

Ferromagnetic Properties of Zn substituted Spinel Ferrites for High Frequency Applications

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Research Type: Review Article

Abstract- This review focuses on two systems, nanocrystalline Zn substituted $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) and $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$, were synthesized using microwave hydrothermal and auto-combustion method respectively. The synthesized powders were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), thermo-gravimetric-differential thermal analysis (TG-DTA) and FTIR. The average particle size was obtained from TEM and it is found to be 17 nm. Zero field cooled (ZFC) and Field cooled (FC) measurements for $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ reveal that samples with $0.6 \leq x \leq 1$ have superparamagnetic behavior at room temperature, which confirms weak interaction between magnetic particles. The blocking temperatures obtained from ZFC-FC curves decreases as Zn concentration increases. Lower reduced remnant magnetization (M_r/M_s) values ($x < 0.5$) suggest that all the samples have uniaxial anisotropy. For $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ bulk densities of the samples were increased with an increase of sintering temperature. The grain sizes of all the samples vary in between 18 nm to 30 nm. The hysteresis loops show high saturation magnetization and low coercivity, indicates that it is a soft material. The incremental permeability (permeability with magnetic field superposition) was influenced by both ΔM and H_c . So these ferrites has the properties and are widely used as electromagnetic wave absorbing materials in the VHF/UHF region and as radar absorbing materials in C-band frequencies.

Index Terms- Spinel Ferrites, Magnetic Properties, Saturation Magnetization, Zero Field Cooling, Blocking Temperature, Permeability, Q-factor, DC-bias-superposition

I. INTRODUCTION

Ferrites have the general formula $(\text{M}_{1-x}\text{Fe}_x)[\text{M}_x\text{Fe}_{2-x}]\text{O}_4$. The divalent metal element M (Mg, Zn, Mn, Fe, Co, Ni, or mixture of them) can occupy either tetrahedral eight (A) or sixteen octahedral [B] sites of a cubic mineral spinel (MgAl_2O_4) structure as depicted by the parentheses or brackets, respectively. For example the structural formula of Co-ferrite is usually written as $(\text{Co}_{1-x}\text{Fe}_x)[\text{Mg}_x\text{Fe}_{2-x}]\text{O}_4$, where x represents the degree of inversion (defined as the fraction of (A) sites occupied by Fe^{3+} cations). Depending on distribution of cations in (A) and [B] sites, ferrites may exist in two extreme states, normal ($x = 0$) and inverse ($x = 1$) or in an intermediate mixed state [1].

Among these materials, spinel ferrite nanoparticles have special importance. They show various magnetic properties depending on the composition and cation distribution. Various cations can be placed in A site and B site to tune its magnetic properties. Depending on A site and B site cations, it can exhibit ferrimagnetic, antiferromagnetic, spin (cluster) glass, and paramagnetic behaviour.

Nanosized ferrites may have extraordinary electric and magnetic properties that are comparatively different from microstructured materials, tailoring them to modern technologies, as well as providing novel applications such as ferrofluids [2], magnetic drug delivery [3], high density information storage [4], photocatalysis [5], gas sensors [6], etc.

Among those spinel ferrites we are interested in Zn substituted mixed ferrites are useful for low and high frequency applications generally for power transformers, power inductors, microwave devices, read and write heads for high speed digital tape, etc. because of their high resistivity, low losses, mechanical hardness, high Curie temperature and chemical stability [7-12].

CoFe_2O_4 has attracted considerable interest because of its large magnetic multi-axial anisotropy, high saturation magnetization, high Curie temperature and extraordinary chemical stability [13-16]. CoFe_2O_4 is predominantly an inverse spinel oxide with Co^{2+} ions mainly on B sites and Fe^{3+} ions distributed, almost equally, between A and B sites [17]. Cobalt ferrite is ferrimagnetic below 790 K (T_N) which suggests that the magnetic interactions in this ferrite are very strong. When Co^{2+} is replaced by Zn^{2+} in $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, Zn^{2+} preferentially occupies the tetrahedral site and the Fe^{3+} ions are displaced to the octahedral sites. Thus, with increasing x , the $\text{Fe}_A\text{-O-Fe}_B$ interaction becomes weak and T_N is expected to decrease. ZnFe_2O_4 is a normal spinel, i.e., $\text{Zn}_A[\text{Fe}_2]_B\text{O}_4$, and it is not ferrimagnetic, but antiferromagnetic due to $\text{Fe}_B\text{-Fe}_B$ interactions only. T_N of ZnFe_2O_4 is very small, 9 K [18]. The absence of magnetic ions on the A site does not permit the antiferromagnetic A-O-B interaction and hence the magnetic interaction in this ferrite is only on the octahedral (B) site. Now as the overall interaction in a ferrite is antiferromagnetic, the only magnetic interaction in ZnFe_2O_4 , i.e., $\text{Fe}_B\text{-Fe}_B$ is antiferromagnetic [19].

Cobalt zinc ferrite is one of the promising soft ferrite used in electronic devices such as transformer cores, electric motors and generators. Cobalt ferrite nanoparticles are suitable for the isolation and refining of genomic DNA, the parting of polymerase chain reaction ready DNA [20, 21] and especially in hyperthermia treatment. Variation in the concentration of the third metal ion like Zn in Co ferrite can easily alter the distribution of Fe^{3+} ion [22]. Zn substituted mixed ferrites (Co-Zn) are chosen due to their high sensitivity of magnetization to temperature for some applications like self-controlled hyperthermia [23-25].

Till now, low-temperature-fired Ni-Cu-Zn ferrites are the most important materials subjected to study the DC-bias-superposition characteristics [26-28] due to their relatively low sintering temperature, high resistivity and good magnetic properties in the high frequency range [29, 30]. But these investigations were mainly focused how to lower sintering temperature of the NiCuZn ferrites by adding various sintering aids or changing the preparation process, improving the electromagnetic properties [31-37] but there are no reports present on pure NiCuZn ferrite which was studied for DC bias superposition. And, moreover, they are the most important soft ferrites used in multilayer chip inductors (MLCIs) and relevant inductive devices [38-40, 29]. In this work, we chose Mn element to replace Cu element in the NiCuZn ferrites, and investigated the effects of 'Mn' on the magnetic properties, especially DC-bias-superposition characteristic.

Studies on spinel ferrites synthesis methods have led to the development of different chemical synthesis techniques, which have a common feature that all reagents are mixed in atomic or molecular level. Most popular methods of bottom-up synthesis approach mentioned above are co-precipitation [41], sol-gel method [42], microemulsion method [43], hydrothermal [44], spray pyrolysis [45], reverse micelle [46], precursor method [47], etc. Complex schedules and low production rate are common problems of these wet-chemical methods [48].

The main advantages of this process over conventional-hydrothermal process are: (a) the rapid heating to treatment temperature saves time and energy, (b) the kinetics of the reaction are enhanced by one to two orders of magnitude, (c) lead to the formation of novel phases, and (d) lead to selective crystallization. Praveena et al. [49-52] have used the microwave hydrothermal (M-H) method to prepare nano-sized powders of various ferrites with large surface area.

Sol-gel auto-combustion synthesis method (also called low-temperature self-combustion, auto-ignition or self-propagation, as well as gel-thermal decomposition), where the chemical sol-gel and combustion process are combined, has shown great potential in the preparation of spinel type ferrite nanomaterials. Generally, this method can be considered as solution combustion technique [53].

II. EXPERIMENTAL

Synthesis of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Ferrites: Nanocrystalline powders with compositions $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) were prepared using microwave hydrothermal route. High purity (sigma, 99.99%) of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were dissolved in double de-ionized water. An aqueous NaOH was added dropwise to the solution until pH (~13) was obtained. The mixture was then transferred into Teflon lined vessel and kept in microwave digestion system (Model MDS-2000, CEM Corp., Mathews, NC). This system uses 2.45 GHz microwaves and can operate at 0-100% full power ($1200 \pm 50\text{W}$). The system is controlled by pressure and can attain maximum pressure of 200 psi, which is equivalent to 194°C . The time, pressure and powder were computer controlled. The products obtained were filtered and then washed repeatedly with de-ionized water, followed by freeze drying overnight. The prepared powders were weighed and the percentage yields were calculated from the actual weight of the salts taken and the amount that was actually crystallized. The particle sizes of as-synthesized powders were estimated by Transmission Electron Microscope (TEM, JEOL). FTIR spectra's were taken on Bruker Tensor 27 model from 4000 to 400 cm^{-1} . The samples were characterized by Phillips PANalytical X'pert powder X-ray diffraction (XRD) with Cu-K_α ($\lambda = 1.5406\text{Å}$) radiation. The lattice constant (a) for the cubic crystal system was calculated using the equation

$$a = d\sqrt{h^2 + k^2 + l^2}$$
 where (h k l) are the Miller indices of the diffraction peak, and 'd' is the inter-planar spacing. The average crystallite size was calculated from Scherer formula $D_m = \frac{K\lambda}{\beta \cos \theta}$ where K is a constant, λ radiation wavelength, β is full width at half maxima (FWHM) and θ is the diffraction angle. The room temperature complex permeability (μ' and μ'') were measured over a wide frequency range from 1 MHz - 1.8 GHz using Agilent RF impedance analyser 4291B. Magnetic measurements were obtained from a super conducting quantum interference device (SQUID) at room temperature (400 K).

