Chapter 5

A Review on Synthesis and Characterizations of Mixed Nickel-Zinc Ferrites

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Abstract

Nanotechnology, when this word comes in mind, it gives deep thought of new development in communication, medical science, intelligent transport system and many more. Ferrites nanoparticles have great significance owing to their amazing chemical and physical properties. In modern era we are developing materials for microwave applications and communication devices. Before the discovery of semiconductor memory chips, ferrites were the major form for electronic memory used in computers. Scientist have been studying and working with nanoparticles in magnetically guided drug delivery. The reactivity of material increases by the use of nanoparticles of that material. The dielectric characteristics of ferrites lean on diverse factors for instance methods of preparations and chemical composition. In various studies it has been found that their conductivity has dependence on temperature, composition and frequency. Among the various kinds of ferrites, Ni–Zn ferrites are viewed as the most adaptable ferrites as a result of their novel characteristics for applications at high frequency. The Ni-Zn ferrites are exploited as core materials in a variety of EM devices as well as have broad range of industrial applications e.g. inductors, microwave devices, power supplies, high and low frequency transformer cores, electromagnetic interference (EMI) suppressions and antenna rods. These broad ranges of applications are owing to their high resistivity, low eddy currents, high saturation magnetization, chemical stability and high Curie

temperature. In view of this, the present chapter deals with the research progress on nickel-zinc ferrites in the bulk as well as nano size.

Keywords

Ni-Zn Ferrites, Dielectric Constant, Saturation Magnetization

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1. Introduction

Around 800 B.C. loadstone was discovered in Greek, which is a non-metallic solid. Such substance was utilized as navigation of North. It was found that loadstone can show magnetic properties. De- Magnate published paper related to study of magnetism in 1600 [1]. This is the origin of the era of ferrites. This word originated from the Lattin word “ferrum” meaning iron. Ferrites are ceramic substance and they are hard and grey or black in color. Ferrite materials consist of ferric ions with oxides. Due to high magnetic moment of ferric ions, ferrites show ferromagnetic properties. Owing to the fact of their moderate resistivity and minimum eddy current loss, they are highly versatile in nature [2]. They have remarkable potential to showcase in electronics, computer, catalysis, telecommunication, radar, pigments, radio, television, video tape.

Ferrites are categorised into four types:

- a) Spinel ferrites
- b) Garnet

c) Ortho-ferrites

d) Hexagonal ferrites

Spinel Ferrites: Spinel ferrites are explained by MFe_2O_4 formula, in which M is described as divalent metal ions.

Figure 1: Spinel ferrites crystal structure having tetrahedral and octahedral sites (Reprinted from reference [3] with kind permission from Elsevier, Copyright 2017, Elsevier.

Spinel ferrites possess two interstitial sites name as tetrahedral (A) interstitial sites and octahedral interstitial sites (B). These interstitial sites have different preferences for different materials [4]. Hence, distribution of metal ions on these interstitial sites changes their properties enormously. Figure 1 illustrates the spinel ferrites crystal structure.

Garnet: Garnet ferrites are explained by $Me_3Fe_5O_{12}$ formula, in which Me is a trivalent ion. The crystal structure is cubic and it contains 8 molecules of $Me_3Fe_5O_{12}$. The ions are distributed over dodecahedral sites, tetrahedral sites and octahedral sites. Fe ions distributed over tetrahedral as well as octahedral sites in 3:2 ratio. Me is occupied by dodecahedral sites and surrounded by oxygen ions. Figure 2 illustrates the spinel ferrites crystal structure.

Figure 2: Garnet ferrites crystal structure (Reprinted from reference [5] with kind permission from Springer, Copyright 2009, Springer).

Ortho-Ferrites: Ortho-ferrites are represented by RFeO_3 , in which R addresses the transition-metal ions or otherwise the rare-earth ions. These ferrites consist of the structure of perovskite (ABO_3), where A addresses the 12-coordinated O^{2-} site where generally the ions of lanthanide series resides while B addresses the site which is generally occupied by the transition-metal ion i.e. Fe^{3+} ions. The crystal structure of orthoferrite is shown in Figure 3. An ideal structure of perovskite structure is purely cubic. At room temperature, the mineral perovskite (CaTiO_3) is known to be orthorhombic and when the temperature is increased above than 900°C then becomes cubic. Other ceramics with the perovskite structure include BaTiO_3 , SrTiO_3 , and KNbO_3 . The magneto-optical characteristics of ortho-ferrites are an immediate result of their structure. Generally, the unit cell of ortho-ferrites is orthorhombic to some extent rather than cubic similar to BaTiO_3 . Although the structural unit cell of ortho-ferrite is nearly cubic, however the angle among the a-b plane and c-axis is larger than 90° to some extent. The cell of orthorhombic has a minor canting ($\sim 0.6^\circ$) in ortho-ferrite unit cell. An illustration of a typical ortho-ferrite is YFeO_3 .

Figure 3: Representation of YFeO₃ unit cell.

It crystallizes orthorhombic unit cell with distorted perovskite structure. The location of Y³⁺ ions plays the major role to distort the structure of perovskite while Fe³⁺ ions reside in the octahedral surroundings. This structure can be imagined as a three-dimensional network of strings of FeO₆ octahedral. One of the anions (O²⁻) forms the common apex of the two adjacent octahedral and display for the super-exchange bond (Fe-O-Fe) between two iron ions. Figure 3 illustrates the YFeO₃ unit cell.

