as prepared’ ferrite samples using BET surface area measurements. The BET surface area was found to be in the range of $27.00-34.45 \pm 1 \text{ m}^2/\text{g}$ and the surface area was found to increase with increase in magnesium content. NH_3/CO_2 -TPD studies determined the presence of acidic and basic sites in the ferrite samples. It was observed that the ‘as prepared’ ferrite possess weak, medium and strong active acidic sites and weak, medium and strongly active basic sites. HR-TEM analysis revealed the morphology of the ‘as prepared’ samples. The HR-TEM images revealed that the ferrite nanoparticles are almost distorted hexagonal in shape and exist as loose agglomerates. Besides, the SAED patterns showed apparent concentric rings and brighter ring is seen for the 311 peak.

The dielectric properties (dielectric constant and dielectric loss tangent) of the ‘as prepared’ $Ni_{0.5}Co_{0.5-x}Mg_xFe_2O_4$ ($x = 0.0-0.5$) ferrites were measured as a function of frequency at room temperature. The dielectric values for all the ferrite samples were found to be higher at lower frequencies which decrease abruptly with increase in frequency. The composition $x = 0.3$ showed the highest values of dielectric constant and we did not get any trend for the dielectric constant with increase in magnesium content. Also, the dielectric loss tangent also did not show any trend with increasing magnesium substitution however the highest value was obtained for $x = 0.2$ composition. Besides, some ferrite samples also displayed the relaxation peaks which could be ascribed to the interfacial polarization and multiple valences of the ionic relaxations. The investigations of the dielectric properties with respect to temperature at four different frequencies 250 KHz, 500 KHz, 750 KHz and 1 MHz from 30°C to 500°C were done. The dielectric constant and the dielectric loss tangent were found to remain constant at lower temperatures and with rise in temperature the values increase abruptly. The dielectric properties (dielectric constant and dielectric loss tangent) were found to decrease with increase in magnesium substitution and the highest values were obtained for $x = 0.0$ composition. The A.C. susceptibility measurements determined the magnetic studies and T_c was found out. The T_c was found to decrease from 809 K to 725 K with increase in magnesium concentration. The composition $x = 0.0$ exhibits single domain particle nature with Hopkinson’s peak, the compositions from $x = 0.0$ to $x = 0.4$ showed a mixture of

superparamagnetic to single domain nature and the composition $x = 0.5$ shows superparamagnetic nature.

The ‘sintered’ analogues of the ferrite samples viz. ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) were checked for their phase purity using the powder XRD technique and the XRD patterns reveal formation of single phasic cubic spinel structure. The values of the lattice constant are in the range of 8.3622- 8.3670 Å and the crystallite sizes were found to increase upon sintering. The Raman spectroscopy also affirmed the formation of single phase spinel ferrites in all the ‘sintered’ ferrite samples.

The dielectric measurements were carried out as a function of frequency for all the ‘sintered’ ferrite samples at room temperature. The dielectric values were found to decrease rapidly upto a certain frequencies and then remain constant. The compositions $x = 0.4$ and $x = 0.5$ showed the highest values of dielectric constant and dielectric loss tangent, respectively and they were not found to show any specific trend with increase in magnesium concentration. The dielectric properties as a function of temperature were evaluated at frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C for all the ‘sintered’ ferrite samples. The ferrites also follow the trend shown by their ‘as prepared’ analogues wherein the dielectric properties at lower temperature were found to remain constant and later were found to increase promptly at certain higher temperature. The dielectric constant and the dielectric loss tangent values were found to be highest for $x = 0.0$ compositions and the values were found to decrease with increasing magnesium content. The Curie temperatures of the ‘sintered’ ferrite samples were found to decrease with increasing magnesium substitution and all the ferrite samples showed multi-domain particle nature.

The ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were tested for their electrochemical performance using CV, GCD and EIS techniques. Three electrode system was used for the analysis after fabricating the ‘as prepared’ ferrites on to a nickel foam. The composition $x = 0.3$ showed the highest values of specific capacitance of 127.32 F/g at a scan rate of 10 mV/s.

Chapter 5

This chapter deals with synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites, characterization, solid state properties and their applications. The ferrite synthesis was

performed using precursor-combustion method and the $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ($x = 0.0-0.5$) precursors were characterized soon after their synthesis since the shelf life of the precursors was very short. The carbon, hydrogen and nitrogen content in the precursors were found out and it was observed that the experimental values of the CHN analysis are in the close proximity with the theoretical values. The IR and TG-DTA-DTG were recorded soon after the precursor synthesis. Besides, hydrazine estimation and isothermal mass loss studies were done along with simultaneously recording of the IR at various temperatures. Thus after carrying out all the characterizations of the precursors the stoichiometry of the precursor was confirmed.

The presence of corresponding metal ions viz. Ni, Co, Zn and Fe in 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrite was confirmed using the MP-AES technique and the experimental data closely matched with the theoretical data. The powder XRD patterns showed formation of cubic spinel ferrites without any impurity element peak. The lattice parameter was found to increase from 8.3502 Å for $x = 0.0$ ferrite to 8.3769 Å for zinc substituted Ni-Co ferrite ($x = 0.5$). The crystallite sizes were found to be in the range of 36–48 nm without any specific trend upon increasing zinc substitution in the nickel cobalt ferrites. The infra-red spectra of the 'as prepared' ferrites showed two characteristic peaks around 400 cm^{-1} and 600 cm^{-1} characteristic of all the spinel ferrites. Raman spectra affirmed the formation of single phase spinel which eliminated the possibility of the presence of extrinsic iron oxide phases.

The oxidation states for all the elements for the 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-0.5$) ferrites were validated using the XPS technique. The deconvoluted spectra for all the elements were plotted after removing the binding energy of carbon 1s. XPS also excludes the possibility of Fe^{2+} in the ferrites. The BET surface area set up was used to measure the N_2 -adsorption-desorption isotherms for all the 'as prepared' ferrites. The values were found to be in the range of $7.0-18.32 \pm 1\text{ m}^2/\text{g}$ and there is no trend as such observed with increase in zinc substitution. The average pore sizes were found to be in the range from 13.63 to 28.53 nm. NH_3/CO_2 -TPD measurements determine the presence of surface active sites on the ferrite surface. It was seen from the plots that the ferrite samples have weak, medium and strong acidic sites and the presence of medium and strong basic sites.

The morphology of the 'as prepared' ferrite samples was evaluated using SEM analysis and the image revealed formation of nanosized ferrites having somewhat spherical

morphology and showing some agglomerations. The EDAX analysis done on ferrite samples confirms the presence of metal ions of Ni, Co, Zn and Fe on the ferrite surfaces. The HR-TEM images reveal nearly cuboidal shaped nanoparticles having varying particle sizes which range from 30-45 nm and which were found to be in good agreement with the powder XRD data. The ferrite samples demonstrate concentric rings in the SAED pattern that are indexed for all the peaks in powder XRD diffraction patterns and the brightest spot was seen for the highest intensity 3 1 1 peak.

The dielectric properties (dielectric constant and dielectric loss tangent) of the 'as prepared' $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) were evaluated at room temperature as a function of frequency. The dielectric values were found to be higher at lower frequencies and later they were found to decrease and ultimately remain constant at a higher frequency. The dielectric constant and the dielectric loss tangent values were found to be highest for $x= 0.0$ composition. The dielectric investigations were also performed as function of temperature at constant frequencies of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C. It was determined that the values were found to remain constant almost up to 300 °C but later tend to increase with temperature for all the ferrite samples. The highest values of dielectric constant and dielectric loss tangents were found to be for $x= 0.0$ composition and the values were found to decrease with increasing zinc substitution ($x= 0.5$).

Furthermore, the magnetic investigations were carried out using A.C. susceptibility measurement set up on all the ferrites. The T_c obtained from it was found to be in the range of 859 K to 809 K and T_c was found to decrease with increase in zinc substitution. For $x= 0.0$, the single domain type of behaviour with Hopkinson's peak was observed while compositions from $x= 0.1$ to $x= 0.4$ showed a mixture of superparamagnetic and single domain particles and $x= 0.5$ compositions showed the superparamagnetic nature of particles. The VSM measurements were also performed to carry out the magnetizations of the 'as prepared' ferrite samples at two different temperatures of 300 K and 60 K. The M_s , and M_r values were found to increase with increase in zinc substitution while the H_c values were found to decrease as the zinc content increases. The K_{eff} was also found to decrease as zinc concentration increases and the values were found to be greater for 60 K VSM analysis as compared to the measurements done at 300 K. The ZFC-FC curves were plotted for two fields of 2000 Oe and 3000 Oe and T_B was found to decrease upon

increasing zinc substitution. The values for T_B were more for 2000 Oe field than the values at the field of 3000 Oe.

The ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites were then sintered at 1000 °C for 10 h and the characterization of the sintered ferrites was done. The powder XRD patterns show sharper peaks in the ‘sintered’ samples. The crystallite sizes increased while the porosity was also found to decrease upon sintering of the samples. The lattice parameter values were found to decrease with increase in zinc content. The Raman IR spectroscopy indicated presence of the pure phased spinel ferrites. The morphology of the ‘sintered’ ferrites was determined using SEM analysis and it was observed that the particles appear as larger agglomerates upon sintering. Besides, EDAX determined the presence of desired elements in the ferrite samples.

The dielectric properties (dielectric constant and dielectric loss tangent) also showed similar trend as that for the ‘as prepared’ ferrite samples when the measurements were done with respect to frequency. The dielectric properties were found to decrease as the frequency increases. For the ‘sintered’ ferrites the dielectric properties did not show any specific trend upon zinc substitution. Moreover, the properties were also evaluated as a function of temperature at four constant fields of 250 KHz, 500 KHz, 750 KHz and 1 MHz from room temperature to 500 °C. No specific trend was seen upon increase in zinc content from the temperature profiles, however the highest values for both dielectric constant and dielectric loss tangent were seen for $x=0.4$ ferrite composition.

The T_c was found to decrease as the zinc content increases for the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites. All the ferrites showed multidomain particle nature. The ‘sintered’ ferrites also exhibit same trend for the VSM magnetic measurements as that of the ‘as prepared’ ferrites i.e. M_r and M_s were found to increase with increase in zinc substitution and H_c values were found to decrease. Besides, K_{eff} was found to decrease with increasing zinc content and the highest values were obtained for measurements done at 60 K. Also, T_B values at both fields of 3000 Oe and 5000 Oe are found to be higher in ‘sintered’ ferrites than the ‘as prepared’ ferrites (done at 2000 Oe and 3000 Oe).

The ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites were then checked for the applications in electrochemistry and as gas sensors. The fabrication of the working electrode was done using nickel foam and the ferrite was deposited on it. The three electrode system was used to evaluate the electrochemical processes such as CV, GCD

and EIS. The composition $x = 0.3$ showed highest value of specific capacitance of 56.98 F/g. The gas sensing applications of the 'as prepared' ferrites were also carried out after preparing the thick films of the ferrite samples and testing gases such as Cl_2 , NO_2 , NH_3 and LPG.

Chapter 3: 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites

Table 6.1 Various parameters for 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0-1.0$) ferrites at different compositions

Compositions →		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Lattice parameter (Å)		8.3693	8.3757	8.3722	8.3666	8.3563	8.3488	8.3468	8.3344	8.3376	8.3393	8.3282
Porosity (%)		45.35	45.37	44.72	44.78	45.48	46.19	45.48	45.00	45.81	44.84	45.81
Crystallite size (nm)		21	20	19	18	18	16	16	17	17	17	15
Surface area (m^2/g)		26.10	27.85	26.06	24.85	27.00	26.80	29.50	30.00	31.50	31.00	30.00
Curie temperature (K)		773	783	789	792	797	821	824	830	839	846	863
Ms	60 K	77.16	72.22	66.58	60.80	53.68	52.97	50.20	47.25	43.09	41.18	40.14
	300 K	72.57	64.58	60.35	58.19	51.44	49.07	46.64	44.47	42.83	37.10	35.46
Mr	60 K	62.86	61.04	53.48	48.24	41.67	36.50	32.68	26.18	22.02	20.15	14.63
	300 K	29.73	24.43	21.24	20.16	16.41	12.00	9.86	7.92	6.28	5.88	4.26
Hc	60 K	13051	12703	12106	11608	10339	9631	8223	6747	4751	2545	376
	300 K	1381	1306	1281	1107	933	711	650	400	299	198	112

T_B	5000 Oe	298	294	288	285	283	278	271	262	231	177	143
T_B	10000 Oe	251	247	240	233	229	223	216	184	165	130	96
Applications												
C_{sp} (CV) (in F/g) at 10 mVs ⁻¹ scan rate		51.47	73.76	61.89	84.95	63.16	69.11	61.41	52.91	62.07	37.35	42.11
C_{sp} (GCD) at 0.1 current density		54.34	91.78	62.64	91.92	72.11	84.57	73.71	61.18	90.12	32.94	32.91
Gas sensing	The maximum gas sensing response is shown by $x=0.0$ composition at 50 °C for 100 ppm of Cl₂ gas with shortest response time of ~ 3 seconds and recovery time of ~ 5 seconds. The thick film with $x=0.2$ composition also showed good response for 100 ppm of NO₂ gas having shortest response and recovery time of ~ 4 seconds and ~ 6 seconds, respectively at 50 °C.											