III. RESULTS AND DISCUSSIONS

Structural and morphological studies: Fig.1 shows powder X-ray diffraction patterns of as-synthesized nanopowders. It shows single-phase cubic spinel structure, without any impurity phases. It is interesting to observe that as Zn concentration is increasing the diffraction peaks become broader indicating the nanosize of the crystals with space group symmetry, $fd\bar{3}m$ [54]. The experimental values of lattice constants are compared with the standard JCPDS-ICDD Cards, for Co ferrite (22-1086 ICDD) and for Zn ferrite (89-1009 ICDD).

Using XRD results, the average crystallite size of the samples was calculated as given in Table 1. When the crystallite size drops from bulk to nanosize, the cation distributions as well as the magnetic properties of the compounds would be altered drastically.

As the Zn^{2+} concentration increases crystallite size decreased from 20 to 15 nm, this result conveys that the introduction of Zn in $CoFe_2O_4$ obstructs the crystal growth, which is based on the entropy stabilization which forms disorder in the spinel structure reported by Sharifi and Shokrollahi [55]. The formation of free energy will be comparable to enthalpy of formation for normal spinels and somewhat more negative for spinels with intermediate or inverse cation distributions [56]. As expected the introduction of zinc in the system, more heat will be liberated, decreasing the molecular concentration at the crystal surface and there by obstructing the crystal growth [57, 41]. It is interesting to note that Zn^{2+} ions in the spinel structure have a very strong preference for tetrahedral sites and Co^{2+} ions have a similar strong preference for octahedral sites. Also Fe^{3+} ions have a stronger preference for the tetrahedral sites as compared to the octahedral sites. As Zn is introduced in the system, it forces Fe^{3+} to occupy octahedral sites and the situation becomes less favourable. The decrease in particle size by increase in Zn content may be explained by the electronic configuration of Co^{2+} ($3d^7$) and its more tendency to interact with ligands and oxygen anions, as compared to Zn^{2+} ($3d^{10}$), which has a complete electronic configuration. The lack of 'd' electron is important because it is very weak in covalent interaction and there is a tendency towards extension between Zn^{2+} and ligand. Furthermore, it is reported by some researchers [58] that the smaller particle sizes of the samples doped with Zn ions are due to the lower bond energy of $Zn^{2+}-O^{2-}$ (159 kJ/mol) as compared with that of $Co^{2+}-O^{2-}$ (384kJ/mol).

The lattice constants of the present samples vary from 8.388 to 8.44 Å and are given in Table 1. It is observed that lattice constant 'a' increases as zinc content (x) increases. This variation can be explained on the basis of difference in ionic radii of the substituted ions. The ionic radii of Zn^{2+} (0.82Å) [59] is larger than that of Co^{2+} (0.78Å) [60] ions. In the present system Zn^{2+} ions are substituted in place of Co^{2+} ions and hence lattice constant increases with Zn content (x).

Using the cation distribution data the mean ionic radius of tetrahedral (A) site (r_A) and octahedral [B] site (r_B) was calculated. It is observed from Fig. 3 that r_A increases and r_B decreases with zinc substitution. The increase in r_A is due to the replacement of Fe^{3+} ions at the tetrahedral A-site by the larger radius Zn^{2+} ions. The decrease in r_B may be due to the increased migration of the larger Co^{2+} ions to the octahedral B-site instead of Fe^{3+} ions.

Transmission electron microscope (TEM) analysis: The Selected Area Electron Diffraction (SAED) ring pattern (Fig. 2a) of the nanoparticles of $Co_{0.4}Zn_{0.6}Fe_2O_4$ is well resolved at (220), (311), (400), (422), (511), (440) reflections, as in XRD pattern. The samples exhibited more or less spherical morphology with uniform size. The lattice spacing of 0.24 nm corresponding to the (311) plane confirms the presence of crystalline $Co_{0.4}Zn_{0.6}Fe_2O_4$ particles (Fig. 2b). From Fig. 2c, TEM images of the particles are well separated from each other. The particle sizes of these samples are compared with those calculated from XRD and are listed in Table 1.

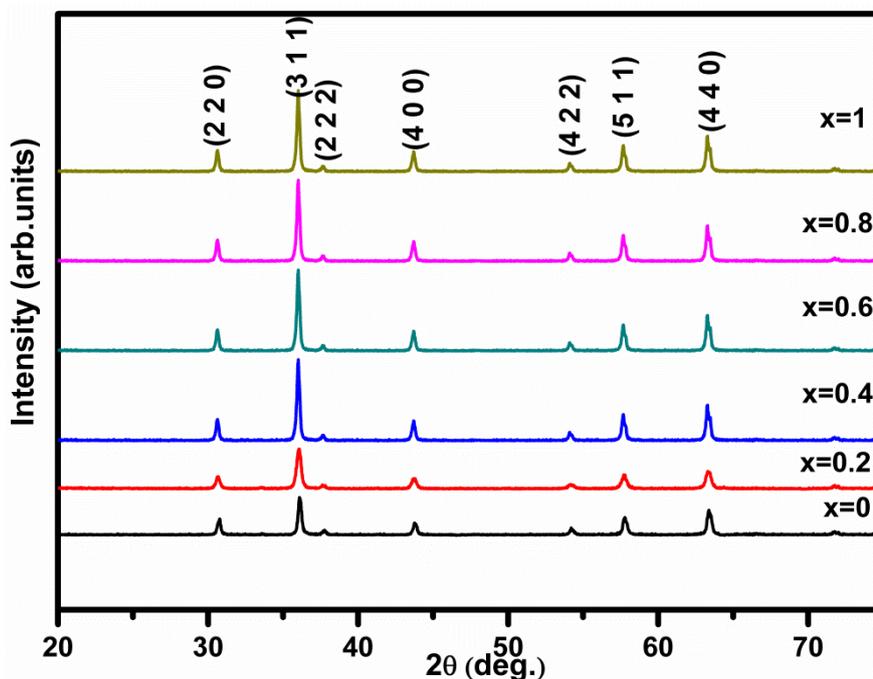


Fig. 1. XRD pattern of the $Co_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) nanoparticles synthesized at temperature 160°C for 15 min.

Table 1. Variation of particle size and lattice constant (*a*) of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$)

Composition 'x'	Particle size (nm) TEM	Particle size (nm) XRD	a (Å)
0	15.2	12	8.388
0.2	14.5	15	8.39
0.4	13.8	18	8.41
0.6	19.4	20	8.42
0.8			8.43
1			8.44

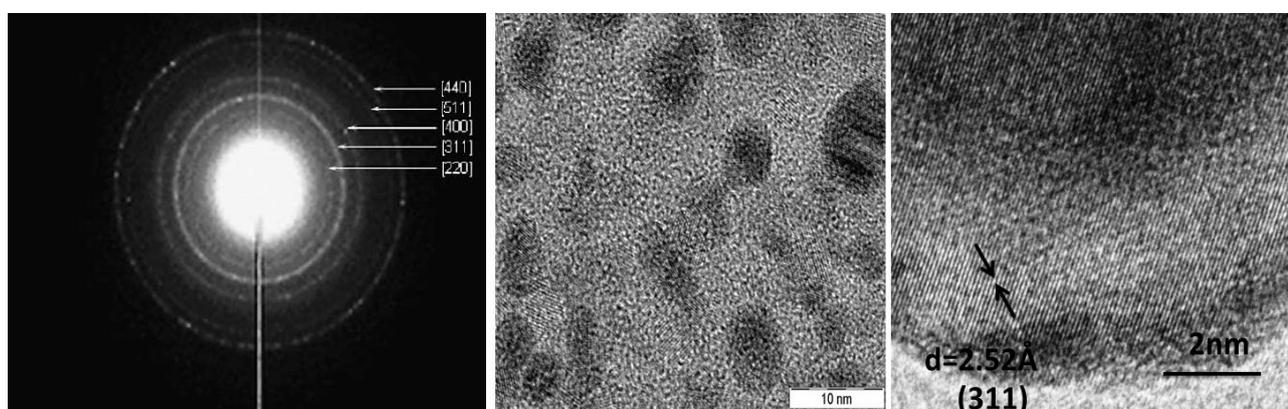


Fig. 2 (a). SAED pattern of $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$. **(b)** High magnification HRTEM image of $\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ showing the (311) oriented lattice planes.

Fourier transform infrared spectroscopy (FTIR): FTIR spectra of as-synthesized nanopowders are presented in Fig. 3. Two main broad metal-oxygen bands are seen in the FTIR spectra of all spinels, and ferrites in particular. The highest one, ν_1 , is generally observed in the range $600\text{--}500\text{ cm}^{-1}$, and it corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site (T_d), $M_{\text{tetra}}\leftrightarrow\text{O}$, whereas the ν_2 lowest band is usually observed in the range $430\text{--}385\text{ cm}^{-1}$, is assigned to octahedral metal stretching (O_h), $M_{\text{octa}}\leftrightarrow\text{O}$ [61-63, 4, 1]. We observed the band at 600 cm^{-1} is assigned as ν_1 ($M_{\text{tetra}}\leftrightarrow\text{O}$), near 400 cm^{-1} , ν_2 ($430\text{--}385\text{ cm}^{-1}$) and below 400 cm^{-1} . The absorption bands observed at ~ 3450 and $\sim 1630\text{ cm}^{-1}$ prove the presence of adsorbed water on the surface of the ferrite nanopowders. The small absorption band at around 1380 and 1720 cm^{-1} in the as-prepared material may be assigned to the unreacted metallic salts and carbonyl respectively. Consequently, the ν_1 band observed at 561 cm^{-1} for ZnFe_2O_4 can be assigned to tetrahedral Zn^{2+} stretching and the ν_2 band observed at 425 cm^{-1} , involves the Fe^{3+} vibration at the octahedral site. The broad band ($3600\text{--}2500\text{ cm}^{-1}$) centered at 3430 cm^{-1} can be assigned to hydrogen-bonded O-H stretching vibration arising from surface hydroxyl groups on nanoparticles and adsorbed water. It seems that the ν_1 band shifts slightly toward the lower wave numbers with increase in 'x' over the composition range and indicating weakening of the metal-oxygen bonds in the tetrahedral sites due to the transition between the extent of normal spinel and inverse structures [64].