Hexagonal ferrites: hexagonal ferrites are further divided into M, Y, W, Z, X and U compounds. All these ferrites have different structure with some similarity with each other.

Table 1: Comparison of various descriptions of the molecular units of hexagonal ferrites (Reprinted from reference[6] with kind permission from Elsevier, Copyright 2012, Elsevier).

Ferrite	Molecular Units	Molecular formula
S	S	CoFe ₂ O ₄
M	M	BaFe ₁₂ O ₁₉
Y	Y	Ba ₂ Co ₂ Fe ₁₂ O ₂₂
W	M+2S	BaCo ₂ Fe ₁₆ O ₂₇
Z	M+Y	Ba ₃ Co ₂ Fe ₂₄ O ₄₁
X	2M+2S	Ba ₂ Co ₂ Fe ₂₈ O ₄₆
U	2M+Y	Ba ₄ Co ₂ Fe ₃₆ O ₆₀

The comparison of various descriptions of the molecular units of hexagonal ferrites is given in Table 1. Ferrites are largely popular in industry because of their huge applications and versatile nature. Among all ferrites, spinel ferrites MFe_2O_4 are quite well known in research field because of their stable structure. As a mentioned earlier, spinel ferrites contain tetrahedral interstitial sites (A) and octahedral interstitial sites (B) with MFe_2O_4 formula. There are total 64 tetrahedral sites and 32 octahedral sites in a unit cell. Cations are distributed differently in different spinel, which is the major cause of variable properties in spinel ferrites and hence their vast application in numerous industries. In consideration of distribution of divalent ions, these ferrites are divided into three categories.

- a) Normal spinel ferrites: when all tetravalent sites are occupied by divalent metal ions and all octahedral sites are occupied by trivalent iron ions $[\text{Fe}^{3+}]$. Such kind of ferrites is known as normal spinel ferrites. For e.g. Ni-Zn ferrites, Mn-Zn ferrites, Zn ferrites, Co-Zn ferrites.
- b) Inverse spinel ferrites: when tetrahedral sites are occupied by trivalent iron ions $[\text{Fe}^{3+}]$ and octahedral sites are occupied by trivalent iron ions as well as divalent ions. Such kinds of ferrites are known as inverse spinel ferrites. For e.g., Ni-Co ferrites, Co ferrites.
- c) Random spinel ferrites: when divalent ions and trivalent iron ions can occupy any octahedral and tetrahedral sites with no fixed proportion. Such ferrites are known as random spinel ferrites. For e.g. $(\text{Mn}^{2+}_{0.8} \text{Fe}_{0.2}^{3+})_A [\text{Fe}_{1.8}^{3+} \text{Mn}^{2+}_{0.2}]_B \text{O}_4$.

Therefore, chemical formula for spinel ferrites can be written as $(\text{M}_{1-a} \text{M}'_a)_A (\text{M}_a \text{M}'_{1-a})_B \text{O}_4$. Where M is divalent ions M' is trivalent ions, A is representing tetrahedral sites, B is representing octahedral sites, If $a=0$ then it is normal spinel ferrite, if $a=1$ then it is inverse spinel ferrite and if $0 < a < 1$ then it is random spinel ferrite

2. Nickel-zinc ferrites

F.A. Hezam et al. [6] prepared $\text{Ni}_{0.5}\text{Mg}_x\text{Zn}_{0.5-x}\text{Fe}_2\text{O}_4$ ($0.0 < x < 0.5$) by co-precipitation method. The size of nano ferrites was found to be 30 nm and structure was cubic spinel. Lattice constant and crystal size was calculated which was observed to be affected with the addition of Mg^{2+} . Magnetization of ferrites was also affected and it was found to be increased with increase in Mg^{2+} ions. Figure 4 illustrates the variation of lattice constant, crystallite size and saturation magnetization with Mg^{2+} ions content.

Figure 4: Variation of lattice constant, crystallite size and saturation magnetization with Mg²⁺ ions content (Reprinted from reference [7] with kind permission from Elsevier, Copyright 2021, Elsevier).

Superparamagnetic properties were showed by all ferrites sample conforming through sample magnetometer techniques. Mg²⁺ and Zn²⁺ have taken tetrahedral site resulting into super exchange interaction between Ni²⁺ and Fe³⁺. J.N. Pavan Kumar Chintala et al. [8] synthesized Ni_{0.65}Zn_{0.35}Fe₂O₄ ferrite by using sol-gel technique. Sample structure was found to be cubic spinel. They found high value of saturation magnetization 176 emu/g at temperature 10 K. R. Verma et al. [9] fabricated Zn_{1-y}Ni_yFe₂O₄ (y= 0.0 to1.0) nano powder. With the help of XRD, sample magnetometer and U-V the structural, magnetic and optical properties were investigated. These studied confirmed that lattice parameter and coercivity decreased, saturation magnetization increased due to more addition nickel ions. Band gap was linearly varied with the concentration of nickel. S. Kumar M V et al. [10] prepared Ni_{1-x}Zn_xGd_{0.1}Fe_{1.9}O₄ (0 ≤ x ≤ 1) with the help of citrate auto-combustion

synthesis process at low temperature. In this study, lattice constant and crystalline size reduces with addition of Zn^{2+} ions. They further reported that Zn ions occupied tetrahedral sites, which raise the tetrahedral site's radius and reduce octahedral site's radius while saturation magnetized has increased and coercivity force has reduced with increase in the concentration of Zn. D. Venkatesh et al. [10] fabricated $\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ (where $x = 0.05$ to 0.25 in steps of 0.05) with citrate gel auto-combustion method. Cubic spinel structure was observed for all samples.