Table 6.2 Various parameters for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$) ferrites at different compositions

Compositions →		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Lattice parameter (Å)		8.3886	8.3837	8.3738	8.3724	8.3679	8.3621	8.3598	8.3581	8.3542	8.3510	8.3482
Porosity (%)		36.22	40.76	39.98	38.98	41.33	42.60	41.48	44.24	44.31	45.23	41.93
Crystallite size (nm)		50	52	49	52	50	46	56	47	47	46	45
Curie temperature (K)		770	780	786	790	793	817	820	825	830	835	850
Ms	60 K	80.36	79.38	72.15	70.80	65.99	67.78	63.39	62.62	58.57	56.45	52.31
	300 K	79.52	78.66	71.69	69.02	63.58	66.25	62.33	57.70	54.43	52.02	47.88
Mr	60 K	63.10	59.05	55.39	53.85	52.61	51.67	47.44	45.76	40.75	33.81	23.50
	300 K	31.25	30.64	29.86	26.81	25.22	24.64	23.85	22.85	20.92	18.65	16.52
Hc	60 K	6393	5595	5361	4070	3718	3623	3155	2569	1091	504	293
	300 K	1066	844	804	719	789	606	554	321	253	178	98
T _B	5000 Oe	344	338	330	328	324	320	311	292	282	256	235
T _B	10000 Oe	295	290	284	283	279	277	229	217	211	206	142

Chapter 4: 'as prepared' $\text{Ni}_x\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites

Table 6.3 Various parameters for 'as prepared' $\text{Ni}_x\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites at different compositions

Compositions $\longrightarrow$	0.0	0.1	0.2	0.3	0.4	0.5
Lattice parameter ($\text{\AA}$)	8.3442	8.3458	8.3476	8.3519	8.3569	8.3593
Porosity (%)	41.36	45.15	42.54	51.11	34.28	33.86
Crystallite size (nm)	21	20	20	20	17	18
Surface area (m^2/g)	27.00	27.88	30.20	32.90	34.20	34.45
Curie temperature (K)	809	798	773	757	748	725
Applications						
C_{sp} (CV) (F/g) at 10 mVs^{-1} scan rate	72.89	55.76	72.63	127.32	48.77	35.05
C_{sp} (GCD) at 0.1 (F/g) current density	79.95	100.42	95.65	316.95	75.98	29.33

Chapter 4: ‘sintered’ $\text{Ni}_x\text{Co}_{0.5-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferritesTable 6.4 Various parameters for ‘sintered’ $\text{Ni}_x\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites at different compositions

Compositions $\longrightarrow$	0.0	0.1	0.2	0.3	0.4	0.5
Lattice parameter ($\text{\AA}$)	8.3622	8.3635	8.3647	8.3658	8.3662	8.3670
Porosity (%)	45.03	34.38	37.38	43.05	31.20	20.41
Crystallite size (nm)	112	120	115	116	111	117
Curie temperature (K)	795	787	762	751	745	720

Chapter 5: ‘as prepared’ $\text{Ni}_x\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferritesTable 6.5 Various parameters for ‘as prepared’ $\text{Ni}_x\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites at different compositions

Compositions $\longrightarrow$		0.0	0.1	0.2	0.3	0.4	0.5
Lattice parameter ($\text{\AA}$)		8.3502	8.3570	8.3584	8.3622	8.3679	8.3769
Porosity (%)		25.96	27.03	27.66	26.47	24.35	13.23
Crystallite size (nm)		43	48	45	43	40	36
Surface area (m^2/g)		18.32	11.48	11.76	10.98	7.00	12.07
Curie temperature (K)		859	856	841	829	813	809
Ms	60 K	55.37	74.10	81.38	88.55	98.26	103.69
	300 K	52.54	56.44	58.26	63.12	67.03	70.57

Mr	60 K	43.21	52.68	54.71	56.89	61.25	63.78
	300 K	16.25	17.26	18.61	21.27	22.81	24.09
Hc	60 K	7965	4399	2803	1818	973	222
	300 K	958	509	251	141	98	63
T _B	2000 Oe	320	315	265	218	165	120
T _B	3000 Oe	291	260	224	184	118	72
Applications							
C _{sp} (CV) (in F/g) at 10 mVs ⁻¹ scan rate		37.72	41.77	37.66	56.98	51.85	28.81
C _{sp} (GCD) at 0.1 current density		34.51	72.64	47.43	118.58	76.12	36.69
Gas sensing		The x= 0.2 ferrite thick film showed highest response towards NO ₂ gas of almost 45 % at 50 °C with better selectivity.					

Chapter 5: 'sintered' $\text{Ni}_x\text{Co}_{0.5-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites

Table 6.6 Various parameters for 'sintered' $\text{Ni}_x\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0-0.5$) ferrites at different compositions

Compositions →		0.0	0.1	0.2	0.3	0.4	0.5
Lattice parameter (Å)		8.3888	8.3837	8.3741	8.3725	8.3686	8.3565
Porosity (%)		19.51	15.03	24.00	14.97	14.54	04.15
Crystallite size (nm)		50	52	52	50	52	51
Curie temperature (K)		817	776	737	703	658	586
Ms	60 K	69.32	81.73	96.03	107.09	111.13	119.36
	300 K	65.70	74.27	76.30	78.32	81.31	83.13
Mr	60 K	22.56	24.87	25.89	26.87	27.12	29.00
	300 K	18.35	19.65	21.56	24.86	25.66	27.45
Hc	60 K	1132	858	360	256	207	146
	300 K	501	356	248	182	59	30
T _B	3000 Oe	340	318	307	286	274	256
T _B	5000 Oe	300	284	255	238	206	195

Appendix I

List of Publications

1. M.U Sawal, V.M.S.Verenkar, An insight into the nanosize and bulk $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites through their comparative study: Structural and magnetic investigations, J. Mater. Sci.: Mater Electron. 32 (2021) 21350-21367.

doi: 10.1007/s10854-021-06639-2

Manuscript under preparation

1. An investigative approach towards designing nanostructured nickel substituted cobalt ferrites as effective gas sensor and supercapacitor electrodes

Appendix II

List of Conference Publication and Workshop Attended

1. M. U. Sawal, V.M.S Verenkar, 'An investigation towards designing nanostructured cobalt substituted nickel ferrite via precursor- combustion triggered synthesis route' (**Poster**), National Conference on Advances in Material Science (AMS-2024) organized by Department of Chemistry & Cluster Research Centre, Khandola in collaboration with Directorate of Higher Education, Government of Goa from 09th to 10th February 2024 (**Third place was awarded for this poster**)
2. M.U. Sawal, V.M.S. Verenkar, 'Exploring the structural, dielectric and magnetic properties of 'as prepared' and 'sintered' nickel substituted cobalt ferrite through its comparative study' (**Poster**), International Conference on Advanced Materials: Properties and Applications (ICAM-2023) organized by School of Physical and Applied Sciences and School of Chemical sciences, goa university from 20th-24th February 2023
3. M.U. Sawal, V.M.S. Verenkar, 'Formulating nanosized nickel substituted cobalt ferrite via combustion-induced route for enhanced gas sensing performance as a selective gas sensor for chlorine gas' (**Poster**), DAE-BRNS 9th Interdisciplinary Symposium on Materials Chemistry (ISMC-2022) organised by DAE Convention centre, BARC Mumbai-400094, India from 07th-10th December 2022.
4. M.U. Sawal, V.M.S. Verenkar, 'An investigative approach towards the comparative study of nanostructured $\text{Ni}_{0.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite with its bulk counterpart synthesized via precursor-combustion triggered route' (**Poster**), DAE-BRNS 23rd Symposium on Thermal Analysis (THERMANS-2022) organized by Department of Physics, Khalsa College, Amritsar, Punjab, India from 03rd-05th November 2022 (**Best poster award**).
5. M.U. Sawal, V.M.S. Verenkar, 'Combustion Triggered Route for Synthesizing Nanostructured Nickel Substituted Cobalt Ferrites: Investigations on their Structure, Morphology, Electric, Dielectric and Magnetic Properties' (**Online mode-Poster**), DAE-BRNS sponsored 8th Interdisciplinary Symposium on Materials Chemistry (ISMC-2020) organized by Chemistry Division, Bhabha Atomic Research center, Mumbai and Society for Materials Chemistry from 17th-19th June 2021
6. M.U. Sawal, V.M.S. Verenkar, 'Employing Tartaric Acid as a fuel for the synthesis of single-phase nano sized $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.2, 0.4, 1.0$) by Combustion method, their characterization and study of the solid-state properties' (**Poster**), 3rd National Conference on New Frontiers in Chemistry- From Fundamentals to Applications-III (NFCFA-2019) organized by Department of Chemistry, BITS PILANI K K Birla Goa Campus, Goa from 20th -22nd December 2019
7. M.U. Sawal, V.M.S Verenkar, 'Employing Tartaric Acid as a fuel for the synthesis of single phase Nano sized Nickel substituted Cobalt ferrite by combustion method, their

characterization and study of the solid state properties' (**Poster**), Two-day workshop on Material Science by Directorate of International Cooperation and Exchange (DICE) and Directorate of Research, Development and Resource Mobilization (DRDRM) organized by University of Porto, University of Coimbra and Goa University from 18th -19th November 2019

Seminars, symposiums, webinars participation

1. Attended a two-day workshop on "Innovating, Designing, Modelling, Characterization and Simulation of Materials and Bio-Molecule using in Silico Solution Suite, Atomistic Simulation Advanced Platform (ASAP), J-OCTA and PRinS' jointly organized by Directorate of Research Development & Resource Mobilization (DRDRM) and Directorate of Internships, Incubation & Industry Partnership (DI3P) on 18th and 19th January 2024
2. Attended a 'ICDD Workshop on Materials Characterization Using Powder X-ray Diffraction' organized by School of Chemical Sciences, Goa University in collaboration with Vivertana Distributors Pvt. Ltd. on 7th and 8th December 2023
3. Attended one day workshop on 'Writing manuscripts & publishing in quality research journals' organised by the Directorate of Internal Quality Assurance (DIQA) on 27th August 2022
4. Attended International conference on 'Science and technology for Society (ICSTS-2022) organized jointly by VMS research foundation, Nagpur and Research for Resurgence foundation on 19th and 20th June 2022
5. Attended a three day workshop on 'X-ray Crystallography' organised by the School of Chemical Sciences and School of Physical and Applied Sciences, Goa University on 21st, 22nd and 23rd July 2022 at School of Chemical Sciences, Goa University
6. Attended a 'National Webinar on Emerging Trends in Heavy Metal Detection Sensors & C-H Functionalization' organized by the Department of Chemistry, DCT's Dhempe College of Arts & Science, Miramar-Goa on 22nd April 2022
7. Attended Online talk at the International webinar on 'Two Dimensional Semiconductor Applications for Green Energy (2D SAGE) by Prof. Giulia Grancini (Italy) at School of Chemical Sciences, Goa University on 10th March 2022
8. Attended a webinar on 'Identify, protect, commercialize your ideas and innovations' organised by the School of Chemical Sciences (SCS), Goa University, Taleigao Goa in association with the Directorate of Internal Quality Assurance (DIQA) on 7th January 2022
9. Attended 'International Webinar on Advances in Materials Chemistry and Applications' organized by the Department of Chemistry, DCT's Dhempe College of Arts & Science, Miramar Goa on 22nd October 2021
10. Attended virtual 'International Conference on Porous Materials for Energy and Environment' (PMEE 2021) organized by Cluster Research Centre, PG & UG Department of

Chemistry in Association with IQAD, Government College of Arts Science And Commerce, Khandola Goa (GCASCK) on 12th and 13th March 2021