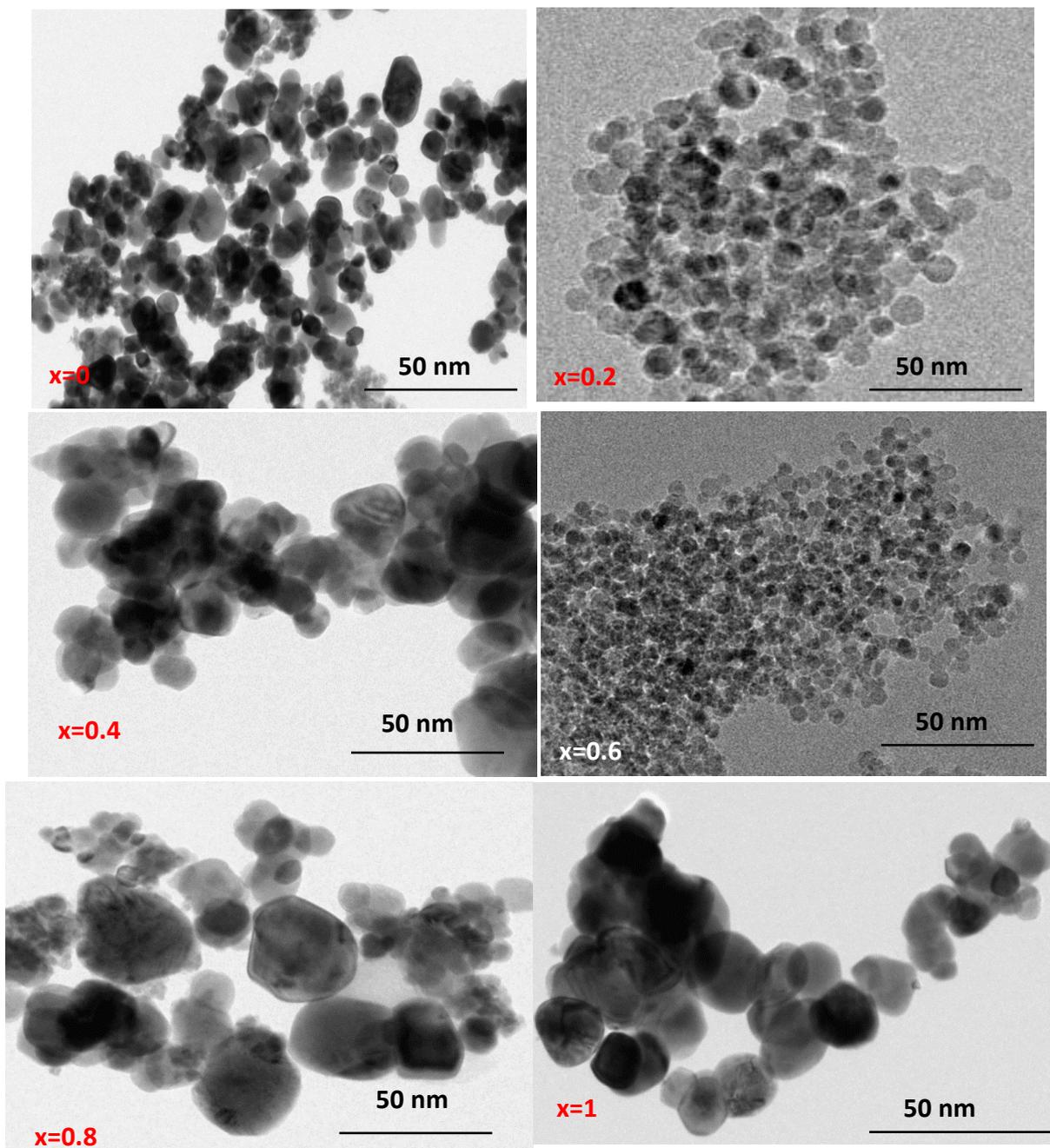


Fig.2c. TEM images of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) nanoparticles.

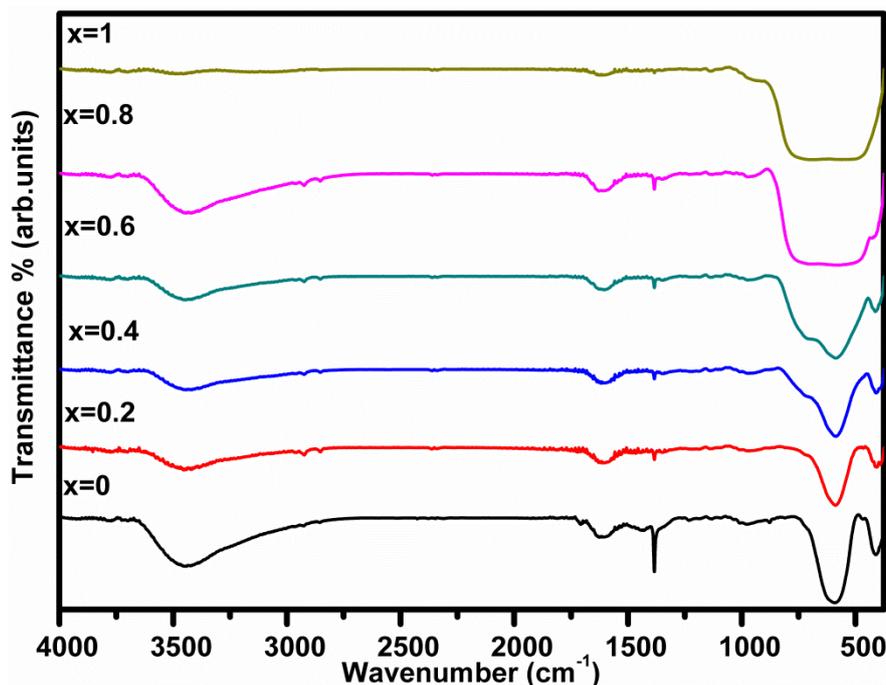


Fig. 3. FTIR spectra for as-prepared $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$).

Frequency variation permeability: Fig. 4(a & b) shows the variation of magnetic permeability components with frequency for $\text{CoZnFe}_2\text{O}_4$ series. The permeability (μ') of ferrite is influenced by wall displacement of magnetization domains at low frequencies, respectively magnetic spin rotation at high frequencies. The highest values of real part of permeability μ' at room temperature belong to $x=0.4$ and $x=0.6$ characterized by highest values of the average grains size and good densification. It is known that high zinc content increases the value of magnetic permeability due to the densification of samples and the increase of magnetic spin rotation contribution [65]. From Fig. 4b could be observed that the lower values of μ'' all the samples. The conduction mechanism in Co ferrite was explained through the existence of simultaneous conduction of n-type ($\text{Fe}^{3+}/\text{Fe}^{2+}$) and p-type ($\text{Co}^{2+}/\text{Co}^{3+}$) which occurs mainly between adjacent B sites, because the distances between metallic cations are sufficiently reduced to facilitate electronic transitions [66].

The real part of permeability spectra for CoFe_2O_4 could be observed that the value of μ' is about 413 at 1MHz and remained constant with an increase of frequency upto 100 MHz. With further increase of frequency the value of μ' is found to increase and shows a relaxation peak at around 108 MHz. From the plots of frequency dependence of imaginary part of permeability (μ'') could be observed that the value of μ'' for all the ferrites are gradually increased with frequency and shows a broad maxima around 108 MHz, where the real part of permeability rapidly decreases, this phenomena is well known as natural resonance [67, 68].

From the complex permeability spectra of CoZn ferrites, it was observed that the real part of permeability (μ') remained almost constant, until the frequency was raised to a certain value and then began to decrease at higher frequency. The imaginary part of permeability (μ'') gradually increased with the frequency and took a broad maxima at a certain frequency, where the real permeability rapidly decreases. This feature is well known as natural resonance [69, 70]. For the chemical composition variation, it was found that the μ' in the low frequency region below 1 MHz decreases with an increase of x , in $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. As 'x' was increased, the natural resonance frequency, where the imaginary permeability had a maximum value, shifts towards higher frequency side.