Table 2: Variation of magnetic and microstructure parameters (Reprinted from reference [10] with kind permission from Springer, Copyright 2019, Springer).

Composition (x)	Remanence M_r (emu/g)	Coercivity H_C (Oe)	Remanence ratio (M_r/M_s)	Grain diameter (nm)	Cation distribution
0.00	4.21	73.93	0.0690	130	$(\text{Zn}_{0.5}\text{Fe}_{0.4}\text{Ni}_{0.1})$ [Ni _{0.4} Fe _{1.6}] O ₄
0.05	13.51	98.64	0.2304	155	$(\text{Zn}_{0.45}\text{Fe}_{0.45}\text{Ni}_{0.1})$ [Ni _{0.4} Fe _{1.55} Cu _{0.05}] O ₄
0.10	10.44	89.72	0.1902	195	$(\text{Zn}_{0.4}\text{Fe}_{0.5}\text{Ni}_{0.1})$ [Ni _{0.4} Fe _{1.5} Cu _{0.1}] O ₄
0.15	12.21	101.67	0.2332	246	$(\text{Zn}_{0.35}\text{Fe}_{0.55}\text{Ni}_{0.1})$ [Ni _{0.4} Fe _{1.45} Cu _{0.15}] O ₄
0.20	9.84	110.54	0.1976	200	$(\text{Zn}_{0.3}\text{Fe}_{0.7})$ [Ni _{0.5} Fe _{1.3} Cu _{0.2}] O ₄
0.25	5.98	83.74	0.1345	183	$(\text{Zn}_{0.25}\text{Fe}_{0.75})$ [Ni _{0.5} Fe _{1.25} Cu _{0.25}] O ₄

Figure 5: Variation of initial permeability and grain size with Cu^{2+} ions content (Reprinted from reference [11] with kind permission from Springer, Copyright 2019, Springer).

The lattice constant and magnetization were observed to be decreased with the addition of Cu^{2+} ions and the maximum magnitude of saturation magnetization (61 emu/g) was found for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ sample. Remanence and grain diameter were investigated to be increased with rise in copper concentration up to $x=0.15$. S. A. Jadhav et al. [12] studied $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrites ($x=0.0$ to 1), which was prepared by sol-gel method. The calculated lattice constant was varied from 8.39 Å to 8.32 Å while the crystalline size was changed from 23 nm to 15 nm. In this study photovoltaic potential of all sample also studied. Resistivity was observed to be decrease with rise in temperature, which showed semiconductor behaviour of all samples.

The increase in saturation magnetization was found with rise in Ni ions. Xiaobing Zhou et al. [13] observed that layer of $\text{Ti}_3\text{C}_2\text{T}_x$ on Ni-Zn ferrite can increase its electrical conductivity 6 times as compared to non-coated Ni-Zn ferrite. Such behaviour shows its huge application in beam-line higher-order mode load in advanced particle accelerators. P. Anantha Rao et al. [14] synthesized $\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 0.4) to investigate its structural, magnetic, morphology and electrical properties. All samples were found to be cubic spinel. With addition of Cd ions, lattice constant was observed to be increased as ionic radius of cadmium is higher as compared to zinc.

However, FESEM study indicated an increase in grain size from 40 nm to 73 nm. FTIR study of samples revealed two major peaks at 600 cm^{-1} and 400 cm^{-1} , which told us that Cd^{2+} ions preferred tetrahedral site. From VSM study, it was found that magnetic saturation was decreased from 89.51 to 71.32 emu/g. In addition to it, remanent magnetization and coercive force were increased from 25.36 to 36.48 emu/g and 32.12 to 41.25 emu/g respectively. In DC resistivity study, semiconductor behaviour was observed in all samples as their resistivity declined with raise in temperature.

Figure 6: FESEM images of $\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ nanoferrites (Reprinted from reference [13] with kind permission from Elsevier, Copyright 2020, Elsevier).

Figure 7: Activation energies of $\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ nanoferrites (Reprinted from reference [13] with kind permission from Elsevier, Copyright 2020, Elsevier).