11. Attended the International Conference on ‘Multifunctional electronic materials and processing (MEMP-2021) organised by C-MET Pune on a digital platform on 8th, 9th and 10th March 2021

12. Attended two days ACT National webinar on ‘Instrumental Methods of Analysis’ (NWIMA 2022) organised by Association of Chemistry Teachers (ACT) in collaboration with Department of Chemistry, Kamala Nehru Mahavidyalaya, Nagpur, India on 17th and 18th October 2020

13. Attended a two-day National e-workshop on ‘Introduction to Origin Software (Data analysis and graphing software)’ organised by the Department of Physics, K.L.E.F., Vijayawada, Andhra Pradesh, India on 29 and 30th September 2020

14. Attended an international webinar on the theme ‘International symposium on materials science and innovation for sustainable society’ organised by Nanomaterial Research Center, Meijo University, DCT’s Dhempe College of Arts & Science, Miramar and Government College of Arts, Science and Commerce, Khandola, under Cluster of Colleges for Research in Chemistry Goa on 26 and 27th August 2020

15. Attended a webinar on ‘Use of Elsevier tools for developing research workflow and academic writing’ organised by the Directorate of Higher Education, Goa in collaboration with ELSEVIER on 18th May 2020

16. Attended a National Symposium on Recent Trends in Condensed Matter Physics and Material Science; (CMPGoa-2020) at the Department of Physics, Goa University on 12th and 13th March 2020

17. Attended one day seminar on the theme ‘Recent Trends in Structural Chemistry’, at the Department of Chemistry, Goa University on 16th February 2019



An insight into the nanosize and bulk $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites through their comparative study: Structural and magnetic investigations

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ABSTRACT

The proposed research work manifests the comparison of nanosized ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite with their ‘sintered’ counterpart concerning their effect on the structural and magnetic properties. This paper conceptualizes the successful synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles by combustion route and their structural characterization viz. powder X-ray diffraction (XRD), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS) studies. The morphological studies like scanning electron microscopy (SEM) and high-resolution-transmission electron microscopy (HR-TEM) proclaimed the cuboidal nature of the particles. The alternating current (AC) susceptibility measurements determined the Curie temperature (T_c), which decreased in the ‘sintered’ ferrite. The vibrating sample magnetometry (VSM) measurements showed an increase in the saturation magnetization and a substantial decrease in coercivity at 300 K and 60 K from nano to bulk ferrite. The temperature-dependent zero-field cooled-field cooled (ZFC-FC) magnetization curves revealed information about the blocking temperature of the ‘as prepared’ and ‘sintered’ ferrites.

1 Introduction

Over the past few decades, ferrite spinels have garnered interest due to their biocompatibility, low toxic nature, brilliant stability, and remarkable sustainability. The exquisite structural, electric, dielectric, and magnetic properties of the bulk and their nanosized counterparts, along with excellent catalytic properties, have laid the foundation for them to make use in unprecedented devices [1, 2]. Prudent

consideration is hence needed to understand the correlation between their structural and physical properties.

Spinel ferrite encompasses a face-centered cubic (fcc) structure comprising of a cubic close-packed oxygen lattice having a general formula, $(\text{M})^{\text{A}}[\text{Fe}_2]^{\text{B}}\text{O}_4$, where M is usually a divalent cation while Fe is trivalent [1, 2]. The structure of spinels consists of two interstitial sites, tetrahedral (A) and octahedral [B], which accommodate the metal cation with oxygen

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coordination. The spinel ferrites are classified as normal, inverse, and random ferrites, considering the distribution of bivalent and trivalent cations in these sites. In the case of the normal spinel ferrites, Fe^{+3} ions occupy the octahedral sites, while M^{+2} ions get accommodated at the tetrahedral sites, resulting in the formula, $(\text{M}^{+2})^{\text{A}}[\text{Fe}_2^{+3}]^{\text{B}}\text{O}_4$. Conversely, in inverse spinel ferrites, half of the Fe^{+3} ions occupy the tetrahedral sites, while M^{+2} ions and the other half of the Fe^{+3} ions occupy the octahedral sites, yielding the formula $(\text{Fe}^{+3})^{\text{A}}[\text{M}^{+2}\text{Fe}^{3+}]^{\text{B}}\text{O}_4$ [3]. The NiFe_2O_4 and CoFe_2O_4 both possess inverse spinel structures [3, 4].

The nanomaterials show overwhelmingly different properties and applications compared to their bulk analogs due to their nano size. The present research scenario predominantly focuses on the potential applications of the magnetic ferrites in supercapacitors [5, 6], catalysis [1, 7–9], gas sensing [10–14], magnetic recording media, high-frequency devices and data storage [15]. The astonishing applications of spinel ferrites propelled researchers from material chemistry to formulate numerous methods for their synthesis. Some amongst them include sol–gel method [3, 4, 16–18], hydrothermal method [15, 19, 20], newly designed precursor-combustion method [21–27], combustion method [28–31], etc.

The magnetic property is one of the significant properties of spinel ferrites, where magnetic domains play a crucial role. A slight variation (reformation) in the domain structure from multidomain to single domain may induce a considerable change in the property, which will result in a change in its applications. Similarly, coercivity is another crucial determining parameter for various applications of the spinel ferrites, dependent on the particle size of ferrites [3, 32, 33]. Thus, with an increase in sintering temperature, the coercivity decreases because of the multidomain particle nature. The high coercivity, good chemical stability, and substantial mechanical hardness make CoFe_2O_4 particularly fascinating, while NiFe_2O_4 possesses a soft magnetic behavior [23].

Numerous adaptations and modifications occur in the magnetic and microstructural properties of the ferrite particles when ground to the nano size. If the particles are exceedingly small, the surface and the fine size effect might cause magnetic properties to become weak, which can be enhanced on calcination and subsequently by sintering. Another problem to

be resolved is the existence of the non-magnetic iron oxide phases, sometimes as a by-product, as these phases might produce secondary effects [34]. Usually, the sintering of the ferrites needs temperature around 1200–1450 °C to take care of these non-magnetic iron oxide phases but, a sintering temperature lesser than 1000 °C is normally employed for fabricating electronic devices [35], thus making the method of synthesis an essential factor to produce impurity-free spinel ferrites. The significance of the present study is the comparison of the ‘sintered’ and the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites, which was prepared by combustion method using relatively unexplored DL-Tartaric acid as a fuel. Though the effect of sintering on the nickel substituted cobalt ferrite and the improvement in the structural and magnetic properties is explored earlier [23, 32], the scope is still there to investigate the magnetic and structural properties in detail.

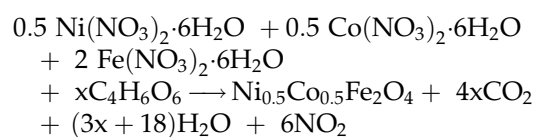
The motive of the present work is to synthesize, characterize, and study the impact of sintering on $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite. The literature reports proclaimed that tartaric acid is rarely used as fuel in the combustion synthesis of the ferrites and hence preferred as a fuel in our present study. Furthermore, we are interested in assessing the influence of particle size change from nano to bulk with increasing sintering temperature. Thus, with this aim in mind, we endeavored to study the variation in the structural and magnetic properties of the nanosized and bulk $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites after optimizing the oxidizer: fuel ratio. The criteria applied for selecting the best oxidizer: fuel ratio after optimization study was the formation of the single-phase spinel ferrites with smaller average crystallite size. The best oxidizer: fuel ratio should ideally generate sufficient heat enough for the spinelization reaction to occur, thus incorporating desired dopants in ferrites [36]. We anticipated that the ferrites under study would exhibit comparably enhanced magnetic properties while changing from the nanoscale to bulk after sintering.

2 Experimental and characterization

2.1 Experimental

The combustion route was employed for synthesizing nickel-doped cobalt ferrite ($\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$), utilizing DL-Tartaric acid as a fuel. The desired stoichiometric

proportions of metal nitrates viz., $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (all AR grades) were used as oxidizers while DL-Tartaric acid as a reducer. Varying ten different oxidizers: fuel ratios, the fuel deficient ratios, viz., 1:0.25, 1:0.375, 1:0.5, 1:0.625, 1:0.75 and fuel-equal/ fuel excess ratios; 1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375 were taken for optimization. All metal nitrates in fixed stoichiometric quantities were weighed, mixed, and heated on the hot plate to obtain the molten melt to which finely ground fuel (with varying ratios) was added. This mixture was later heated with continuous stirring on a hot plate till it ignites, undergoing combustion, and forms powdered nanoscale ferrites. The powder was homogenized by grinding and then calcined at 500 °C in the air for 5 h in a muffle furnace to eradicate any unburned carbonaceous species. All the ferrites obtained with a varying oxidizer to fuel ratios were then ground for 2 h and later checked for phase purity concerning the formation of spinel phase by recording their powder X-ray diffraction (XRD) patterns. The study of the fuel ratios (fuel deficient and fuel excess) is discussed later in Sect. 3.1. The 'as prepared' ferrites were then pressed into pellets and pre-sintered at 800 °C for 5 h. Later, the pellets were ground into fine powder by grinding for 2 h and were pelletized again using 5-ton pressure for 5 min and sintered at 1000 °C for 10 h. N5C5FA and N5C5FS are the respective notations given to the 'as prepared' and the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles. Figure 1a shows the schematic illustration of the entire synthesis procedure. The probable reaction occurring during the combustion synthesis can be summed up as below:



2.2 Characterization techniques

The thermal properties such as thermogravimetry (TG) and differential thermal analysis (DTA) of solidified melt (containing fuel mixed with metal nitrates) were studied using simultaneous TG-DTA thermal analyzer of Netzsch STA 409PC (Luxx) make at a heating rate of 10 °C/min in zero air between 30 and 800 °C. Rigaku Miniflex X-Ray diffractometer

(bearing monochromatized Cu-K α radiations filtered through Ni absorber ($\lambda = 1.5418 \text{ \AA}$) confirmed the phase purity of the optimized, 'as prepared' and 'sintered' spinel ferrites. Shimadzu Fourier transform infra-red (FTIR) Prestige-21 spectrophotometer recorded the infra-red spectra. Inductively coupled plasma-atomic emission spectroscopy technique performed on ACROS Simultaneous ICP spectrometer having an R. F. generator of 1.6 kW at 27.12 MHz determined the elemental compositions of the ferrites. JEOL-make field emission transmission electron microscope of model JEM 2100F assessed the particle size of the 'as prepared' ferrite. The scanning electron microscope (SEM) with the EDAX facility of Carl Zeiss make (Model No. EVO1) was employed to study surface morphology, along with elemental analysis of the 'as prepared' and the 'sintered' ferrites, respectively. The oxidation states of the elements in ferrites were determined using an X-ray photoelectron spectrometer of the make PHI 5000 Versa Prob II, FEI, Inc. ADEC Embedded Technology & Solutions Pvt. Ltd conducted the thermal variation study of normalized alternating current (AC) susceptibility of the ferrites. Quantum design-make cryogen-free Versa Lab Vibrating Sample Magnetometer (VSM) evaluated the magnetic measurements as a function of the applied field (M-H) at 60 K and 300 K operating at an externally applied magnetic field of 3 T. The same instrument conducted the magnetization measurements as a function of temperature (M-T), the Zero-field cooled-field cooled (ZFC-FC) measurement with the fields of 250, 500, 1000, 5000, and 10,000 Oe in the temperature range of 60–350 K.

3 Results and discussion

3.1 Studies of optimization of metal nitrates to fuel ratios

3.1.1 Thermal analysis of the 1:0.75 optimization ratio

Figure 1b depicts the TG-DTA plot of the solidified molten mixture of metal nitrates and fuel in the ratio of 1: 0.75, respectively, which gave information about the decomposition temperature. The TG plot shows a continuous mass loss, initially up to around 120 °C due to the loss of water associated with metal nitrates represented by two small endothermic peaks in DTA.