Room temperature M-H loops: Fig. 5 shows the variation of magnetization with the applied field. All prepared samples at room temperature exhibit ferrimagnetic coupling. As zinc is introduced in the system, it pushes Fe^{3+} ions from tetrahedral A sites to octahedral B sites [71]. This causes the increase in magnetization of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. That is, while the magnetic moment of the A site decreases due to increase of non-magnetic Zn

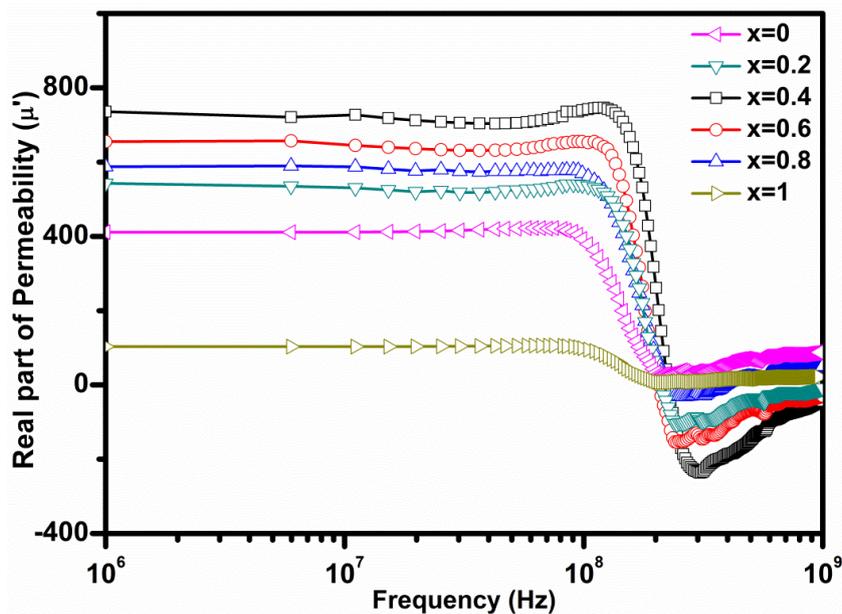


Fig 4a. Frequency variation of real part of permeability of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$).

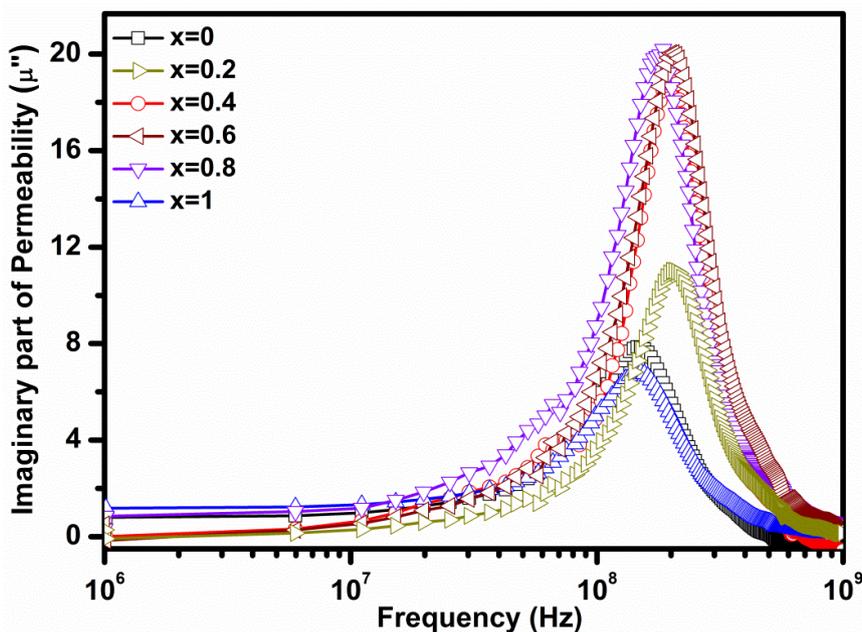


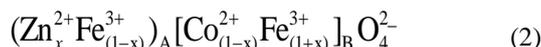
Fig 4b. Frequency variation of imaginary part of permeability of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$).

ions in the A site, the magnetic moment of the B site increases due to increase of Fe^{3+} ions in B site. Therefore, in the present study, when the Zn concentration increases from 0 to 0.2, total magnetization ($M_{\text{oct}} - M_{\text{tet}}$) of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ increases due to the increase of inter-sublattice A–B super-exchange interaction between the magnetic ions of the sublattices A and B. This increase in saturation magnetization with Zn concentration from $x = 0.0$ to $x = 0.2$ is in good agreement with Neel’s collinear two-sublattice model [72]. Further, with increase in the Zn concentration from $x = 0.2$ to $x = 1.0$, the saturation magnetization gradually decreases from 79.04 emu/g to 26.04 emu/g. The results obtained are in well accordance with the earlier reported values [73, 74]. The coercivity also decreases with Zn concentration which is attributed to the non-magnetic character of Zn ion. Since more Zn ions replace with Co ions by increasing ‘x’, the saturation magnetization and coercivity both decrease.

According to Neel's two sublattice model of ferromagnetism the magnetic moments of ions on the tetrahedral (A) and octahedral (B) sites are aligned antiparallel to each other and spins have collinear structure. Therefore, the theoretic magnetic moment per formula unit in μ_B , n_B^t , is described as

$$n_B^t(x) = M_B(x) - M_A(x) \tag{1}$$

where $M_B(x)$ and $M_A(x)$ are the B and A sublattice magnetic moments in μ_B , respectively. The cation distribution of the $Co_{1-x}Zn_xFe_2O_4$ can be written as



As a function of Zn concentration, the theoretical magnetic moment values, n_B^t , of the $Co_{1-x}Zn_xFe_2O_4$ were calculated using the cation distribution given in Eq. 2 and the ionic magnetic moments of Fe^{3+} , Co^{2+} , and Zn^{2+} as $4.85\mu_B$, $2.78\mu_B$ and $0\mu_B$, respectively. The experimental values of the magnetic moments (n_B^e), per unit formula in Bohr magneton (μ_B), were calculated according to the relation [75]:

$$n_B^e = \frac{M_w \cdot M_s}{5585} \tag{3}$$

where M_w is the molecular weight, M_s is the saturation magnetization and 5585 is the magnetic factor. The variation of the theoretic magnetic moment and experimental magnetic moment (n_B^t and n_B^e , respectively) with respect to Zn composition for $Co_{1-x}Zn_xFe_2O_4$ is represented in Table 2. It is observed from the table that the theoretical magnetic moment increases linearly as a function of Zn concentration, and also the experimental magnetic moment, increases with Zn concentration of up to $x = 0.2$, and then gradually decreases with further increase in Zn concentration. This increase in n_B^e with Zn concentration of up to $x = 0.2$ can be attributed to the Neel's collinear two-sublattice model. However, this model is unable to explain the decrease of n_B^e (and hence M_s) with Zn concentration for $x > 0.2$. The decrease in n_B^t (and hence M_s) for $x > 0.2$ which results from the existence of non-collinear spin arrangement in the system could be explained on the basis of the three-sublattice model suggested by Yafet and Kittel [76].

When higher Co^{2+} ions are substituted by Zn^{2+} ions in the $Co_{1-x}Zn_xFe_2O_4$, the magnetic ions of tetrahedral A site are so much decreased, the dominant inter-sublattice A-B super-exchange interaction becomes weaker and hence the intra-sublattice B-B super-exchange interaction strengthens, which in turn results in occurrence of random spin canting on the B site with respect to the direction of spins of the A site. Therefore, it is reasonable to conclude that the canted (non-collinear) spins lead to a decrease in the values of the experimental magnetic moment (and thus the magnetization) with Zn concentration for $x > 0.2$.

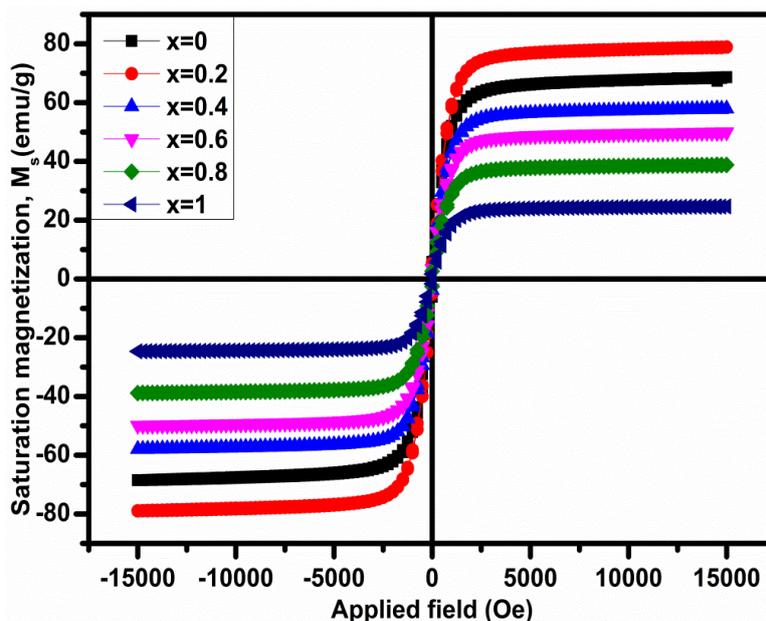


Fig. 5. The magnetic hysteresis loops of $Co_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) at room temperature.

Table 2. Data of saturation magnetization (M_s) for RT, magnetic moment (experimental and theoretical), Y–K angle (α_{YK}), blocking temperature (T_B) for $Co_{1-x}Zn_xFe_2O_4$ system.

'x'	M_s (emu/g) RT	n_B^e (μ_B)	n_B^t (μ_B)	T_B (K)
0	68.71	3.12	2.98	-
0.2	79.04	3.25	4.2	-
0.4	57.7	2.56	5.9	350
0.6	50.82	2.12	7.2	245
0.8	39.12	0.98	8.8	110
1	26.04	0.2	10.05	49.5

M-T analysis: Fig. 6 shows zero field cooled (ZFC) and field cooled (FC) curves of $Co_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) measured in the temperature range of 10 - 400 K under an applied field of 50 Oe. Firstly, the samples were cooled down without any external magnetic field and then the magnetization of samples was recorded during heating up to 400 K under an applied field of 50 Oe. Later, the samples were cooled down again in an applied field of 50 Oe and then it was recorded during heating up to 400 K under an applied field of 50 Oe. As the temperature increases in ZFC measurement, firstly, the magnetic zero field cooling (MZFC) increases and then reaches a maximum value at specific critical temperature, which is called the blocking temperature (T_B). Above T_B in the unblocked region, the MZFC monotonically decreases with increasing temperature. This is the characteristic behaviour of super-paramagnetic materials.