Moreover, activation energy increased initially till $y = 0.1$, afterwards it showed downward trend. A. Bajorek et al. [15] did detailed study of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite, which was fabricated by co-precipitation method. Crystalline size was found to be 14 nm to 20 nm. FTIR confirmed the occupancy of iron on octahedral and tetrahedral sites. Superparamagnetic property was discovered in the magnetization study. Magnitude of coupling constants derived from mean field theory gave proof of opposite magnetization between tetrahedral interstitial sites and octahedral interstitial sites [15]. M.V.S. Kumar et al. [16] synthesized $\text{Ni}_{1-x}\text{Zn}_x\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($0 \leq x \leq 1$, $y = 0.1$) samples with low temperature citrate precursor combustion method. In this study, it was observed that Gd ions preferred octahedral sites in crystal structure. Also, all sample found to have cubic spinel structure. FE-SEM revealed the presence of porosity in all ferrite samples. Zn ions enhanced the hopping between octahedral and tetrahedral site, which increase the ac conductivity of ferrite samples. Additionally, DC resistivity & Curie temperature were investigated to be decreased with the addition of Zn ions. Such behaviour described the increased hopping between Fe^{2+} and Fe^{3+} . T. Dippong et al. [17] synthesized $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4/\text{SiO}_2$ ferrites by sol gel method. With the help of thermal analysis, they have confirmed the formation of nickel-zinc and ferrous ions-succinate precursors around 200°C . Crystalline size, lattice

parameter, magnetic saturation, coercivity and remanence were studied and they all changed their value with Ni content. Super paramagnetic property was observed in all samples.

Figure 8: FE-SEM micrographs of typical samples (a) $x = 0.0$, (c) $x = 0.4$ unirradiated and (b) $x = 0.0$, (d) $x = 0.4$; γ -irradiated for $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ NPs (Reprinted from reference [19] with kind permission from Springer, Copyright 2018, Springer).

M.M. Kothawale et al. [18] studied properties of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrites prepared by Microwave-assisted combustion method. Samples were having large surface to volume ratio with strain value ranges between 9.4×10^{-4} to 3.0×10^{-4} . The crystalline size varies from 51 to 69 nm. In FTIR data absorption bands found at 610 cm^{-1} , 550 cm^{-1} , 450 cm^{-1} , 375 cm^{-1} . The highest value of magnetic saturation was 82.49 emu/g for $x = 0.6$. A high value of saturation magnetization (M_s) is supposed to be the most vital requirement of magnetic recording, magnetic refrigeration, magnetic fluid, permanent magnet material, magnetic resonance imaging, and the magnetic core material. S. Kumar et al. [19] studied $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites synthesized through facile solution combustion technique. They analysed XRD, FTIR, VSM of all the samples. In magnetic study, magnetic saturation was found to be maximum at $x=0.3$ with 38.73 emu/g value, afterwards its value

decrease. Also, with increase in concentration of Zn ions, ferrimagnetic behaviour changed into super paramagnetic nature. V.K. Mande et al. [20] prepared $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$, (Ni-Zn-Cr) nanoparticles with $x=0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 with the help of sol gel auto combustion method. Also, irradiation effects of Co-60 source on each ferrite were investigated.

Figure 9: FTIR spectra for (a) unirradiated and (b) γ -irradiated $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ NPs
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XRD confirmed the cubic spinel structure of both radiated and irradiated sample. FTIR confirmed the metal oxide bond with its absorption peaks. FE-SEM showed that irradiated samples have some distorted morphology as compared to non-irradiated

sample. The dielectric properties were found to decrease with the rise in zinc and Cr^{3+} ions for both the cases i.e. without and with irradiation. S. Ikram et al. [21] prepared $\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Cd}_{0.2}\text{Fe}_{2-b}\text{La}_b\text{O}_4$ ($b = 0.0-0.21$) cubic spinel ferrite through sol-gel auto combustion synthesis process. Effect of La on the properties of ferrite sample were studied and it was found that lattice constant was increased till $b = 0.105$ and then decreased. Absorption bands were observed to be at 540.8 cm^{-1} and 490.8 cm^{-1} , which confirmed the tetrahedral interstitial and octahedral interstitial sites in ferrites. Magnetic saturation, remanence has decreased with the addition of La ions. AC conductivity was found to increase at lower frequency and at higher frequency it is found to decrease. Such type of ferrite is suitable for microwave absorbing applications. M. Kuru et al. [22] synthesized $\text{Ca}_x\text{Ni}_{0.75-x}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.5$ and 0.75) by adopting chemical co-precipitation synthesis process. In XRD investigation, lattice parameter varied from $8.334\text{ \AA}$ to $8.538\text{ \AA}$ and crystal structures were cubic spinel for all samples. Afterwards, crystalline size was measured, which varied between 12 nm to 27 nm . Dielectric properties also studied for different temperature and frequencies. AC conductivity was observed to be decreased with the addition of calcium ions. They observed that grain boundaries have profound role in conductivity. Pathania et al. [23] synthesized $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{W}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) with the help of co-precipitation method. From SEM, cubic spinel structure was confirmed. They investigated the application of ferrite samples in hydrogen gas sensing at concentration 1000 ppm in a temperature range $80-300$ degrees Celsius. Platinum coating has been made on ferrite pellets by sputtering technique which increased the resistivity. High sensitivity, cheaper price, longer stability, high selectivity and quick response at lower temperature proves that such sensor have numerous advantages in industrial applications. K. S. Ramakrishna et al. [24] prepared $\text{Ni}_x\text{Cu}_{0.1}\text{Zn}_{0.9-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) ferrite nano particles with co-precipitation method. Exchange interaction and magnetocrystalline anisotropy was observed to increase with the substitution of Ni^{2+} ions. It was observed that magnetocrystalline anisotropy constant was temperature dependant as it decreased with increase in temperature. Jean-Luc Mattei et al. [25] synthesized $\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Co}_{0.2}\text{Fe}_y\text{O}_{4-\delta}$ where $y = 1.98$ and $y = 2.3$ by using chemical co-precipitation method. They analysed its application in antenna. At frequency higher than 700 MHz , both samples were found not suitable for antenna applications. However, frequency lowers than 700 MHz , they are well suited for such applications as dielectric loss was quite low. M. M. Ismail et al. [26] studied $\text{Ni}_{1-a}\text{Zn}_{a-2b}\text{Li}_b\text{Fe}_{2+b}\text{O}_4$, where ($0 \leq a \leq 0.5$) and ($b = 0, 0.01, 0.02, 0.03$, and 0.04) ferrites by preparing with sol-gel method. They calculated lattice constant which was observed to be increased with the addition of zinc and decreased with the rise of lithium ions. From SEM, crystalline shape came out to be smooth, spherical and its size came out to be larger than the calculated from XRD data. This suggested the agglomeration in nano