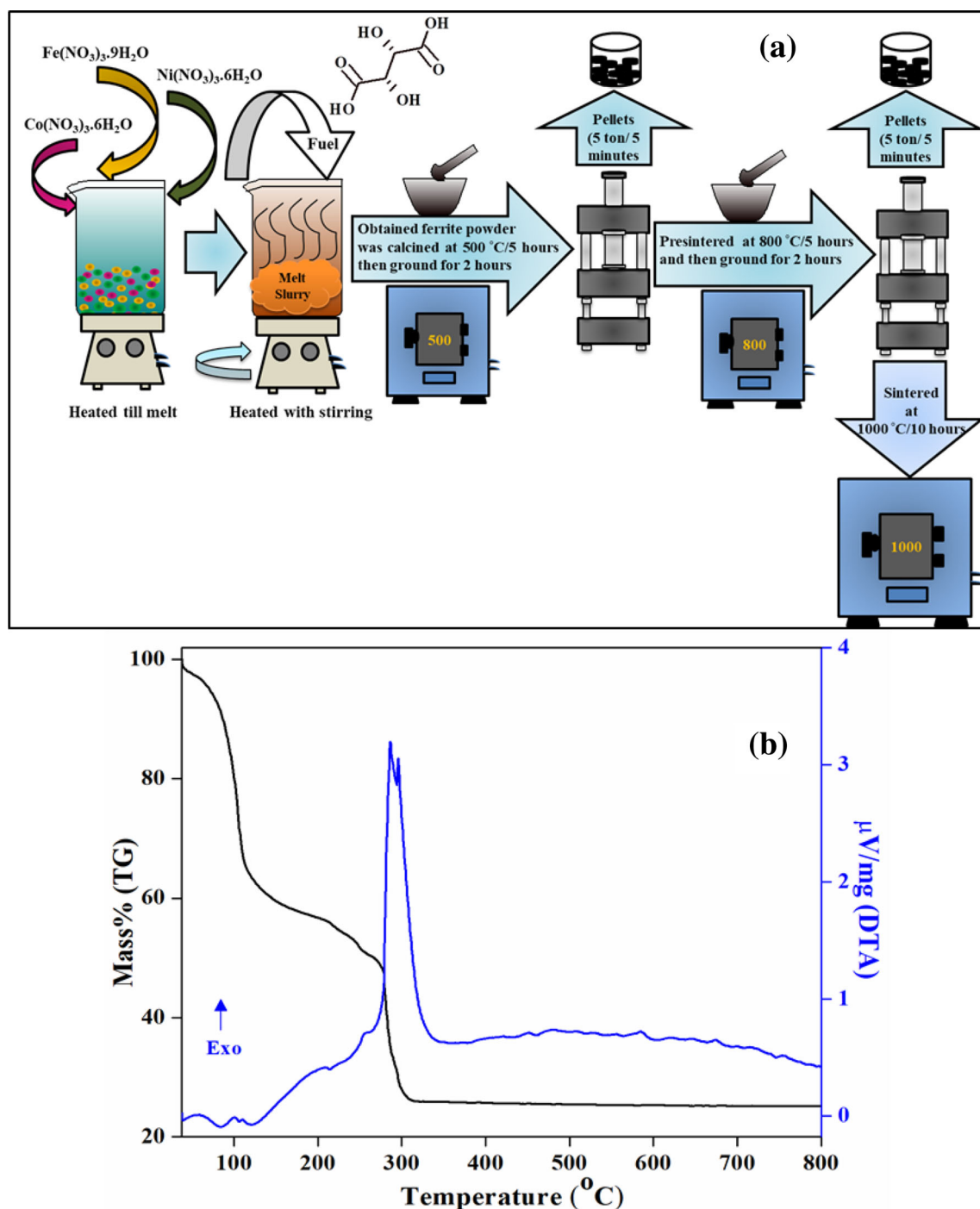


Fig. 1 **a** The scheme illustrating the combustion synthesis procedure of the ‘as prepared’ and the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites. **b** The TG-DTA plot of the solidified melt comprising of metal nitrates: fuel ratio of 1:0.75

A mass loss with a peak in DTA at 310°C is due to the combustion of the nitrates with fuel exothermically to form mixed metal oxide. Beyond the temperature of 310°C , the TG plot did not show any substantial weight loss. Hence all the auto-combusted samples (having different metal nitrates to fuel ratios)

were calcined at a little higher temperature (than the combustion temperature) at 500°C to ensure that all the carbonaceous impurities are entirely removed from the final product viz. the mixed metal oxide.

3.1.2 XRD studies of the product obtained from optimization of the metal nitrates to fuel ratios

Figure 2a and b reveal the powder XRD patterns of calcined and uncalcined ferrites, respectively, from metal nitrate fuel deficient and metal nitrate fuel excess fuel ratios. The XRD patterns before calcination indicate the broad nature of the peaks due to the smaller particle size and lower crystalline nature of the particles. However, on calcination at 500 °C, the broadness of the peaks decreases, and the peaks become sharper, demonstrating an increase in the crystallinity. The XRD patterns of all the ferrites (with different metal nitrates: fuel ratios) after calcination showed monophasic cubic spinel structure, confirming the phase purity. The lattice parameters (a) of all the calcined ferrites were found to be between 8.3302 and 8.3519 Å [Table 1]. The average crystallite sizes (D) of all the ferrites with different metal nitrate: fuel ratios were calculated using Scherrer's formula and tabulated in Table 1. The ferrite having a 1: 0.75 fuel ratio was found to have the smallest average crystallite size and highest lattice parameter and thus was chosen for the synthesis of the 'as prepared' and 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites.

3.1.3 Infra-red studies of the product obtained from optimization of the metal nitrates to fuel ratios

Infrared spectra of all the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites synthesized by varying metal nitrates: fuel ratios were studied in the range of 4000–350 cm^{-1} . Figure 3a, b demonstrates the room temperature FTIR spectra of all the ferrites prepared (with fuel deficient/equal and fuel excess ratios), wherein each spectrum exhibits two prominent absorption bands in the range between 398 and 402 cm^{-1} (ν_2) and 593–601 cm^{-1} (ν_1) [Table 1]; which are indicative of typical cubic spinel ferrites [37] affirming the formation of the cubic spinel ferrites. The absorption band at $\sim 600 \text{ cm}^{-1}$ (ν_1) attributes to cation–anion bond ($\text{M}_\text{A}\text{--O}$) stretching vibrations at tetrahedral sites, and the frequency band at $\sim 400 \text{ cm}^{-1}$ (ν_2) corresponds to cation–anion bond ($\text{M}_\text{B}\text{--O}$) stretching vibrations at octahedral sites of the ferrite samples. The variation in the $\text{Fe}^{+3}\text{--O}^{2-}$ bond distances for tetrahedral and octahedral complexes shows a shift in band positions [38].

3.1.4 AC susceptibility studies of the product obtained from optimization of the metal nitrates to fuel ratios

AC susceptibility technique provides information about three types of magnetization domains, viz. the superparamagnetic (SP), single-domain (SD), and multi-domain (MD) [39]. In SP materials, the rise in temperature does not allow the magnetic domains to orient in one direction that creates chaos and contributes very little to the magnetization. In multi-domain, the magnetization domains properly orient in one direction. However, an increase in temperature contributes heavily to magnetization. The single-domain particles have magnetization values lying between SP and MD materials. AC Susceptibility measurements examined the Curie temperature of all the ferrites obtained with different fuel ratios (fuel deficient and fuel excess ratios). The fuel deficient ratios exhibited a purely SD nature of the particles (Fig. 4a), while the fuel excess ratios tend towards SD-MD particles (Fig. 4b) with the majority of the particles of SD nature. Among the different fuel ratios, the ratio chosen for further synthesis was 1:0.75, possessing a single-domain particle nature.

3.1.5 VSM studies of the product obtained from optimization of the metal nitrates to fuel ratios

The magnetic studies of all ferrites prepared by varying oxidizer to fuel ratios were performed using a vibrating sample magnetometer (VSM) at an applied field of 3 T. Figure 5a, b demonstrates the room temperature VSM plots of magnetic moment v/s magnetic field of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ synthesized using fuel deficient and the fuel excess ratios carried out at 300 K (RT). The VSM magnetization curves verify that all the ferrites exhibit ferromagnetic-like behavior [40] due to appreciable coercivity, as seen in the inset pictures (Fig. 5a, b). The fuel ratio 1: 0.25 shows the lowest saturation magnetization value, despite that its crystallite size is determined to be higher in comparison with the ferrite obtained using the ratio of 1:0.75. Hence, the fuel ratio of 1:0.75 chosen for the further synthesis of the ferrite sample (under the present study) was based on its minimal crystallite size. Table 1 reveals the values of the saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c). The M_r and H_c values range

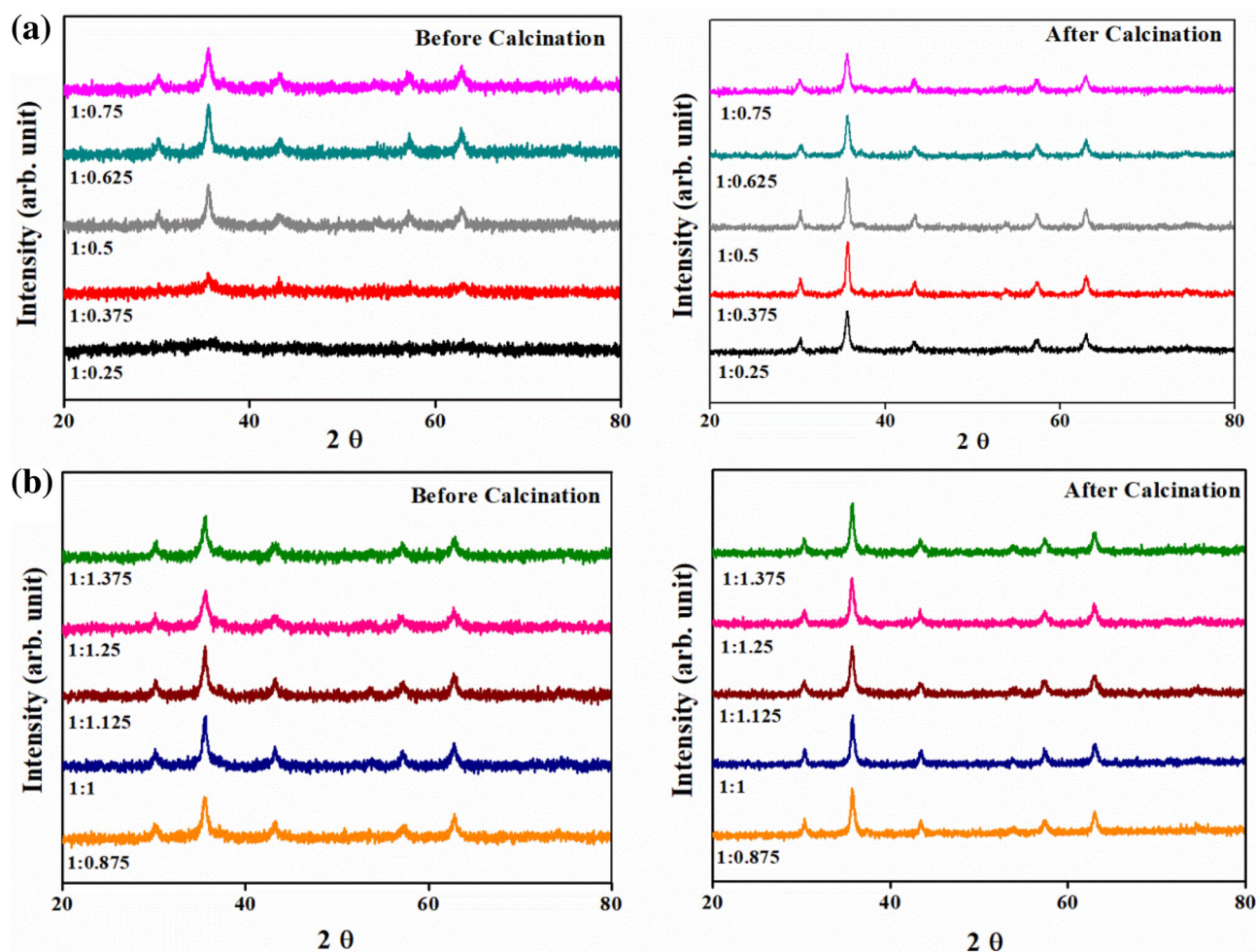


Fig. 2 The XRD powder patterns for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite synthesized before and after calcination at 500 °C by varying metal nitrates: fuel ratios **a** 1:0.25, 1:0.375, 1:0.5, 1:0.625 and 1:0.75 and **b** 1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375

Table 1 The saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c), Curie temperature (T_c), IR frequencies (ν_1 and ν_2), the average crystallite size (D) and lattice parameter ($\text{\AA}$) for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite synthesized by varying metal nitrates: fuel ratios