It is clear from Fig. 6, only the samples with Zn concentration of $0.6 \leq x \leq 1.0$ show super-paramagnetic behaviour at RT indicating that the magnetic interactions between the particles are weak and these samples can be regarded as good candidates for biomedical applications. The ZFC and FC measurements of all the samples except for the samples with Zn concentration ($x = 0.0$ and 0.2) show an irreversible magnetic behaviour below the temperature, called irreversibility (T_{irr}) temperature. T_{irr} is defined as the temperature at which the ZFC and FC curves split from each other and corresponds to the blocking temperature of the largest nanoparticles in the super-paramagnetic systems [77].

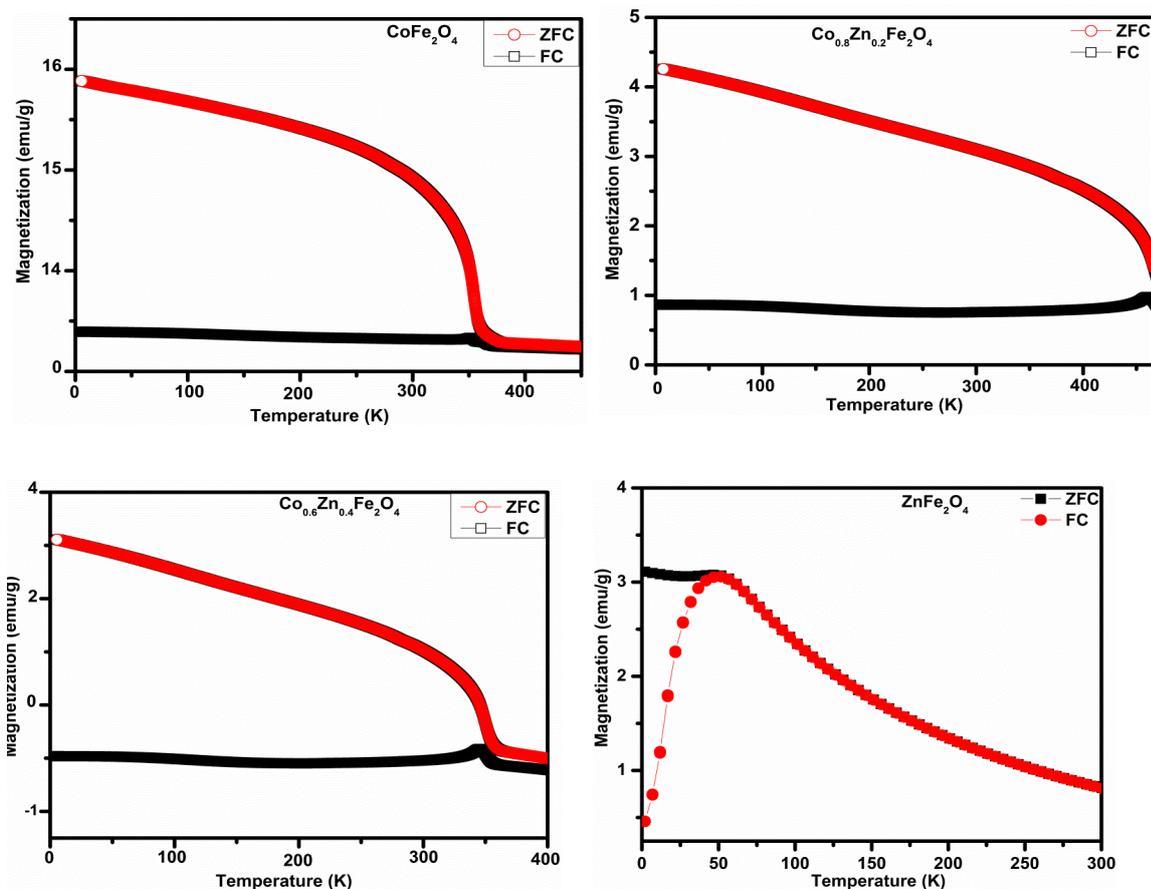


Fig. 6. Zero field cooled (ZFC) and field cooled (FC) curves of the $Co_{1-x}Zn_xFe_2O_4$ under an applied magnetic field of 50 Oe.

Fig. 7 shows the variation of the coercive field (H_c) as a function of temperature. It could be easily seen that H_c strongly depends on both Zn concentration and temperature. Also H_c substantially increases with decreasing temperature. This is due to increase of effective magnetic anisotropy with decreasing temperature because the content of the Co^{2+} ions on the octahedral (B) sites increases with decreasing temperature [78]. In this study, the coercive field value of pure cobalt ferrite is 12585 Oe at 10 K, which is much larger than that of bulk $CoFe_2O_4$ (about 5 kOe at 5 K). At low temperatures, the frozen surface spins resulting from coating material are strongly pinned with ordered core spins by exchange interactions and thus extra energy is needed to switch the ordered core spins. This interaction in the present system could be the reason for increase in coercive field at low temperatures [79]. Similar results have been reported in metal-substituted ferrite particles [80, 81].

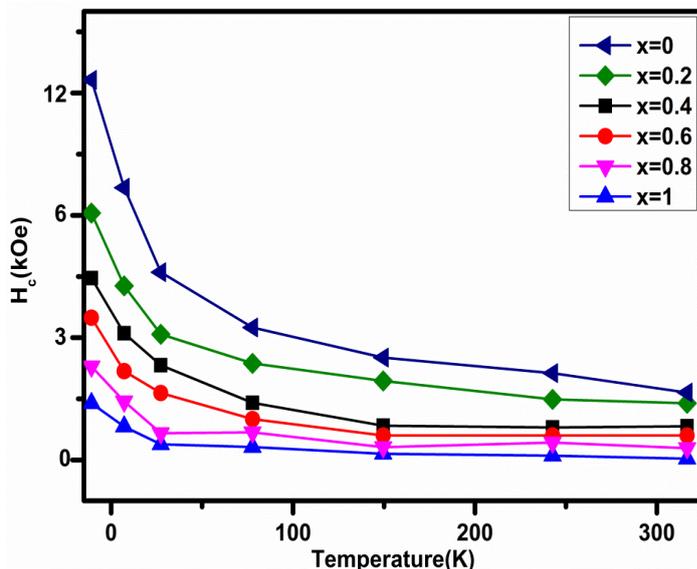


Fig. 7. Temperature dependence of the coercive field for $Co_{1-x}Zn_xFe_2O_4$.

Fig. 8 shows the variation of the coercive field (H_c) and effective magnetic anisotropy constant (K_{eff}) with respect to Zn concentration at room temperature. It can be easily seen from figure that H_c and K_{eff} decrease with increasing Zn concentration. According to the Stoner-Wohlfarth model, H_c for an assembly of non-interacting 3D random particles is given by $H_c = 0.985 K_{eff}/M_s$ for uniaxial anisotropy and $H_c = 0.64 K_{eff}/M_s$ for cubic anisotropy. It was found from the M_r/M_s results that all the samples in this study have uniaxial anisotropy. Therefore, to calculate the K_{eff} , the relation $H_c = 0.64K_{eff}/M_s$ was used. As shown in Figs. 5, 7 and 8, H_c is almost negligible at room temperature for $0.6 \leq x \leq 1.0$, indicating the existence of super-paramagnetic behaviour for only these samples. The coercive field is associated to the strength of the magnetic field that is required to overcome the anisotropy barrier. According to the Stoner - Wohlfarth theory, magnetic anisotropy energy (E_A) for non-interacting single-domain particles is given by

$$E_A = KV \sin^2 \theta \tag{5}$$

where K , V , and θ are magnetic anisotropy energy constant, volume of the particles and the angle between magnetization direction and the easy axis of a nanoparticles, respectively. With reducing of magnetic anisotropy, the magnetic anisotropy energy barrier (E_A) decreases, which causes lower external magnetic field for spin reversal. The strong magneto-crystalline anisotropy of cobalt ferrite is mainly due to the presence of Co^{2+} ions in the octahedral (B) sites of the spinel structure [82]. When the Zn concentration increases in cobalt ferrite the concentration of the Co^{2+} ions in the octahedral (B) sites decreases, which leads to decrease in effective magnetic anisotropy. Therefore, in this study, the effective magnetic anisotropy, K_{eff} and accordingly H_c of the samples decrease with increasing Zn concentration. The decrease of K_{eff} and H_c with increasing Zn concentration is generally expected behaviour in metal-substituted ferrite particles [83, 80].

