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Review Article

Ni-Cu-Zn Ferrite Research: A Brief Review

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Abstract

The temperature at which the ferrite is sintered critically depends on the chemical composition. The electromagnetic properties are dependent on the densification and microstructure. Substitutions and addition of sintering aids is an attractive approach to enhance the electromagnetic properties. Various compositions in the system $Ni_{1-x-y}Cu_xZn_yFe_2O_4$ were investigated. Cu is used to decrease the sintering temperature. However, Cu decreases the resistivity, which is not desirable for its high frequency applications. So, optimization of Cu content is necessary. Different ranges of electromagnetic properties have been reported with various Zn concentrations. Optimization of Zn concentration with respect to Ni and Cu is essential to achieve desirable electromagnetic properties. Influence of rare earths has also been reported. The investigations showed an improved densification in Ni-Zn and increased permeability in Cu-Zn ferrite by Sm substitution. La substitutions showed an improved resistivity in Ni-Zn ferrites. Similarly, these substitutions may improve the electromagnetic properties in Ni-Cu-Zn ferrites. V_2O_5, MoO_3 and Bi_2O_3 were reported to be the most widely used sintering additives. Bi_2O_3-WO_3 and V_2O_5-MoO_3 mixed additives were better than the individual additives in Ni-Cu-Zn ferrite, respectively. Further research is needed on the mixed sintering additives in the system V_2O_5, Bi_2O_3 and MoO_3 for the ferrites.

Keywords: Additives; Ferrite preparation; Ni-Cu-Zn ferrite; Rare Earth; Sintering aids.

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1. Introduction

Ferrites constitute a special branch of ferrimagnetics. The term ferrite denotes a group of iron oxides, which have the general formula MO. Fe_2O_3, where, M is a divalent metal ion such as $Mn^{2+,}$ $Fe^{2+,}$ Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+} or Cd^{2+}. The typical ferrite is magnetite,

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Fe_3O_4 (on $FeO.Fe_2O_3$), which has been a well known magnetic oxide since ancient time. The ferrites were developed into commercially important materials chiefly during the year 1933-1945 by Sonek [1] and his associates at the Philips Research Laboratories in Holland. In a classical paper published in 1948, Neel [2] provided the theoretical key to an understanding of the ferrites.

Ferrites are important materials both from application point of view as well as theoretical point of view. One of the reasons of being ferrites are interesting is their high resistivity. The resistivity of ferrites varies from 10^2 to 10^{10} ohm-cm which is about 15 orders of magnitude higher than that of iron [3]. This outstanding property of ferrites makes them highly demandable for high frequency applications. Other reasons which make Ferrites to be the most important are their applicability at higher frequency, lower price, greater heat resistance and higher corrosion resistance. Along with the technological advances in a variety of areas, the demand for soft magnetic materials increases day by day.

Among the soft magnetic materials, polycrystalline ferrites have received special attention due to their good magnetic properties and high electrical resistivity over a wide range of frequencies; starting from a few hundred Hz to several GHz. Spinel type ferrites are commonly used in many electronic and magnetic devices due to their high magnetic permeability and low magnetic losses [4, 5] and also used in electrode materials for high temperature applications because of their high thermodynamic stability, electrical resistivity, electrolytic activity and resistance to corrosion [6, 7]. Moreover, these low cost materials are easy to synthesize and offer the advantages of greater shape formability than their metal and amorphous magnetic counterparts. Almost every item of electronic equipment produced today contains some ferrimagnetic spinel ferrite materials. Loudspeakers, motors, deflection yokes, electromagnetic interference suppressors, radar absorbers, antenna rods, proximity sensors, humidity sensors, memory devices, recording heads, broadband transformers, filters, inductors, etc are frequently based on ferrites.

Properties of ferrites are dependent upon several factors such as composition, method of preparation, substitution and doping of different cations, sintering temperature and time, sintered density, grain size and their distribution [8, 9]. Apart from the fact that they have very complex structures, their physical properties themselves are dependent on a number of valence electrons of the divalent or trivalent metal ions of tetrahedral (A) and octahedral (B) sites. Several attempts have been made to enhance the qualities of ferrites by employing various methods. The most general method is the incorporation of same suitable nonmagnetic/diamagnetic impurities at the A or B sites. This method enables them to acquire improved electrical, magnetic and optical properties.