Metal nitrate: fuel ratio	M_s	M_r	H_c	T_c	IR frequency		Average crystallite size (nm)	Lattice parameter (Å)
	(emu/g)	(emu/g)	(Oe)	(K)	M-O _{tet}	M-O _{oct}		
					ν_1	ν_2		
					(cm ⁻¹)	(cm ⁻¹)		
1:0.25	44.80	15.15	680	825	601	399	18	8.3495
1:0.375	51.06	17.51	653	817	597	401	21	8.3402
1:0.5	51.64	16.71	781	826	596	402	21	8.3440
1:0.625	49.26	14.71	715	804	600	400	18	8.3385
1:0.75	48.64	14.25	711	821	601	399	16	8.3519
1:0.875	48.21	13.90	676	822	600	401	19	8.3374
1:1	48.74	15.25	773	813	596	398	18	8.3403
1:1.125	45.2	13.07	617	820	597	399	17	8.3406
1:1.25	49.0	15.73	730	817	593	400	23	8.3305
1:1.375	50.39	16.03	820	814	594	398	21	8.3302

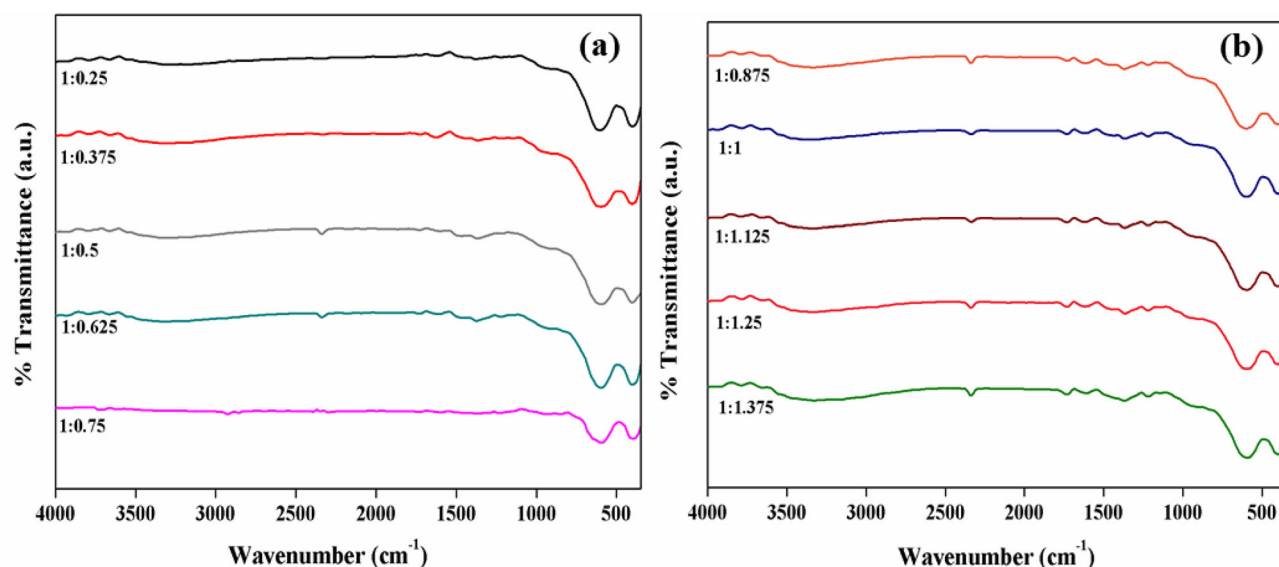


Fig. 3 The FTIR spectra for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite synthesized by varying metal nitrates: fuel ratios with **a** fuel deficient optimization ratios (1:0.25, 1:0.375, 1:0.5, 1:0.625 and 1:0.75) and **b** fuel excess optimization ratios (1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375)

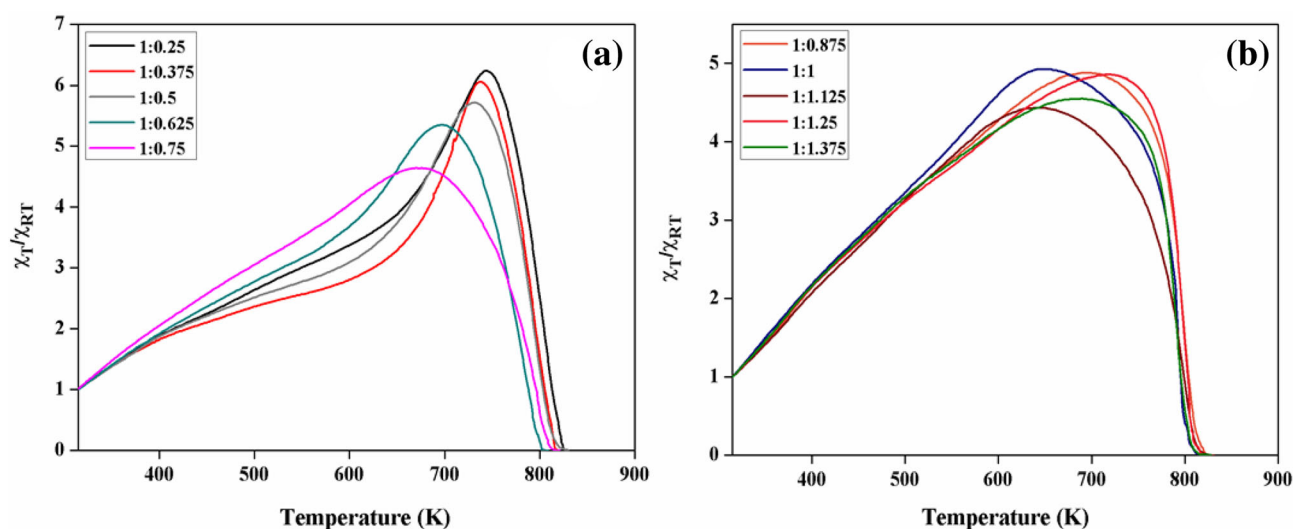


Fig. 4 Plots of variation of normalized AC susceptibility as a function of temperature for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite synthesized by varying **a** fuel deficient optimization ratios (1:0.25, 1:0.375, 1:0.5,

1:0.625 and 1:0.75) and **b** fuel excess optimization ratios (1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375)

from 13.07 to 16.71 emu/g and 617 to 820 Oe, respectively, for the ferrites obtained from different oxidizer to fuel ratios.

3.2 Structural properties of the 'as prepared' and 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

The $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite was synthesized by the combustion method using the metal nitrate (oxidizer)

to DL-tartaric acid (fuel) ratio of 1:0.75. The ferrite powder thus obtained was homogenized by grinding and then calcined at 500 °C in the air for 5 h in a muffle furnace to get rid of any unburned carbonaceous species. This $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite sample is given notation as the 'as prepared' ferrite (N5C5FA). The 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite (N5C5FS) was prepared from the 'as prepared' ferrite following the procedure mentioned in Sect. 2.1.

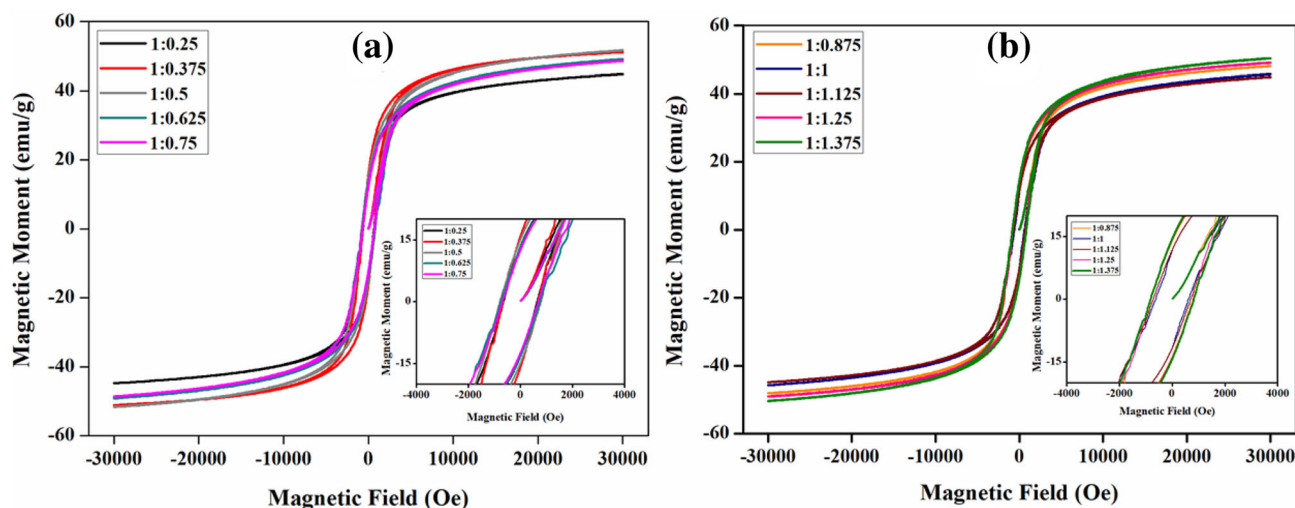


Fig. 5 The room temperature VSM plots of magnetic moment v/s magnetic field of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ synthesized using **a** varying fuel deficient optimization ratios (1:0.25, 1:0.375, 1:0.5, 1:0.625 and

1:0.75) and **b** fuel excess optimization ratios (1:0.875, 1:1, 1:1.125, 1:1.25 and 1:1.375)

3.2.1 XRD studies of the 'as prepared' and 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

The XRD diffraction patterns in Fig. 6a portray the structural characteristics of the 'as prepared' and 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites. The characteristic diffraction peaks in the diffractogram for both 'as prepared' and 'sintered' ferrites correspond to the hkl planes of spinel structure viz. (220), (311), (400), (422), (511), (440) and (533), which are closely matching with JCPDS card no. 01-088-380, thereby confirming the formation of impurity-free $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites. The Scherrer equation computed the average crystallite size (D) of ferrites as mentioned below:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

wherein ' λ ' specifies the incident wavelength of $\text{Cu-K}\alpha$ radiation of characteristic X-rays, ' β ' relates to the full width at half maximum (FWHM) in radians and ' θ ' is the Bragg's diffraction angle. The broadness of the XRD peak of the 'as prepared' ferrite (inset in Fig. 6a) points at the nanosize nature of the particle compared to the 'sintered' ferrite [41]. The broadness is further validated from the average crystallite size calculated [Table 2] using Scherrer's equation [4] for both the 'as prepared' and 'sintered' ferrites.

The lattice constant ' a ' of both the ferrites was calculated using the following equation [21]:

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (2)$$

where ' a ' denotes the lattice parameter, d_{hkl} is the interplanar distance, and (hkl) are the miller indices. The comparison of lattice parameters of both the 'as prepared' and 'sintered' ferrites (tabulated in Table 2) indicates an increase in lattice parameter (8.3488 Å for 'as prepared' and 8.3715 Å for the 'sintered' ferrite) with sintering which is the trend also observed by Gibin et al. [42]. They studied the effect of sintering on $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ synthesized by co-precipitation method and reported the lattice parameter values for the 'as prepared' and 'sintered' ferrite as 8.384 and 8.396 Å, respectively. The reduction of surface tension of nanocrystalline material with an increase in the particle size is the reason for an increase in the lattice parameter [43]. The average crystallite size (demonstrated in Table 2) of the 'as prepared' N5C5FA ferrite was lesser in comparison with the 'sintered' N5C5FS ferrite. Usually, a decrease in the particle size can cause a further subside in the lattice parameter in ferrite nanoparticles. The change in the coordination numbers of oxygen with the cations and the contribution from the excessive volume of the grain boundaries [44] are the two reasons for a decrease in the lattice parameter. The factors such as strain, surface pressure, defects like vacancies or interstitial defects, the finite-size effect of Madelung energy, and some more factors are the principal contributors in deciding the trends (increasing or decreasing) with the crystallite size variation of the nanoparticles [45].