At blocking temperature (T_B), the magnetic anisotropy energy barrier of the single-domain nanoparticles, $K_{eff} V$ is overcome by thermal energy kT_B , where K_{eff} and V are magnetic anisotropy energy constant and volume of the particles, respectively, k is the Boltzmann constant and T_B is the blocking temperature and then the spins fluctuate randomly above T_B . The T_B values of the samples are listed in Table 2. It is observed from the ZFC and FC measurements in Fig. 6 that the T_B of only the $0 \leq x \leq 0.2$ is higher than 400 K because of higher effective magnetic anisotropy and T_B of $0.4 \leq x \leq 0.6$ gradually decreases with increasing Zn concentration. It is known that the blocking temperature depends on the effective magnetic anisotropy. As seen from Fig. 6, the anisotropy constant continuously decreases as a function of Zn concentration. Therefore, the blocking temperature decreases with increasing Zn concentration. It has been widely reported that the magnetic interactions such as dipole-dipole interactions between the particles and exchange interactions between surface spins and core spins of the nanoparticles play an important role in determining the magnetic properties of the particles [84, 85]. The stronger dipolar interactions also result in the increase in the

blocking temperature. As well as a decreasing magnetic anisotropy, and a weakening of dipolar interactions at high Zn concentrations is another reason for the reducing blocking temperature.

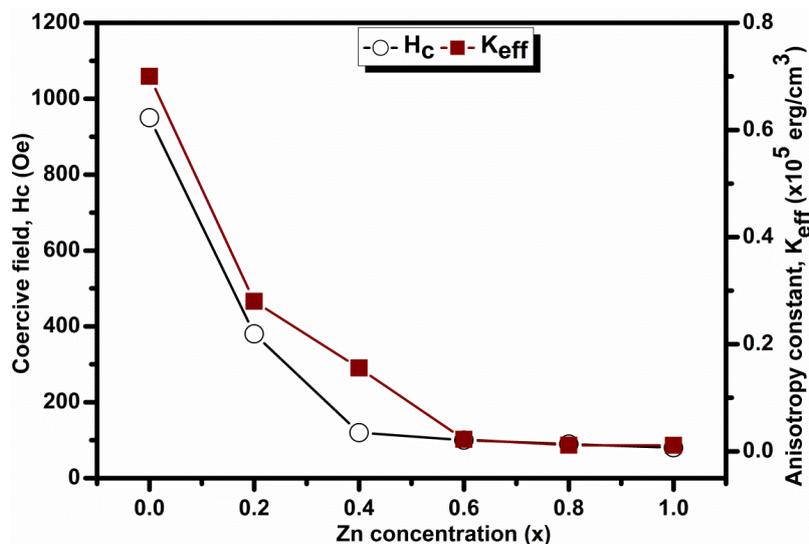


Fig. 8. Composition dependence of coercive field (H_c) and effective magnetic anisotropy constant (K_{eff}) of $Co_{1-x}Zn_xFe_2O_4$ at room temperature.

Synthesis of $Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe_2O_4$

The energy to form the Ni-Zn-Mn ferrite nanocrystallites is provided by oxidation-reduction process of thermal precursor and fuel in the sol-gel auto-combustion process [86]. Metal nitrates were employed in this process as they have a dual role of being a soluble cation source and the oxidant [87]. Citric acid was used with 2 important roles: the fuel for the combustion reaction and as a chelating agent to form complexes with metal ions, preventing the precipitation of hydroxylated compounds [88].

The materials used were nickel nitrate hexahydrate (99.99 %, Aldrich), zinc nitrate hexahydrate (98%, Aldrich), manganese nitrate hexahydrate (99.5%, Aldrich), iron nitrate monohydrate (98%, Aldrich) and citric acid monohydrate (99%, Merck, India). The synthesis was achieved by mixing stoichiometric proportions of the respective nitrates and citric acid. For each nitrate, was taken a solution called citrate precursor. First citric acid was dissolved in distilled water in the ratio 1:3 (mol %) relative to the corresponding metal nitrate under magnetic stirring and heating to 60°C. The next step was to add mass nitrate still under magnetic stirring and heating until complete formation of the metal complex reaction with citric acid, forming metallic citrate resulting in a clear and stable solution. With constant stirring the pH of the solution was adjusted to about 7 with ammonia. The resulting mass was subjected to auto-combustion on a hot plate at 200°C for 2h, there by releasing the large amount of gases (CO_2 , H_2O , N_2), and auto-combustion occurred giving rise to a dark brown ferrite powder. And the powder was subsequently ground for further heat treatment and structural characterizations.

The TG/DTG curve was obtained in a thermo-balance Perkin Elmer Model TGA 7 HT in a nitrogen atmosphere at a heating rate of 5°C/min in the temperature range 25-1100°C. To confirm the phase formation for the as-prepared samples, a Phillips PANalytical X'pert powder X-ray diffractometer (XRD) was used, with Cu K_α (radiation wavelength $\lambda = 1.54\text{\AA}$). The particle size and morphology of the powders were studied using the transmission electron microscope (Model JEM-2010, JEOL, Tokyo, Japan). The ferrite powders were pressed into pellets and toroidal specimens using a 1500 Kg/cm² pressure by adding polyvinyl alcohol (PVA) 2 wt% as binder. Here we have made an attempt of optimizing the sintering temperature of this particular composition $Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe_2O_4$, sintering at 400, 500, 600 and 700°C for 4h using conventional sintering method. Magnetic measurements were made using a vibrating sample magnetometer (VSM), Lakeshore 7500, USA. The incremental permeability and Q-factor under dc-bias-superposition conditions were measured by means of a precision LCR meter (Agilent 4284A) with a dc bias current source (N9936A).

Results and Discussions of $Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe_2O_4$ Ferrite

Thermo-gravimetric analysis: Fig. 9 shows the thermo-gravimetric analysis of $Ni_{0.4}Zn_{0.2}Mn_{0.4}$ ferrite. The TGA-DTG curves indicate that the degradation of dried gel show multi-step weight loss. The first stage of degradation can be observed between 26 and 200°C, with respect to the output of waste water which is adsorbed on the material during the synthesis step, the step of degradation can be best viewed through the DTG curve, which should be the derivative of the TGA, broadens the mass losses that are subtly displayed in the TGA curve.

The second stage of degradation occurs between 200-550°C, which is related to structural water and traces of NO, NO₂, CO and CO₂. The third stage of degradation occurs between 550 and 1000°C, this loss is related to the output of volatile organics still remaining in the material after 1000°C. A continuous line in the TGA curve is related to the end of the degradation of organic matter and the formation of oxides can be observed indicating formation of 100% crystalline phase and ceramic yield of about 90%.

In aqueous chemistry, the degree of condensation varies with different ligand types and the formation of ligands in turn depends on the pH region [89]. As the pH value of the aqueous solution was modified to 7, better condensation process during hydrolysis provided single step decomposition to form the nanocrystallites. The weight loss for precursor occurs in two steps. In fact, O-H groups, carboxyl group and NO₃⁻ ions exist in the dried gel [90]. The first weight loss represents the water vaporization of O-H groups. In the second step, a large weight loss represents the decomposition of carboxyl, NO₃⁻ ions and NH₄NO₃, and at the same time, auto-combustion occurred. The decomposition of NH₄NO₃ supplied oxygen to accelerate the combustion reaction [91]. As the decomposition of NH₄NO₃ is endothermic process, the combustion temperature is decreased and the amount of heat generated in the combustion process is also decreased. Therefore, the decomposition of NH₄NO₃ favours the formation of small size crystallites in this synthesis.

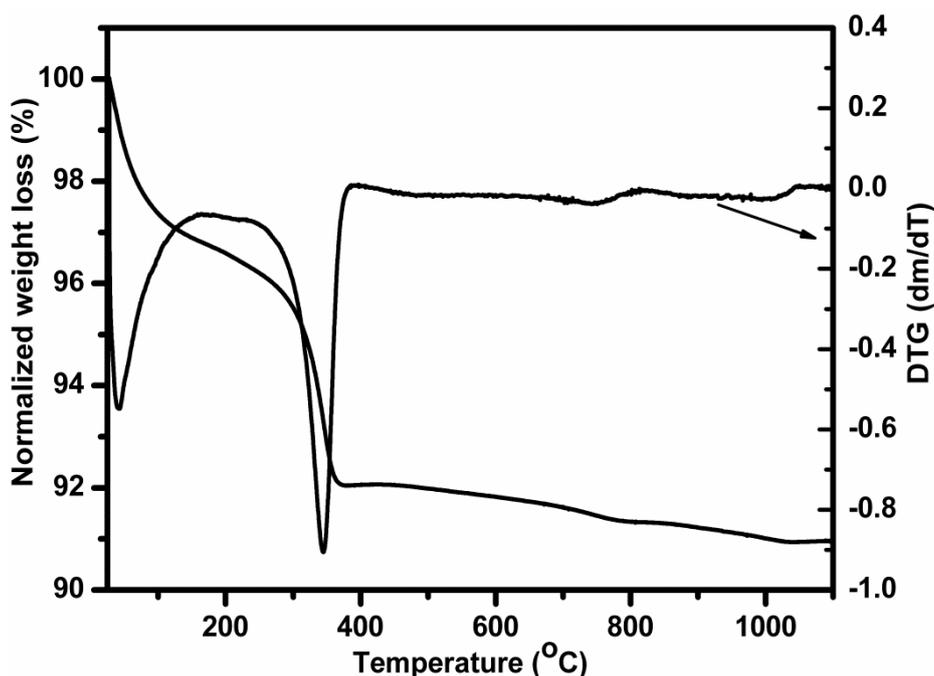


Fig. 9. TGA-DTG of Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe₂O₄ of dried gel.

X-ray diffraction and Rietveld refinement: Fig.10. shows the X-ray diffraction of ferrite Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe₂O₄ sintered at 300°C, 400 °C, 500°C, 600°C and 700°C for 4h. The peaks indicate the formation of single phase spinel. The formation of single phase spinel type was achieved by controlling the atmosphere using argon. By analyzing only the ferrite phase, an increase in peak intensity with increasing calcination temperature can be noted. This is due to the fact that diffusion occurs more readily at higher temperatures, resulting in better organization of the system, which increases the amount of crystalline phase formation observed in the diffraction peaks with better definition and more intensity.