particles. Poisson ratio value was calculated and its value was 0.35, this attribute to isotropic theory and also high stability of the materials. Reduction of elastic constant with the addition of zinc and lithium suggested that interatomic bonding was reducing continuously. As Ni with d^8 configuration and Fe with d^5 configuration replaced with Zinc with d^{10} configuration and lithium with s^2 configuration, which described that totally and half-filled shells are more stable and they don't contribute in bond formation whereas partially filled ions such as nickel are good at making strong bond with oxygen. M. V. S. Kumar et al. [27] did research on $(\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Gd}_b\text{Fe}_{2-b}\text{O}_4; b = 0, 0.1, 0.15, \text{ and } 0.2)$ ferrite sample, which was prepared by low-temperature citrate gel auto-combustion synthesis process. Initially lattice constant and crystalline size was reduced with addition of Gd^{+3} substitutions and then it started increasing. Porosity also declined with the addition of Gd^{+3} concentrations, which was depicted by FESEM. Hopping was observed between $\text{Fe}^{+3} \leftrightarrow \text{Fe}^{+2}$ ions. Such behaviour raised capacitance value. Gd^{+3} replaced the Fe^{+3} ion at B site, while Fe^{+3} occupied A site, which attribute to enhanced dielectric constant. Magnetic saturation value was maximum at $b=0.1$ with 53.80 emu/g and sample showed super paramagnetic value as remanence was quite low. M.K. Anupama et al. [28] prepared $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (where, $x = 0.0, 0.2, 0.4, 0.6, 0.8 \text{ \& } 1$) ferrites with the use of solution combustion method. It was observed that with the addition of Zn ions, ferromagnetic properties have reduced as Zinc is diamagnetic in nature. EPR spectrum examined at room temperature and lands g factor varied from 2.23 to 1.95 with the increase in Zn concentration. This value confirmed that exchange interaction between Fe^{3+} , Ni^{2+} and Zn^{2+} metal ions were not symmetric. T.A. Taha et al. [29] prepared $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4/\text{C}$ ($x=0.0, 0.1, 0.3, 0.5 \text{ and } 0.7$) ferrites through self-combustion synthesis process at temperature. All ferrites exhibit cubic spinel structure and lattice constant, crystalline size and density of samples increased as zinc concentration increased. Also, radius of octahedral site was decreasing as zinc concentration was decreasing. However, tetrahedral site radius remained same. A-O-B interaction in spinel ferrites contributed to net magnetic behaviour. When Nickel ion, which is ferromagnetic in nature, was replaced by zinc ions, which is diamagnetic in nature, then magnetic saturation value reduced. Dielectric constant was also decreasing with frequency. Its maximum magnitude was observed for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ sample, which indicate that this ferrite is best suitable for microwave absorbers fabrication. A. Pathania, et al. [30] synthesized $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{W}_b\text{Fe}_{2-b}\text{O}_4$ ($b = 0.0, 0.2, 0.4, 0.6, 0.8 \text{ \& } 1.0$) ferrites with the help of co-precipitation method and sintered at 850 degree Celsius. Maximum saturation magnetization was found to be 28.05 emu/g and its value was decreased with the replacement of iron ions with non-magnet tungsten ions. Resistivity of samples was found to decline from $2.2 \times 10^5 \text{ } \Omega \text{ cm}$ to $1.9 \times 10^5 \text{ } \Omega \text{ cm}$. Activation energy also reduced from magnitude 0.0264 to 0.0221 eV. Semiconductor behaviour was also observed in all the samples. M.A. Islam et al. [31]

fabricated $\text{Li}_{0.35-0.5x}\text{Ni}_{0.3}\text{Zn}_x\text{Fe}_{2.35-0.5x}\text{O}_4$ ($x= 0.00-0.40$ in steps of 0.10) ferrites with the help of sol- gel auto combustion method, which was sintered at 1100 degree Celsius. In XRD investigation, crystalline size was observed to be 23 nm to 37 nm, which was calculated by Scherrer formula. Lattice constant has also increased with the addition of zinc ions. Other parameters like permeability, magnetization and quality factor also showed increasing trend with the increase in zinc content. The highest value of initial permeability was found to 254 for $\text{Li}_{0.15}\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.15}\text{O}_4$ sintered at temperature 1523 K, which was 6 times as compared to parent composition. Dielectric loss also declined six times as compared to parent sample. Moreover, increasing trend in lattice parameter and decreasing trend in Neel temperature showed that there was weakening in A-B interaction with the increase of zinc concentration.