Fig. 6 **a** The powder XRD patterns of the ‘as prepared’ (N5C5FA) and ‘sintered’ (N5C5FS) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites with inset figure depicting an expanded view of the 311 peaks. **b** The IR spectra of the ‘as prepared’ (N5C5FA) and ‘sintered’ (N5C5FS) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

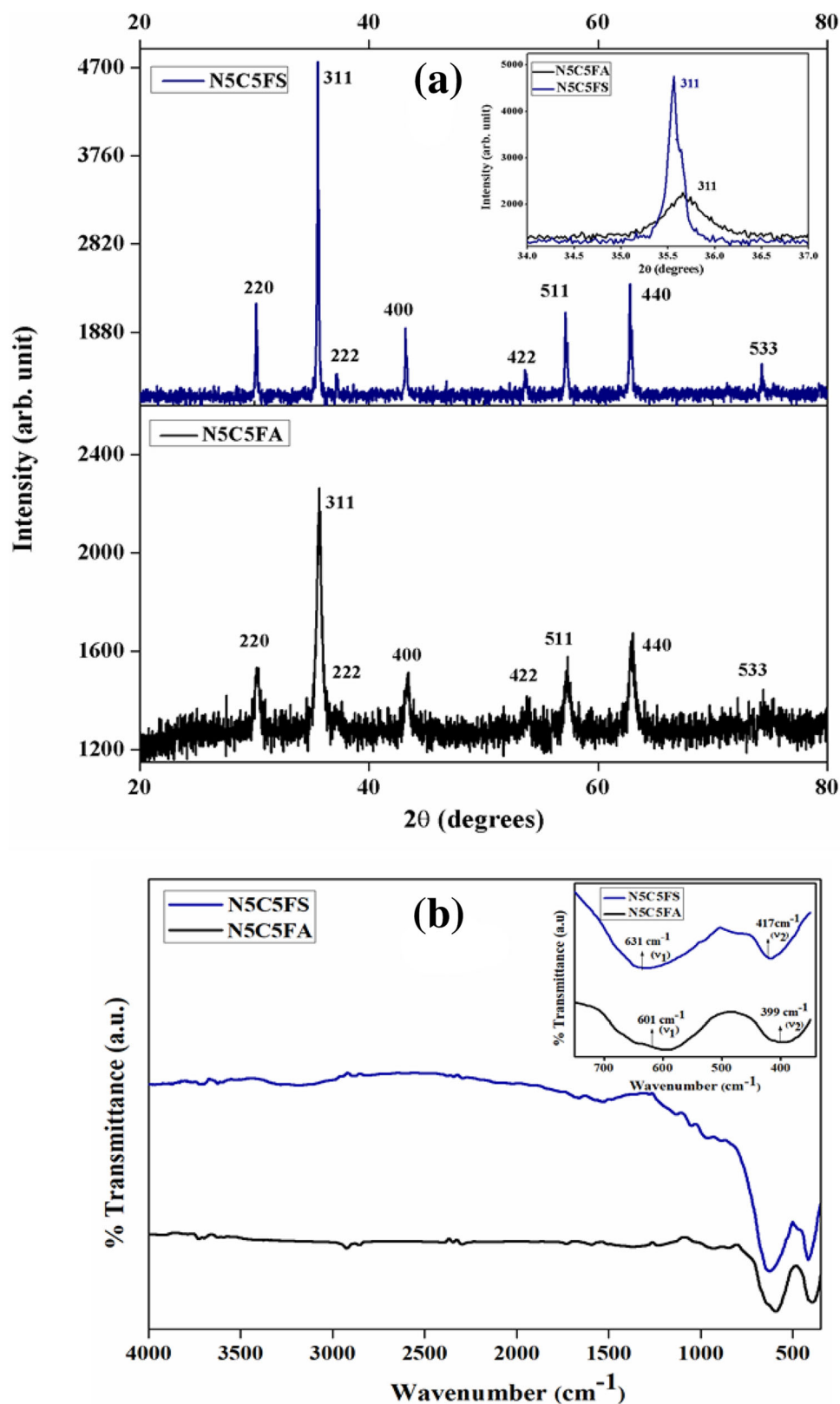


Table 2 The average crystallite size (D), lattice parameter (a), measured density (d_m) theoretical density (d_x), porosity (P), Curie temperature (T_c) and IR frequencies of the ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

Ferrite	Crystallite size (D) (nm)	Lattice parameter ‘ a ’ (Å)	Measured density (d_m) (g/cm^3)	Theoretical density (d_x) (g/cm^3)	Porosity (P) (%)	T_c (K)	IR frequencies	
							M-O _{tet} ν_1 (cm^{-1})	M-O _{oct} ν_2 (cm^{-1})
N5C5FA	17	8.3488	2.8797	5.3523	46.19	821	601	399
N5C5FS	53	8.3715	3.3738	5.3118	36.48	817	631	417

The measured density (d_m) is estimated using the formula [19] given below in Eq. 3.

$$d_m = \frac{8M}{N_A a^3} \quad (3)$$

where 8 is the number of formula units in a unit cell, M is the molecular weight of the formula unit, N_A is Avogadro’s number (6.023×10^{23} atoms/mole), and a^3 is the volume of the unit cell for the cubic spinel system.

The below-mentioned formula evaluated the theoretical density (d_x) of the ‘as prepared’ and ‘sintered’ ferrites [21].

$$d_x = \frac{m}{\pi r^2 h} \quad (4)$$

wherein m is the mass of the pellet, r is the radius, and h is the height of the pellet. The porosity (P) was calculated for both the ‘as prepared’ and ‘sintered’ ferrites using the following formula.

$$P(\%) = \frac{d_m}{d_x} \times 100 \quad (5)$$

Table 2 enumerates the measured and theoretical density along with the porosity of both the ferrites. The results suggest that there is a decrease in porosity with an increase in sintering temperature. The diminution in the number of pores at the elevated temperature is responsible for the subside in porosity because of the agglomeration of grains due to an increase in effective grain area contact, thereby increasing further densification leading to a decrease in porosity [46].

3.2.2 Infra-red Studies of the ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

The IR spectra of the ‘as prepared’ (N5C5FA) and ‘sintered’ (N5C5FS) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites were recorded between 350 and 4000 cm^{-1} as depicted in

Fig. 6b. The absorption bands at ν_1 (601–631 cm^{-1}) and ν_2 (399–417 cm^{-1}) ascribe to the stretching vibrations at tetrahedral sites and octahedral sites, respectively in both the ‘as prepared’ and ‘sintered’ ferrites [Table 2]. The inset figure (Fig. 6b) shows a slight shift in the peak towards a higher wavenumber with an increase in sintering temperature. Massoudi et al. [3] observed the same trend wherein they stated that the shift in the peak might be due to alteration in microstructure with increased temperature; which is perhaps due to FeO_6 octahedron getting reformed to FeO_4 tetrahedron, and this reformation can be associated with intensified covalent nature of the $\text{Fe}^{+3}\text{--O}$ bond at A-site than at the B-site. This behavior is justified based on the bond distances of the Fe--O bond at the A-site being smaller than at the B-site [38].

3.2.3 Chemical composition study of the ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

Table 3 presents the experimental percentages of metal ions in the ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites obtained from the ICP-AES analysis compared with the theoretical ones. The experimental percentages of metal ions in both the ‘as prepared’ and the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites are in close agreement with the theoretically computed percentages confirming the formation of stoichiometric $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites.

3.2.4 X-ray photoelectron spectroscopy (XPS) study of the ‘as prepared’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

XPS studies affirmed the oxidation states of all the elements of the ‘as prepared’ N5C5FA and ‘sintered’ N5C5FS (not presented here) ferrites. The full scan XPS spectra and the deconvoluted core level XPS scans of Ni 2p, Co 2p, Fe 2p, and O 1s of the ‘as

prepared' N5C5FA ferrite are pictorially illustrated in Fig. 7 using the XPS PEAK 41 software. It is seen from Fig. 7 that Ni, Co, Fe, and O are present in the 'as prepared' ferrite sample without any impurity element except the carbon that may have deposited on the surface during the sample preparation. The entire spectral data were throughout calibrated for charge correction for carbon 1 s peak with a fixed value of 284.8 eV [47].

The Ni $2p_{3/2}$ peak is observed (Fig. 7a) at the binding energy value of 854.9 eV, whereas the peak for Ni $2p_{1/2}$ is exclusive at 872.5 eV [48]. The corresponding satellite peaks appear at 861.7 and 880.1 eV for Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively [49], affirming Ni is in the + 2 oxidation state in 'as prepared' ferrite. The characteristic binding energy peaks observed at 795.5 and 780 eV (Fig. 7b) for Co $2p_{1/2}$ and Co $2p_{3/2}$, respectively [18], confirmed that cobalt exists in the + 2 oxidation state. Additionally, the satellite peaks at binding energies of 786.8 and 802.7 eV validate the existence of Co in the + 2 oxidation state. Two peaks at binding energies of 779.7 and 782.3 eV denote respective octahedral and tetrahedral bonding of Co^{+2} with oxygen [50].

The high-resolution XPS peaks (Fig. 7c) observed, respectively, at 725.4 eV and 710.2 eV are attributed to the Fe $2p_{1/2}$ and Fe $2p_{3/2}$, having a satellite peak at a binding energy of 716.8 eV. A satellite peak witnessed at the binding energy of 8 eV higher than the main peak viz. Fe $2p_{1/2}$ is typical for Fe in a trivalent oxidation state [47, 51]. The peaks at 710.2 and 712.2 eV confirm the Fe^{+3} ion distributions, respectively, at the octahedral and the tetrahedral sites [18]. Figure 7d indicates the binding energy of the oxygen species equivalent to O 1 s at 529.7 eV, which is assigned to the contribution of lattice oxygen, whereas the peak observed at higher binding energy (531.3 eV) attributes to lower coordinated lattice oxygen suggesting structural defects [11, 16].

Table 3 Percentages of nickel, cobalt, and iron present in 'as prepared' and 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

Elements	Experimental %		Theoretical %
	N5C5FA	N5C5FS	
Ni	12.30	12.05	12.54
Co	12.18	11.9	12.56
Fe	47.9	46.9	47.63

3.3 Morphological studies of the 'as prepared' and the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites:

3.3.1 Scanning electron microscopy and EDS mapping analysis

The respective SEM images of 'as prepared' and the 'sintered' $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites are presented in Fig. 8a and b in addition to their histograms of particle size distribution and EDAX spectrum. The SEM images reveal that both the samples have nanosized cuboidal shaped grains with a notable tendency of coalescence and agglomeration. This cohesion of the grains attributes to their magnetic interactions [24]. The nanosized nature of particles can be imputed to the generation of a considerable number of gases during the combustion process, obstructing to a certain magnitude the agglomeration of nanoparticles resulting in porous materials [2]. On sintering, however, the nanoparticles merge consequently, the agglomerates having larger particle sizes. The respective histograms derived from the SEM images approximated the maximum average particle size for the 'as prepared' ferrite obtained in the range of 50–80 nm and that of the 'sintered' ferrite around 80–140 nm. The Energy dispersive X-ray (EDX) spectra of both the 'as prepared' and the 'sintered' ferrites demonstrate the peak positions of corresponding constituent elements viz. Ni, Co, Fe, and O within the resolution limit of EDAX [2].

3.3.2 High-resolution-transmission electron microscopic analysis

The HR-TEM Microscopic analysis of the 'as prepared' ferrite illustrates that particles are nearly cuboidal shaped [42] with uneven size distribution exhibiting considerable agglomeration arising due to magnetic interactions between the particles [31]. The typical histogram depicted in Fig. 8c furnished the details about the maximum particle sizes in the range of 10–20 nm, which closely correlates with the average crystallite size obtained from Scherrer's formula using XRD. Figure 8c (III and IV) shows a TEM image of a nanoparticle with its SAED pattern. The associated SAED pattern of the 'as prepared' ferrite shown in the figure portrays concentric rings bearing bright spots in the diffraction pattern, justifying the crystalline nature of the nanoparticles with