It could be seen from the table 3 that as the sintering increases there is increase in the average crystallite size (D) from 30 nm to 40 nm. Increasing the sintering temperature causes a greater diffusion between grains, increasing the average size of the crystals. The value of lattice constant increases from 8.271 Å to 8.298 Å with an increase of sintering temperature and the lattice parameters are matching well with the reported values.

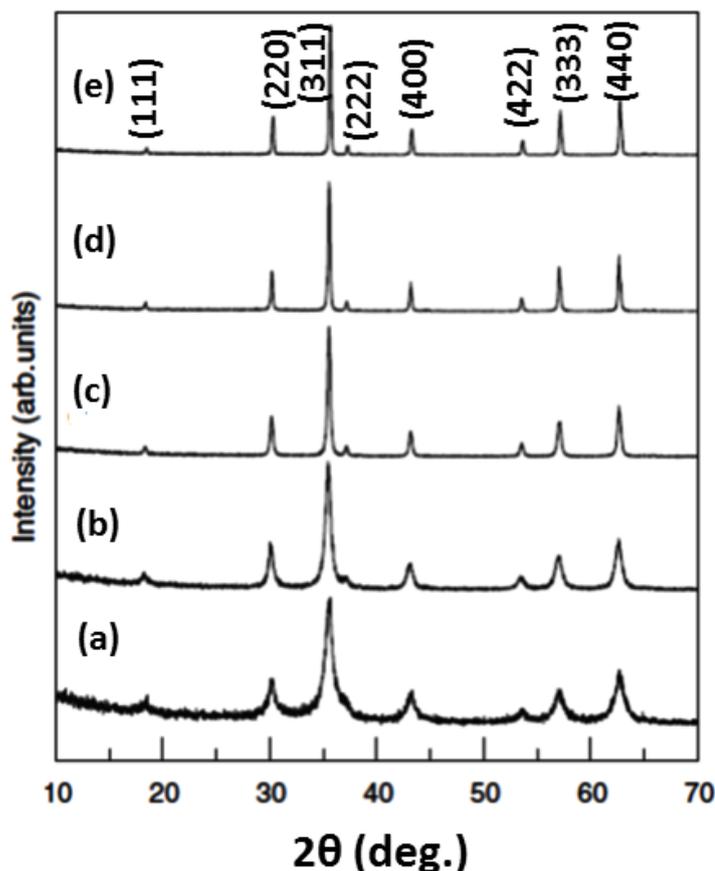


Fig. 10. XRD patterns of $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ powder sintered at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

Table 3. Values of lattice constant, strain, bulk and x-ray densities, porosity, and crystallite size.

Temperature	Lattice Constant (Å)	Lattice constant (Å) from refinement	Strain (%) from refinement	Bulk density(d_b) (g/cc)	X-ray density(d_x) (g/cc)	Porosity (%)	Particle size (nm) TEM
As-prepared	8.271	8.26	1	4.61	5.02	9	18
400°C	8.283	8.27	0.2	5.02	5.22	4	22
500°C	8.286	8.28	0.1	5.15	5.30	3	24
600°C	8.293	8.29	0	5.36	5.45	2	26
700°C	8.298	8.30	0	5.60	5.50	2	30

Transmission Electron Microscopy: Fig. 11(a-d) shows the TEM images of $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ sintered at different temperatures, which demonstrates that these samples are in nano-regime. TEM images show better crystallinity as well as regular shape (spherical) and size of particles. However, the crystalline powders are easy to form agglomerates due to nanosize effect and intrinsic magnetism. In order to disperse particles, samples are grinded. The grain size estimated from TEM pictures is slightly lower than the calculated crystallite size. The average particle size from TEM studies was found to be around 18-30 nm. The lattice spacing of 0.32 nm corresponding to the (311) plane is shown in Fig. 11(e). The d-values computed from the XRD and the SAED pattern (Fig. 11(f)) matches well with the standard d-values of Ni-Zn ferrite [92] (JCPDS #00-052-0278).

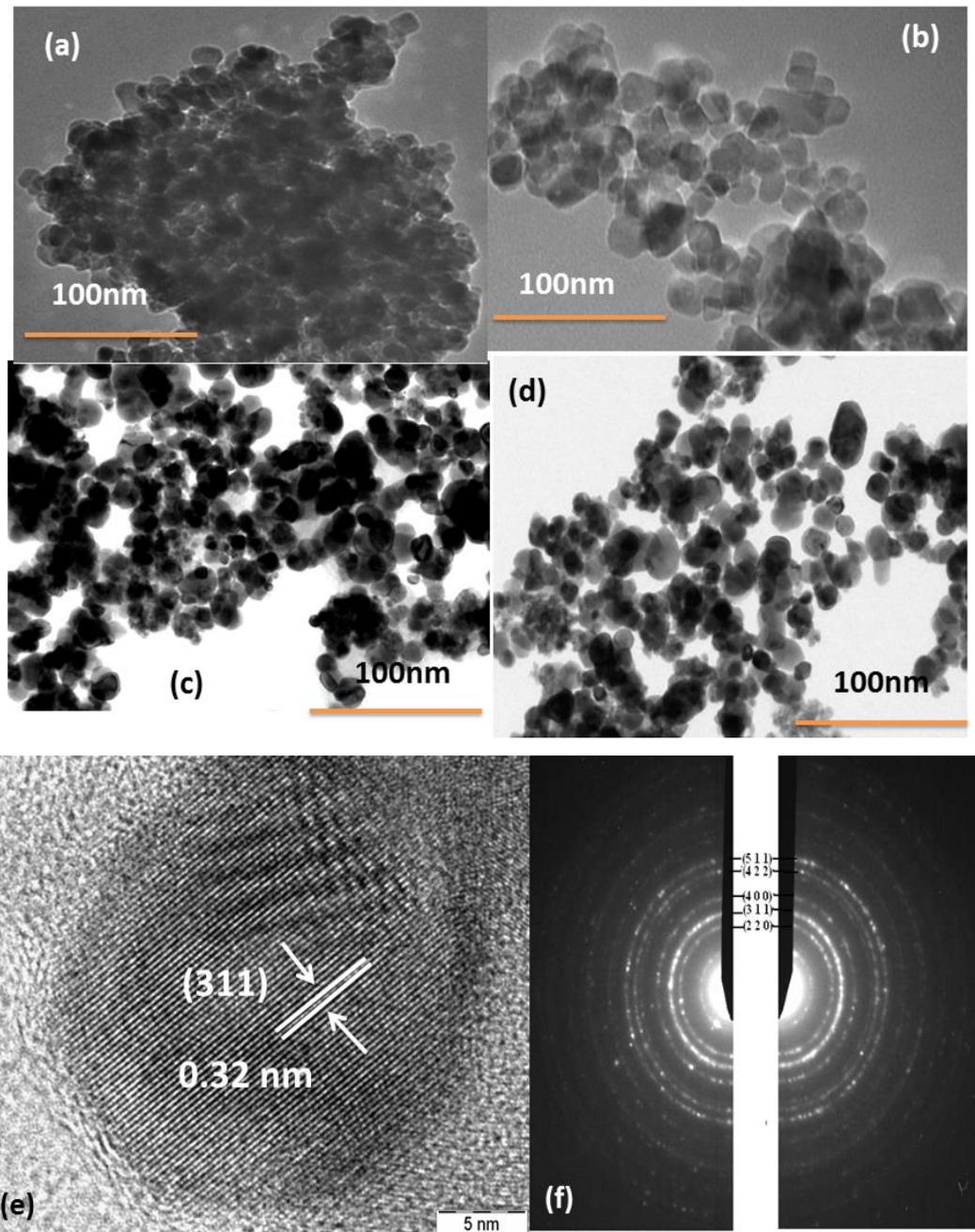


Fig. 11. TEM images of $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$: (a) as-prepared powder, (b) sintered at 500°C, (c) 600°C, (d) 700°C, (e) High magnification HRTEM image of 700°C showing the (311) oriented lattice planes of $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$, and (f) SAED pattern of d-spacing matched with XRD.

Room temperature M-H loops: Fig. 12 shows the dependence of the magnetization as a function of applied magnetic field through the hysteresis loops for $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ sintered at different temperatures. The loops are exhibiting low power loss and low coercivity. The low losses in the reversal magnetic field indicate that it is a soft magnetic material being disengaged little energy to reverse the magnetic moment. The magnetic parameters such as saturation magnetization, remnant magnetization, and coercive field, calculated from the hysteresis curve are arranged in the Table 4. The saturation magnetization values increased with increasing sintering temperature, ranging from 23.91 to 55.80 Am^2/Kg , to the powders sintered at 400 to 700°C for 4h, respectively. The same happened with the coercive field, changing from 4.79 to 6.39 kA/m for the sintered powder samples. The squareness factor (M_r/M_s) also monotonically increases with sintering temperature (Table 4), suggesting an increase in magneto-crystalline anisotropy. We believe this increase in magneto-crystalline anisotropy is most likely due to improvement in crystal order and structure, expected in samples sintered at high temperatures.

The samples had some differences in size after sintering, to truly test their dc-bias-superposition characteristics, the equivalent length of each sample was calculated first. To this end, each wire sample was wound on a reel of 20 turns. According to the

equation: $NI = Hl_e \Rightarrow H = \frac{NI}{l_e}$, where N is the number of wire turns, I is the current, H is the magnetic field, and l_e is the equivalent length of the cores, we could change to compensate the difference in equivalent length of each sample and to ensure that all samples were subject to the same dc-bias-superposition magnetic field.