Figure 10: Variation of the specific surface area and specific surface area to volume ratio of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ samples with crystallite size (Reprinted from reference [32] with kind permission from Elsevier, Copyright 2016, Elsevier).

S.P. Dalawai et al. [32] fabricated $\text{Ni}_x\text{Zn}_{1+y-x}\text{Fe}_{2-2y}\text{Sn}_y\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ and $y = 0.1, 0.2$). In XRD investigation, lattice constant was observed to be similar with parent sample. However, bond lengths at tetrahedral site were decreased due to increase nickel concentration while, bond length for octahedral site remained same. FTIR confirmed the formation of octahedral as well as tetrahedral site. Particle size varied between 20 nm to 60 nm. All samples showed semiconductor behaviour. Moreover, DC resistivity observed to be decrease with nickel content till $x=0.6$ and an increase was found in the same after $x = 0.6$.

Activation energy also showed the similar trend till $x=0.6$ with the increase in nickel ions. M. Ashtar et al. [33] prepared $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0.1, 0.2, 0.3, 0.4$) by using sol-gel synthesis process. The specific surface area as well as specific surface area to volume ratio was found to increase by means of decline in the size when the chromium was doped in nickel-zinc nanospinel ferrite. AC conductivity has increased with the increase in frequency. A. Thakur, et al. [34] $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ through chemical co-precipitation synthesis process, which was sintered at temperature 800°C and 900°C for 3 hours. The magnitude of saturation magnetization was found to increase from 73.88 to 89.50 emu/g as a variable of sintering temperature telling their potential applications in high frequency devices. M. Veena et al. [35] prepared $\text{Ni}_{1-x}\text{Zn}_x\text{Dy}_y\text{Fe}_{2-y}\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8, 1.0$) ($y=0.0$ and 0.1) nanospinel ferrites by novel combustion technique then all samples were irradiated with ^{60}Co gamma radiation with total exposure dose 31 KGy having rate 6.1 KGy/h. XRD of all samples revealed nano size of ferrites. Presence of dysprosium was observed at lower angle with extra peak before and after irradiation since DyFe_2O_3 is present in ferrites.

Also, as Dy^{3+} concentration increases, intensity of peaks reduced. There is a little shift in peaks because of irradiation. Migration of ions in interstitial sites leads into disorder in irradiated samples. Because of irradiation, intensity and broadening of peaks has reduced. As Dy^{3+} with ionic radii 0.092 nm has placed in the position of Fe^{3+} with ionic radii (0.067 nm), which results into raised in lattice parameter from 0.831 nm value to 0.836 nm. Increase in lattice parameters tells that dysprosium ions take octahedral sites. When samples were irradiated, lattice parameter was observed to be enhanced. Dielectric constant was also investigated as function of frequency and concentration for all samples. The value of dielectric constant, loss tangent and ac conductivity was observed to increase with the increase in zinc ions, and then it attained a constant value and found to decrease thereafter. Dielectric constant and ac conductivity both increased in irradiated nano-ferrites.

Figure 11: Variation of the ac conductivity as a function of frequency for of Cr^{3+} doped Ni-Zn ferrites (Reprinted from reference [32] with kind permission from Elsevier, Copyright 2016, Elsevier).

Figure 12: XRD pattern of $\text{Ni}_{1-x}\text{Zn}_x\text{Dy}_y\text{Fe}_{2-y}\text{O}_4$ nanoferrites (a–b) before irradiation (c–d) after irradiation (Reprinted from reference [34] with kind permission from Elsevier, Copyright 2016, Elsevier).

Figure 13: Variation of dielectric constant for $Ni_{1-x}Zn_xDy_yFe_{2-y}O_4$ nanoferrites (a–b) before irradiation (c–d) after irradiation (Reprinted from reference [34] with kind permission from Elsevier, Copyright 2016, Elsevier).

Figure 14: Variation of ac conductivity for $Ni_{1-x}Zn_xDy_yFe_{2-y}O_4$ nanoferrites (a–b) before irradiation (c–d) after irradiation (Reprinted from reference [34] with kind permission from Elsevier, Copyright 2016, Elsevier).

Sarveena et al. [36] prepared $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_x\text{Cu}_y\text{Fe}_{2-x-y}\text{O}_4$ through sol-gel method. Particle size was reduced from 20 nm to 18 nm and lattice parameter raised from 8.348 Å to 8.406 Å.

Figure 15: Variation of magnetization with temperature and Curie temperature with composition for $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_x\text{Cu}_y\text{Fe}_{2-x-y}\text{O}_4$ ferrites (Reprinted from reference [35] with kind permission from Elsevier, Copyright 2016, Elsevier).