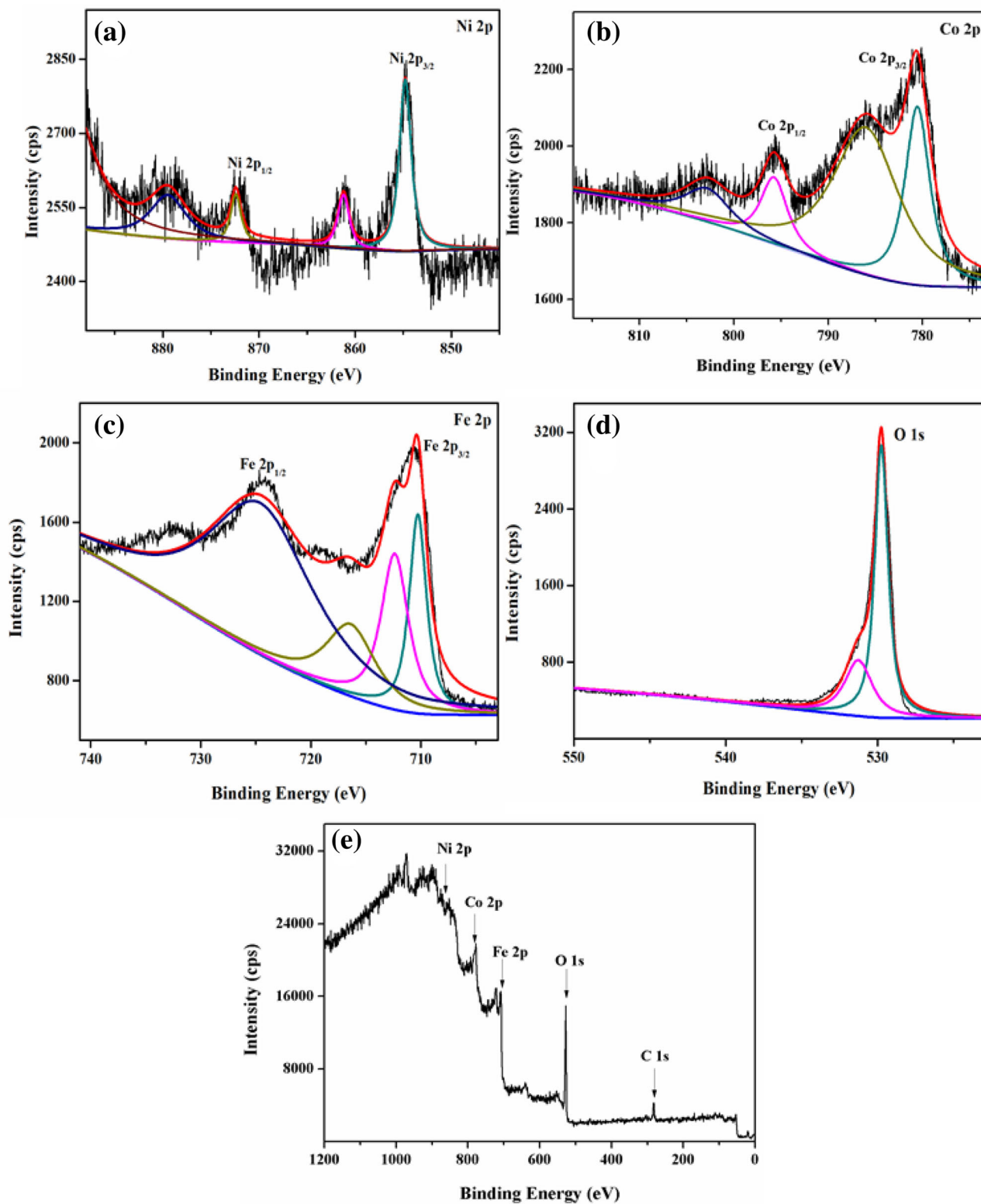


Fig. 7 The deconvoluted XPS spectra of **a** Ni 2p **b** Co 2p **c** Fe 2p **d** O 1s and **e** full scan XPS spectrum of 'as prepared' ($\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$) ferrite

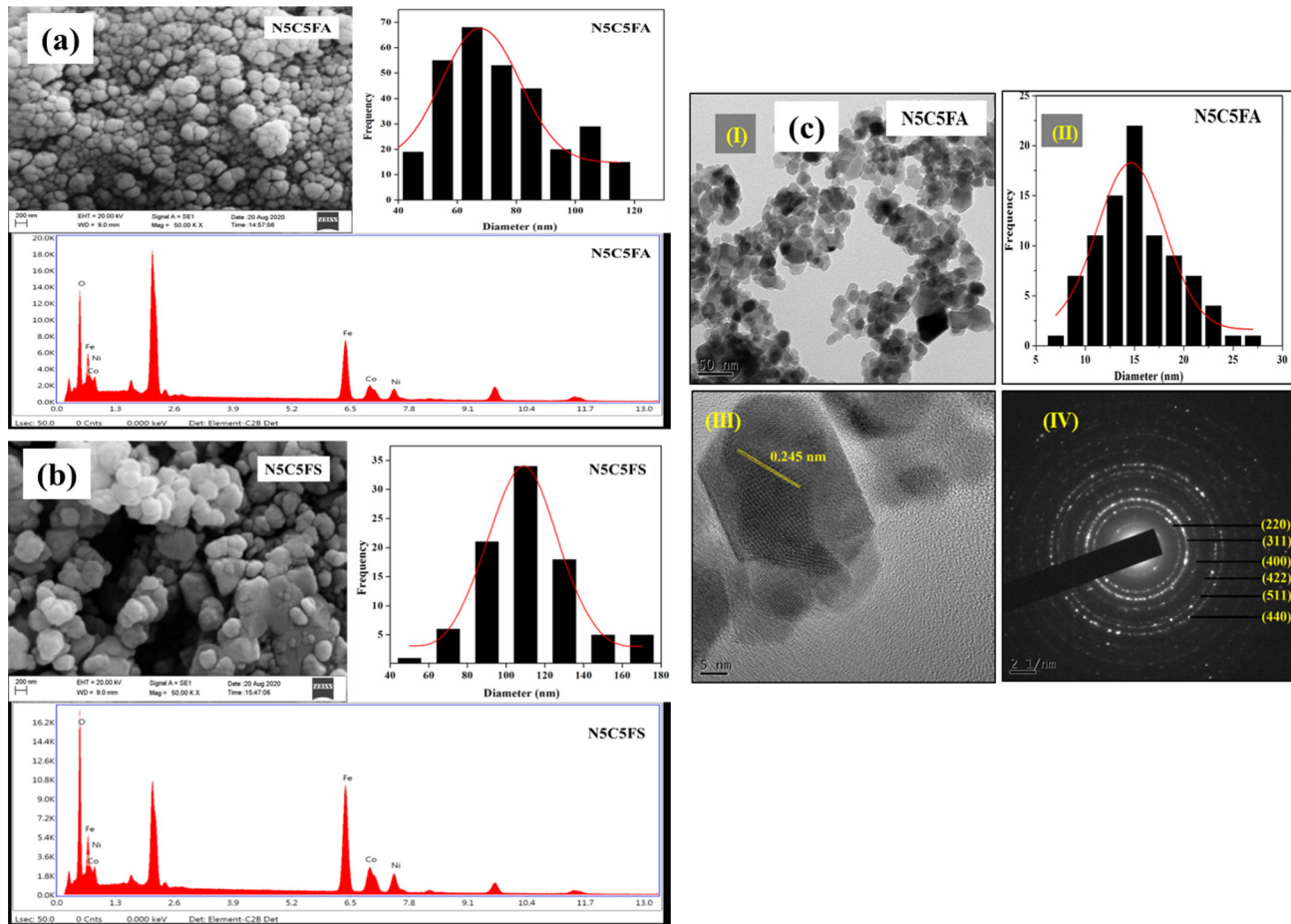


Fig. 8 The SEM micrograph, histogram of particle size distribution and EDAX spectrum of **a** ‘as prepared’ (N5C5FA) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite **b** ‘sintered’ (N5C5FS) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite **c** (I) HR-TEM micrograph of ‘as prepared’ (N5C5FA)

$\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite (II) typical histogram representing particle size distribution (III) HR-TEM images of a single $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle and (IV) its SAED pattern

agglomeration [22, 52] exhibiting the brightest spot for the highest intensity (311) peak.

3.4 Magnetic properties of the ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

3.4.1 AC susceptibility of the ‘as prepared’ and ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

Figure 9 demonstrates the temperature variation of normalized AC susceptibility measurements of the ‘as prepared’ and the ‘sintered’ $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites from room temperature to 600 °C. The temperature variation of normalized AC susceptibility curve of the ‘as prepared’ ferrite (N5C5FA) shows a continuous linear increase in susceptibility as temperature increases with a peak at high temperature and subsequently a linear fall indicating predominantly

single-domain particles [18, 53]. In the ‘sintered’ ferrite (N5C5FS) contrarily, there is a slow initial increase followed by a sharp increase at the higher temperatures culminating into a sharp peak (Hopkinson peak) just before the Curie temperature (T_c) and a sharp fall after that at T_c , suggestive of single domain-multidomain (SD-MD) type of particles behavior. The increase at the Hopkinson peak is a competing process of thermo-magnetic randomization; and the magnetic ordering by boundary wall domain expansion as thermal energy increases. Thermal fluctuations responsible for the rise in the magnetic alignment and the increasing ease of magnetization mutually compete with increasing temperature [53].

The Curie temperature (T_c) is the temperature at which there is a transition from ferromagnetic to paramagnetic, viz. a transition from the ordered

alignment of the magnetic spins to the random alignment [54]. As the particle size decreases from bulk to nano, the particles get converted from multi-domain to single domain to SP in ferromagnetic and ferrimagnetic materials with the corresponding change in T_c [55]. Table 2 represents the Curie temperatures of both the 'as prepared' and the 'sintered' ferrites, implying comparably higher values of the T_c of 'as prepared' ferrite compared to the 'sintered' ferrite. The T_c observed to be 821 K for the 'as prepared' ferrite is higher than 753 K, obtained in the earlier reports by the precursor-combustion method [26]. The alteration in the lattice cation distribution of tetrahedral and the octahedral sites is responsible for the fall in the T_c with an increase in the particle size (as seen from SEM images), which is probably because of the strength of the exchange interactions [3]. The initial increase in normalized AC susceptibility of single-domain particles with an increase in temperature ascribes to the inadequacy of sufficient thermal energy for disturbing the aligning spins, confirming the ferrimagnetic behavior of the ferrites. However, above T_c , there is adequate thermal energy available which disturbs the alignment, thus causing a decrease in susceptibility values [56].

3.4.2 VSM studies of the 'as prepared' and 'sintered' $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites

The vibrating sample magnetometer (VSM) was used to study the magnetic properties of the 'as prepared' and 'sintered' $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites. Figure 10a and

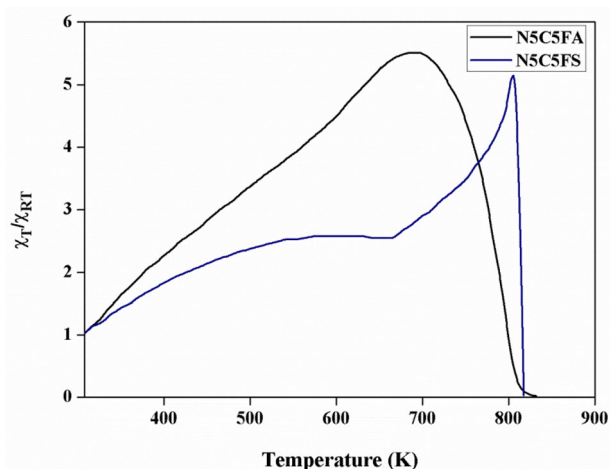


Fig. 9 Plots of variation of normalized AC susceptibility as a function of the temperature of the 'as prepared' (N5C5FA) and 'sintered' (N5C5FS) $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites

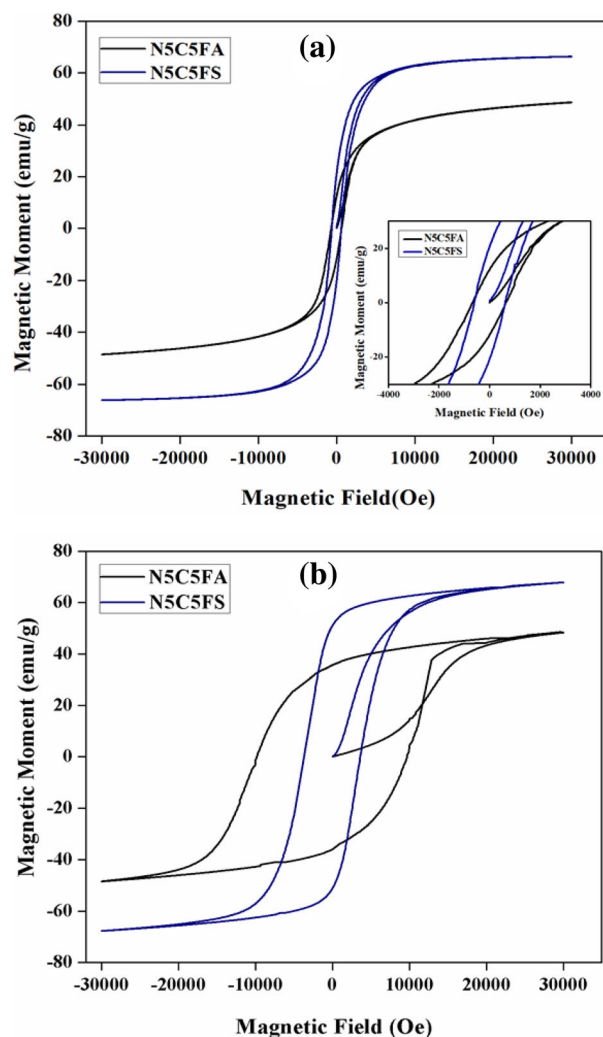


Fig. 10 Hysteresis loops of 'as prepared' (N5C5FA) and 'sintered' (N5C5FS) $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites at **a** 300 K and **b** 60 K

b demonstrate the M-H curves of the 'as prepared' (N5C5FA) and the 'sintered' (N5C5FS) ferrites, respectively, at room temperature (300 K) as well as at 60 K, in a maximum applied magnetic field strength of 3 Tesla. The values of saturation magnetization (M_s), remanent magnetization, (M_r), coercivity (H_c), squareness ratio (M_r/M_s), magnetic moment (η_B), and magnetocrystalline anisotropy (K_{eff}), blocking temperatures (T_B) at the fields of 5000 and 10,000 Oe of 'as prepared' and 'sintered' $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrites are presented in Table 4.