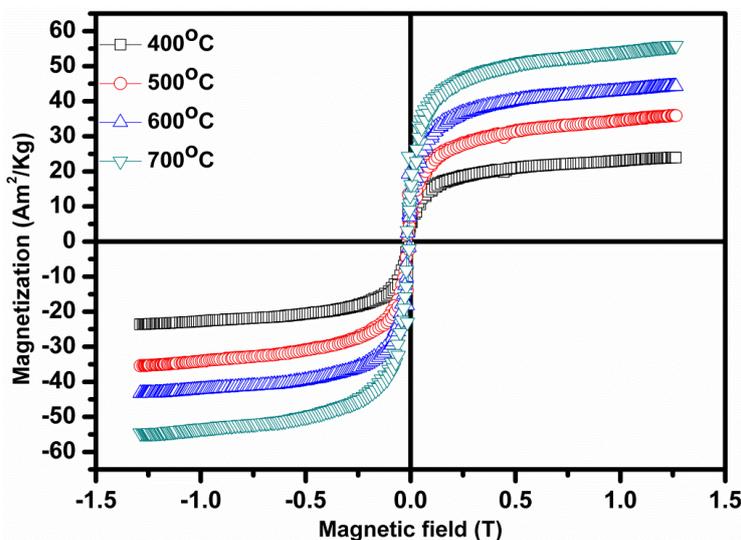


Fig. 12. Magnetic Hysteresis loops of $Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe_2O_4$

Table 4. Remnant magnetization (M_r), saturation magnetization (M_s) and coercive field (H_c) of $Ni_{0.4}Zn_{0.2}Mn_{0.4}Fe_2O_4$ sintered at different temperatures. As temperature increases M_r , M_s and H_c increase.

Temperature	M_s (Am^2/Kg)	M_r (Am^2/Kg)	H_c (kA/m)	$\Delta M(M_s - M_r)$ (Am^2/Kg)	M_r/M_s
400°C	23.91	9.10	4.79	14.81	0.38
500°C	35.87	13.43	5.58	22.44	0.37
600°C	44.26	19.01	5.90	25.25	0.42
700°C	55.80	24.44	6.39	31.36	0.43

Magnetic field dependent permeability: Fig. 13 shows the variation of incremental permeability (tested at 100 kHz) with superposition magnetic field. Permeability first increased for all the samples as the sintering temperature increased, without dc-bias-superposition, which was mainly due to the increase of sintered density and average grain size. With increasing dc-bias-superposition magnetic field, the permeability of all samples decreased continuously.

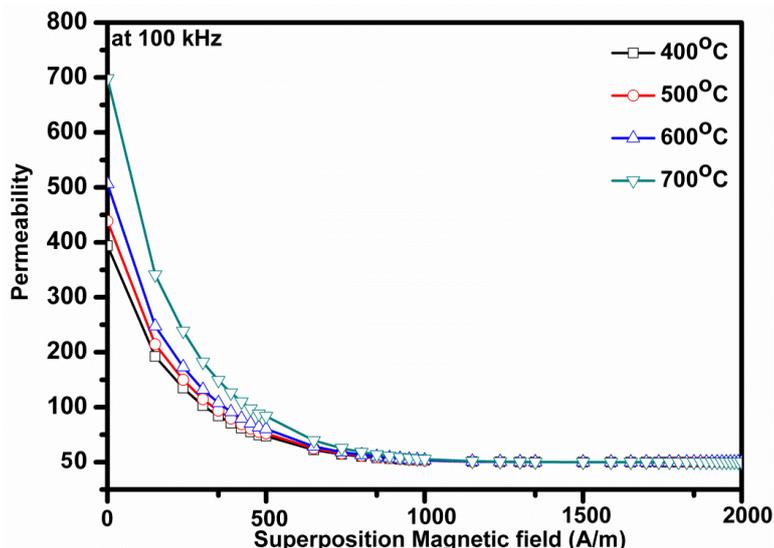


Fig. 13. Variation of permeability with superposition magnetic field.

Magnetic field dependent quality factor: Fig. 14 shows the variation of Q-factor (tested at 100 kHz) with superposition magnetic field for the four samples. The Q-factor first increased with the superposition magnetic field, attaining a maximum at 600 A/m, and then it continuously decreased upon further increasing the superposition magnetic field for all samples. Hence, it could be concluded that a sample that was well sintered and had an even and relatively small average grain size was favourable for attaining better performance in terms of dc-bias-superposition characteristics [93].

To demarcate the intrinsic relationship between microstructure and dc-bias-superposition characteristics, M_r , M_s , H_c and density of the samples were measured. The sample sintered at 400°C has low values of M_s and M_r owing to the fact that it was not well sintered. As the sintering temperature increases, all the parameters M_r , M_s and H_c increase as well as the density also rises, minimizing the porosity of the samples.

It is known that higher M_s and ΔM favour a higher incremental permeability [94]. As the temperature increases, permeability increased and the behaviour is explained above. The Q-factor is determined by density and microstructure. Higher density favours a higher Q-factor. The microstructure with an even and single domain grain size also favours a higher Q-factor. According to Snoek's law, permeability is inversely proportional to the cut-off frequency of ferrites. And the frequency at which the Q-factor attained the maximum value is proportional to the cut-off frequency of ferrites.

In this study, the Q-factor was tested at 100 kHz, although this was not the frequency at which the peak Q-factor appeared. The samples could attain higher Q-factor values at less than 100 kHz. With the increase of superposition magnetic field, incremental permeability decreases; the cut-off frequency and the frequency at which the peak Q-factor appeared gradually shifted to higher values. Hence, with appropriate superposed magnetic field, the frequency at which the peak Q-factor appeared just shifted to 100 kHz, so the Q-factor increased. Thereafter, the frequency at which the peak Q-factor appeared shifted to higher values, so the Q-factor at 100 kHz also gradually decreased.

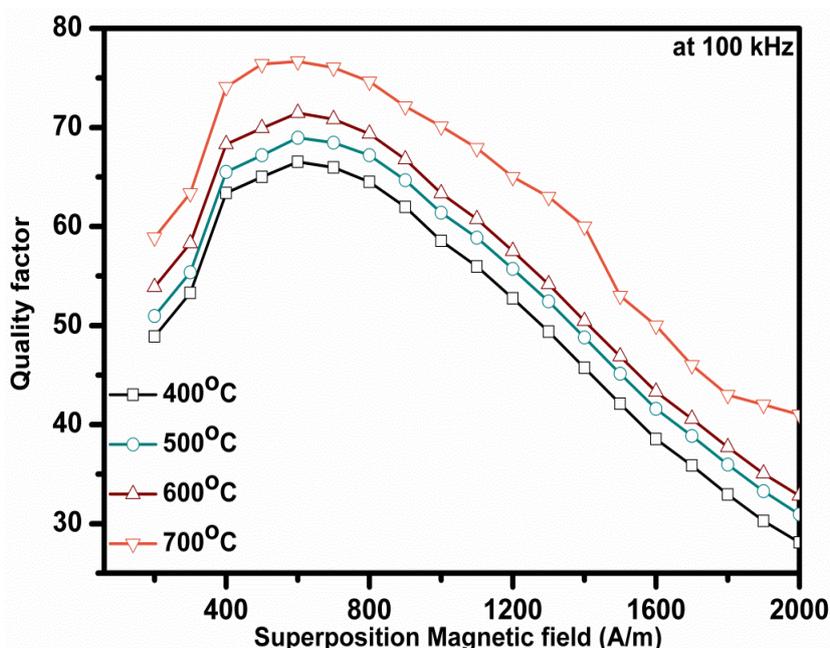


Fig. 14. Variations of Q-factor with superposition magnetic field.

IV. Conclusions

The presence of Zinc ions causes appreciable changes in the structural and magnetic properties of Zn-substituted CoFe_2O_4 synthesized by microwave hydrothermal route. All the nanocrystals exhibit cubic spinel structure. This extensive study of magnetic properties of Co-Zn ferrites confirms that these materials are suitable and good candidates for hyperthermia applications. Zero field cooled (ZFC) and Field cooled (FC) measurements reveal that samples with $0.6 \leq x \leq 1$ have super-paramagnetic behaviour at room temperature, which shows weak interaction between magnetic particles. The blocking temperature obtained from ZFC-FC curves decreases as Zn concentration increases. Lower reduced remnant magnetization (M_r/M_s) values ($x < 0.5$) suggest that all the samples have uniaxial anisotropy. It was found that the effective magnetic anisotropy, the coercivity and remnant magnetization continuously decrease with increasing Zn concentration. The blocking temperature decreases with Zn concentration.

The results specify that the auto-combustion method was effective in getting the single phase of $\text{Ni}_{0.4}\text{Zn}_{0.2}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$. The average crystallite size increased linearly with the calcination temperature. Increasing the crystallite size is related to increased diffusion effect caused by the increase of the sintering temperature. The hysteresis loops showed soft magnetic behaviour. Consequently,

the sample that was well sintered and had a microstructure that consisted of relatively small and even grains favoured the attainment of better dc-bias-superposition characteristics, including permeability and Q-factor. With the addition of Mn to Ni-Zn ferrites, there is not much change in its structure, but it increases its permeability and it is stable up to 600 kA/m of dc-bias superposition magnetic field; so these materials can be used in high frequency power applications as they have very high resonant frequency.

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