This was in good agreement with theoretical measurements. While studying magnetic behaviour, it was observed that magnetic saturation has reduced as well as in electric behaviour, Curie temperature also reduced with the addition of copper and cobalt ions, which were weakening the tetrahedral and octahedral site interaction. J.S. Ghodake et al. [37] prepared $\text{Ni}_{0.60-x}\text{Zn}_{0.35}\text{Co}_x\text{Fe}_{2.05}\text{O}_4$ by using citrate nitrate combustion method. Lattice

constant has increased from 8.09 Å to 8.12 Å as well as crystalline size has increased from 39 nm to 52 nm with the substitution of cobalt ions. Further, in the investigation of magnetic characteristics, increase in retentivity, remanence force and magnetic saturation was observed. Such behaviour was explained on the basis of replacement of Ni^{2+} (low magnetic moment) with Co^{2+} ions (high magnetic moment), which enhanced the A-B interaction. In addition to it, the initial permeability was decreased with the variation of frequency.

Table 3: Summary of structural properties of Ni-Zn ferrites.

Sample	Lattice constant	Crystalline size	Reference
$\text{Ni}_{0.5}\text{Mg}_x\text{Zn}_{0.5-x}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.5$)	8.39 to 8.40 Å	8-23 nm	[6]
$\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$	8.3765 Å	43.13 nm and 38.02 nm	[7]
$\text{Zn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$)	8.33 to 8.43 Å	27.5 to 30.6 nm	[8]
$\text{Ni}_{1-x}\text{Zn}_x\text{Gd}_{0.1}\text{Fe}_{1.9}\text{O}_4$ ($0 \leq x \leq 1$)	8.35 to 8.40 Å	77.6 to 93.2 nm	[9]
$\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ (where $x = 0.05$ to 0.25)	8.36 to 8.39 Å		[10]
$\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	8.34 to 8.40 Å	15 to 23 nm	[11]
$\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4$	8.3894 to 8.4878 Å	42.68 to 40.45 nm	[13]
$\text{Ni}_{(1-x)}\text{Zn}_x\text{Gd}_y\text{Fe}_{(2-y)}\text{O}_4$ ($0 \leq 1 \leq y = 0.1$)	8.354 to 8.404 Å	77.63 to 93.2 nm	[15]
$\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Cd}_{0.2}\text{Fe}_{2-y}\text{La}_y\text{O}_4$ ($y = 0.0-0.21$)	8.439 to 8.465 3 Å		[20]
$\text{Ca}_x\text{Ni}_{0.75-x}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ ($x=0, 0.25, 0.5$ and 0.75)	8.334 and 8.538 Å,	12 nm and 27 nm	[21]
$\text{Ni}_x\text{Cu}_{0.1}\text{Zn}_{0.9-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$)	8.429 to 8.399 Å	22.4 to 21.3 nm	[23]
$\text{Ni}_{1-x}\text{Zn}_{x-2y}\text{Li}_y\text{Fe}_{2+y}\text{O}_4$, ($0 \leq x \leq 0.5$) and ($y= 0, 0.01, 0.02, 0.03$, and 0.04)	0.839 to 0.835 nm	41.9 to 41.935 nm	[25]
$(\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4; y = 0, 0.1, 0.15$, and $0.2)$	8.3156 to 8.3259 Å		[26]

$\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4/\text{C}$ ($x=0.0, 0.1, 0.3, 0.5$ and 0.7)	8.260 to 8.397 Å	18.50 to 36.00 nm	[28]
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{W}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ & 1.0)	8.3730 Å		[29]
$\text{Li}_{0.35-0.5x}\text{Ni}_{0.3}\text{Zn}_x\text{Fe}_{2.35-x}\text{O}_{4-x}$ ($x=0.00-0.40$)		23 to 37 nm	[30]
$\text{Ni}_{(x)}\text{Zn}_{1+y-x}\text{Fe}_{2-2y}\text{Sn}_{(y)}\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$; $y = 0.1, 0.2$)	8.436 to 8.302 Å	36 nm	[31]
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0.1, 0.2, 0.3, 0.4$)	8.400 to 8.389 Å	56 to 11 nm	[32]
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$		38.36nm to 42.16nm	[33]
$\text{Ni}_{1-x}\text{Zn}_x\text{Dy}_y\text{Fe}_{2-y}\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8, 1.0$) ($y=0.0$ and 0.1)	0.8310 nm to 0.8356 nm		[34]
$\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_x\text{Cu}_y\text{Fe}_{2-x-y}\text{O}_4$ ($x=0.0, 0.1, 0.2$) & ($y=0.0, 0.05, 0.05$)	8.348 Å to 8.406 Å		[35]
$\text{Ni}_{0.60-x}\text{Zn}_{0.35}\text{Co}_x\text{Fe}_{2.05}$ ($x=0.0$ to 0.4)	8.09 Å to 8.12 Å	39 nm to 52 nm	[36]

Table 4: Magnetic properties of mixed Ni-Zn ferrites.