The saturation magnetization (M_s) in the 'sintered' ferrite is higher than the 'as prepared' ferrite at both temperatures, which was also reported by Rana et al. [57]. In the present study, the M_s values for the 'as

prepared' ferrite at 300 K and 60 K are 48.64 emu/g and 51.7, respectively, which are higher than the M_s value of 41 emu/g and 52.42 emu/g at 300 K and 2 K, respectively, reported in the literature [32]. Similarly, for the 'annealed' ferrite, the reported M_s values [32] are lower at 300 K (55.24 emu/g) and 2 K (64.66 emu/g) as compared to the 'sintered' ferrite in the present study [Table 4]. The nanoparticles possess spin glass-like layers or canted (disordered) spin on their surfaces, which emerges as a consequence of a higher fraction of surface-to-volume ratio of atoms in smaller particles. The spin-canting in the nano ferrites originates because of the alteration of cation distribution on account of the chemical disorder, which modifies super-exchange interactions and the confinement effect at the nanoscale level. This modification breaks the symmetry, which gradually produces broken exchange bonds at the surface of the nanoparticles [32]. As a consequence of the spin-canting effect, even at a high applied magnetic field, the particles do not possess any saturation hence leading to the lowering of saturation magnetization in the smaller particles [58]. Moreover, the decrease in temperature led to an increase in the M_s value owing to the minimized thermal variation effects at low temperature (60 K) than at 300 K on the magnetic ions [59], as depicted in Table 4.

Nevertheless, the coercivity (H_c) and magnetocrystalline anisotropy (K_{eff}) show a reverse trend at both temperatures. It is lower in the 'sintered' ferrite than in the 'as prepared' ferrite. The large values of the magnetic anisotropy accredit to the non-stoichiometric divalent cation distribution. The 'as prepared' ferrite encompasses a considerable amount of Ni^{+2} ions at the A-site compared to most Ni^{+2} ions in 'sintered' ferrite occupying the B-site [32]. The M-H plots at both 60 K and 300 K showed higher H_c for the 'as prepared' ferrite than the 'sintered' ferrite. This trend is because the H_c depends on the grain

size; the smaller the grain size more the coercivity. The decreasing values of H_c with increasing sintering temperature are due to the transformation of single-domain particles to the multidomain nature of the particles. Das et al. [19] reported the same trend in their studies. This decrease is the result of the contribution from microstrain, shape anisotropy, and magnetocrystalline anisotropy. The H_c values at 300 K and 60 K are found to be 711 Oe and 9598 Oe, respectively, for the 'as prepared' ferrite. Coutinho et al. [23] also observed a similar trend wherein H_c at 310 K and 50 K were 1703 and 16,073 Oe, respectively. The remanent magnetization, found to increase with an increase in the particle size, suggests a tendency towards the cubic anisotropy with an increase in the particle size [60]. However, M_r value decreased drastically with an increase in temperature, from 60 to 300 K in both the 'as prepared' and 'sintered' ferrites.

The magnetocrystalline anisotropy constant (K_{eff}) for the uniaxial system given as:

$$H_c = \frac{0.985K_{\text{eff}}}{M_s} \quad (6)$$

The strong anisotropy of cobalt ferrites is because of Co^{+2} ions present in the octahedral sites of the cubic spinel. With the rise in the temperature, Co^{+2} ions shift from octahedral to tetrahedral sites. This shift leads to a decrease in the Co^{+2} ions in the octahedral sites. Thus, in both 'as prepared' and 'sintered' ferrites, the K_{eff} decreases with an increase in temperature [23]. We found the values of K_{eff} of the order of 10^5 erg cm^{-1} , which are in agreement with the reported values [23, 32]. The theoretical magnetic moment per formula unit in terms of Bohr magneton (η_B) has been calculated by the formula as follows:

$$\eta_B = \frac{M_W \times M_s}{5585} \quad (7)$$

Table 4 Saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c), squareness ratio (M_r/M_s), magnetic moment (η_B), and magnetocrystalline anisotropy (K_{eff}), blocking temperatures (T_B) at the

Ferrite	Temperature (K)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	M_r/M_s	η_B (μ_B)	K_{eff} $\times 10^5/\text{erg cm}^{-1}$	T_B (Oe)	K
N5C5FA	60	51.7	35.80	9598	0.69	2.17	5.03	278	223
	300	48.64	14.25	711	0.29	2.04	0.35		
N5C5FS	60	67.78	51.67	3623	0.76	2.84	2.49	320	277
	300	66.25	24.64	606	0.37	2.78	0.40		

fields of 5000 and 10000 Oe of the 'as prepared' (N5C5FA) and 'sintered' (N5C5FS) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrites

where M_W and M_S are molecular weight and saturation magnetization of the ferrite sample [3], respectively. The magnetic moment values are tabulated in Table 4.

The impact of morphological features on the magnetic properties of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite was studied by performing temperature-dependent (MT) field cooled (FC) and zero-field-cooled (ZFC) magnetization measurements employing VSM in an external applied magnetic field of 10,000 Oe in the temperature range of 60–350 K for both, the ‘as prepared’ (Fig. 11a) and ‘sintered’ (Fig. 11b) ferrites. While carrying out the ZFC measurements, the ferrite nanoparticles first were cooled to 60 K without any application of an external magnetic field (250, 500, 1000, 5000, and 10,000 Oe). Later the ferrite nanoparticles were heated to 350 K by concurrently evaluating the magnetization (M_{ZFC}) under an externally applied magnetic field. Likewise, while executing the FC measurements initially, the nanoparticles were cooled down in the presence of the applied field by simultaneously noting the magnetization (M_{FC}) while warming up to 350 K under the applied magnetic field.

Figure 11a and b exemplifies that in the ‘as prepared’ and ‘sintered’ ferrites, the FC curve is having an almost temperature-independent type of behavior at low temperature, which suggests the existence of magnetic interparticle interactions having long-range, that results in a magnetically ordered state with high anisotropy [60]. However, M_{ZFC} exhibits a decrease with a decrease in temperature. This decreasing tendency of M_{ZFC} implies that spins of the transition metal ions at ambient temperature in octahedral and tetrahedral sites deviate from antiparallel alignment and, thus the lattice possesses either a canted or partially misaligned spin structure [23], which might be due to the nano-sized nature of the ferrite samples. With the temperature rise, there is a reduction in thermal fluctuations and orientation of spins to reduce the canting angle and are aligned to ferrimagnetic structure [45]. The variation in magnetization behavior is a pointer towards wide particle size distribution, confirmed from HR-TEM and SEM, domain state, and magnetic anisotropy energy concerning the temperature [30]. As the temperature rises, the magnetization of the samples first reaches up to a broad maximum at a specific temperature, also called the blocking temperature (T_B), and then it

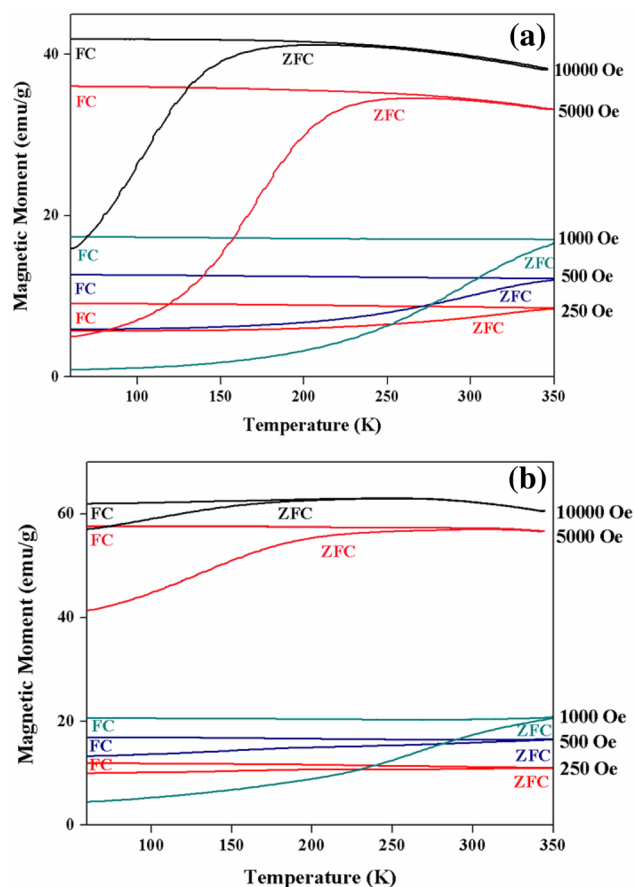


Fig. 11 Temperature-dependent (M-T) and FC magnetization curves at fields of 250, 500, 1000, 5000 and 10,000 Oe of **a** ‘as prepared’ (N5C5FA) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ and **b** ‘sintered’ N5C5FS $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$

decreases. With increasing temperature, M_{FC} decreases continuously, which might be due to the gathering of the magnetic monodomain particles [60]. The magnetic irreversibility observed at the higher fields, known as the irreversibility temperature (T_{irr}), is defined as the temperature at which both M_{ZFC} and M_{FC} meet. Due to saturation of the spins, T_B and T_{irr} are obtained at the higher fields (5000 and 10,000 Oe). Table 4 shows the T_B values of both ‘as prepared’ and the ‘sintered’ ferrites.

The blocking temperature decreased with an increase in the externally applied field in ‘as prepared’ and the ‘sintered’ ferrites. The blocking temperature increases with an increase in the grain volume, which might be due to the formation of agglomerates with increasing sintering temperature, as discussed by Szczygieł et al. [61]. The T_B values in cobalt substituted nickel-zinc ferrite system under the applied field of 500 Oe is found to be 289 K [30]

which is higher than 278 K obtained under the applied field of 5000 Oe. The M_{ZFC} and M_{FC} curves in case of both the 'as prepared' and 'sintered' ferrites under lower applied magnetic fields show bifurcation of the FC and the ZFC curves, and thermo-magnetic irreversibility over an entire temperature range, suggesting magnetically non-homogenous system despite; the material is chemically homogeneous [23].

4 Conclusion

Conclusively, monophasic nanosized 'as prepared' $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrite was successfully synthesized by a combustion synthesis route employing tartaric acid as fuel and subjected to sintering. The crystallite size increased with sintering for the $Ni_{0.5}Co_{0.5}Fe_2O_4$ ferrite as determined by the powder XRD technique and the XPS studies confirming the oxidation states of all the elements in the ferrites. A comparative assessment of the structural properties of 'as prepared' and the 'sintered' ferrites was done by SEM for morphology, along with energy dispersive spectroscopy (EDAX), which determined the presence of all the elements in the samples and high-resolution-transmission electron microscopy (HR-TEM), signifying nanosized cuboidal nature of the ferrite samples. AC susceptibility investigations revealed an increase in the Curie temperature, with multidomain particle nature for the 'sintered' ferrite. The magnetization (VSM) studies disclosed an increase in the saturation magnetization values with sintering. The ZFC-FC curves showed bifurcation of the FC and ZFC curve over an entire temperature range of 60–350 K in lower applied magnetic fields, specifying a magnetically non-homogenous system. However, T_B and T_{irr} are observed at higher applied magnetic fields of 5000 Oe and 10,000 Oe.

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Declarations

Conflict of interest The authors declare that there are no conflict of interest about the submission of the manuscript which are relevant to this content.

Ethical approval The authors declare that the ethical standards are maintained while writing this manuscript.

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