Sample	Magnetic saturation (Ms) emu/g	Coercivity (H_c) Oe	Remnant (M_r) emu/g	Reference
$\text{Ni}_{0.5}\text{Mg}_x\text{Zn}_{0.5-x}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.5$)	44 to 53	-	-	[6]
$\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$	176	26.27	5.20	[7]
$\text{Zn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0.0-1.0$)	8.21 to 30.48	570.8 to 172.06	-	[8]
$\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ (where $x = 0.05$ to 0.25)	45 to 61,	-	-	[10]
$\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	44.26 to 14.48	2.94 to 284.53	0.0125 to 11.320	[11]
$\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4$	89.51 to	32.12 to	25.36 to	[13]

	71.32,	41.25,	36.48	
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	45.44 to 80.66	0.007 to 0.005	1.93 to 3.43	[14]
$\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4/\text{SiO}_2$	0.72 to 29.28	-	-	[16]
$\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Cd}_{0.2}\text{Fe}_{2-y}\text{La}_y\text{O}_4$ ($y = 0.0-0.21$)	40.31 to 34	71.85 to 54.37	5.2 to 3.25	[20]
$\text{Ni}_x\text{Cu}_{0.1}\text{Zn}_{0.9-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$)	23.87 to 36.67	24.09 to 64.99	-	[23]
$\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4/\text{C}$ ($x=0.0, 0.1, 0.3, 0.5$ and 0.7)	44.90 to 47.48	175.71 to 71.38	6.39 to 2.79	[28]
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{W}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ & 1.0)	28.05	-	-	[29]
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	73.88	33.00 to 48.07	89.50	[33]

3. Applications

(a) Inductors

Predominant application of ferrite is used as inductors in several electronic devices such as filters, impedance matching, and low noise amplifiers etc. Recently, ferrite has gain popularity in passive functional devices in which multilayer of ferrite has been used. Such devices have high degree of integration density as well as the ferrite provides large permeability for operation. However, it is necessary to find a method in which density and purity of films can be controlled. Sol gel and spin coating synthesis seemed promising for such requirements [38]. Layered ferrite electronic devices have numerous advantages such as they can easily convert magnetic field into voltage by using magnetostriction, they provide high sensitivity at such small size with almost zero power consumption. One example of this is $(\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $x = 1-0.5$)/lead zirconate-titanate ($\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$) ferrite [39]. This ferrite was prepared by tape casting with eleven layers.

(b) High frequency applications

Ferrite have been utilizing for telecommunication and radar at higher frequency. Ferrite are far better than metal in terms of penetration of electromagnetic fields [40]. Ferrites

application in monitoring, audio-video electronic devices, industrial automation are becoming increasingly popular. Using iron is not an effective option nowadays because of its size and cost. Ferrites provide low eddy current losses, sufficient permeability for power conversion. Microwave absorption when magnetic field is low is getting attention is recognised as LFA. In this application, ferromagnetic material with anisotropy field is required. Results obtained by a research on Ni-Zn ferrite have been quite promising for such applications [41].

(c) Power

Power delivery can also be enhanced by using ferrites. In computers, TV, all sorts of machinery require power for their operations. SMP (Switched mode Power supply) is one of the leading power sources nowadays. By decreasing eddy currents in ferrites, efficient in terms of power can be increased. Recently study of Mn-Zn and Ni-Zn is getting attention for such uses, in which $Mn_xNi_{0.5-x}Zn_{0.5}Fe_2O_4$ has been synthesised with the help of citrate precursor technique. However, its applications at high temperature need to be studied. With increase in Ferrous ions at higher temperature by controlling its state through oxidation, Ni-Zn and Mn-Zn ferrite can also provide numerous power supplies at low as well as high temperature [42]. Miniaturization also required in such area in order to compete with demand of integrated thin films around 200°C. Therefore, a new method for synthesizing transformer can also be given with the help of such devices [43].

(d) Electromagnetic interference suppression

Requirement of high-speed digital devices are increasing drastically in computers, mobile phones, scanners etc. wireless communication is responsible for raising demand of electric and magnetic field. Such communication is known as electromagnetic interference [44]. Noise is one of the biggest issues in electromagnetic interference. Such problems can be reduced by making low pass filters, when frequency becomes greater than circuit frequency. There are many proposed methods to build such devices by using ferrites [45]. Apparently, miniaturization leads to increase in the use of ferrites for suppressors. Ni-Zn ferrites have been using for same application at frequency range 20-200 MHz.

(e) Biosciences

In many living organisms, magnetic particles can easily be found at nano scale. Such magnetic particles have better properties as compared to the magnetic particles that have been prepared in laboratory. Biogenic magnetic nanoparticle possesses perfect crystallography and morphology. These magnetic particles can be utilized for therapeutic applications e.g. MRI also known as magnetic resonance imaging, superparamagnetic behaviour is required as such particles are able to change the speed of proton decay,

which is working principle of MRI [46]. Energy coming from hysteresis loss of ferrite have tendency to treat cancer tissues, which is known as hyperthermia. When enzymes, antibodies become immobilized, then these immobilized components can be target and extracted from specific place through external magnetic field [47].

Conclusions

In this chapter, we have tried to provide the basic information of ferrites and then included the recent reported work done so far on the substituted Ni-Zn ferrites along with the applications of these ferrites in various fields. We have proposed Ni-Zn ferrite as suitable and potential candidate for diverse applications.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgment

The authors are grateful to the research and scientific community who have made relentless efforts to bring novel data in the fields and topics of research and development discussed in this review. This work did not receive any funding.

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