Ni-Cu-Zn ferrite system is a widely used ferrite material system in various electromagnetic devices. Some of the important properties of Ni-Cu-Zn ferrite are high resistivity, high permeability and comparatively low magnetic losses. These properties make this ferrite system very attractive. In this paper we have represented a review of different growth techniques of Ni-Cu-Zn ferrite system and effect of incorporation of different elements and additives.

2. Literature Review

2.1. *Different methods of ferrite preparation*

Spinel ferrites are prepared through various methods like solid state reaction method [10]; high energy ball milling method [11]; sol-gel method [12]; chemical co-precipitation method [13]; microwave sintering method [14]; auto combustion method [15], conventional ceramic technique [16], conventional two-step synthesis method [17] etc. Ni-Cu-Zn ferrite has been synthesized through solid state reaction method by many investigators [18-25]. In this method, different metal oxides are mixed and calcined to get ferrite powders. However, mechanical mixing of different oxides is hardly intimate and homogeneous and hence it results in composition fluctuation at every stage of processing that also persists after sintering [26]. Solid state process requires calcination temperature more than 750°C for phase formation and sintering temperature more than 1000°C to achieve better densification. At this high sintering temperature, evaporation of Zn leads to the formation of chemically inhomogeneous material [27]. Chemical methods overcome some limitations of solid state reaction method.

Co-precipitation process was used to synthesis of Ni-Cu-Zn ferrites by many researchers [28-30]. Hsu *et al*. [28] obtained crystalline ferrite particles with particle size of about 30 nm. Rahman *et al.* [29] reported that the average crystallite size of dried ferrite powder was 10 nm and crystallite size influenced the coercivity.

Modak *et al*. [30] reported that the coercive field for the ferrite with particle size 12 nm was interestingly low (87 Am^{-1}) and the saturation magnetization was moderately high (~ 50 Am^2kg^{-1}).

Krishnaveni *et al.* [31] synthesized $Ni_{0.53}Zn_{0.35}Cu_{0.12}Fe_2O_4$ ferrite nano-powders by co-precipitation method using microwave–hydrothermal reaction system. The particle size of the synthesized powder was 10-30 nm.

Ghodake *et al*. [32] reported the synthesis of $(Ni_xZn_yCu_{1-x\ -y}Fe_2O_4$ ferrites by co-precipitation technique using oxalate precursors.

Sol-gel method was used to synthesis the ferrite by Zahi *et al*. [33], Yan *et al*. [34] and Nam *et al*. [35]. Nam *et al*. [35] observed nano-sized spherical Ni-Cu-Zn ferrite having particle size 10-20 nm by this method.

These chemical methods have some disadvantages. They, have multiple step pathways that are time consuming, require expensive alkoxide precursor material and are highly pH sensitive which require special attention for complex systems like Ni-Cu-Zn ferrites [36]. The auto combustion method has the advantages of using inexpensive precursors and low external energy consumption and resulting nano-sized, homogeneous, highly reactive powder.

Several researchers prepared Ni-Cu-Zn ferrite [34, 37-40] including various other ferrites like Mg-Cu-Zn [41], Mg-Cu [42] and Ni-Zn [43, 44] by auto combustion method to produce nano-precursor. Generally, metal nitrate salts are used as reactant and glycine [45], urea [44] and citric acid [37] are used as fuel in auto combustion method. Citric acid

is preferred because both glycine and urea contains N_2 and releases extra amount of pollutant N_2 gas during combustion reaction. Auto combustion process has been proved to be a simple and economic way to prepare nano-scale ferrite powders [37]. Nano-structured materials offer novel properties. It decreases the free energy during sintering due to increasing surface area which is the main driving force for lowering the sintering temperature of particles. By proper tuning of the particle size, it is possible to optimize the desired properties like electrical, magnetic, optical, thermal, mechanical etc [46].

2.2. *Improvement of electromagnetic properties*

Many investigators have focused their attention on the improvement of electromagnetic properties of the ferrite by divalent ions substitution. Generally, the divalent metal ions (M^{2+}); Ni, Zn, Cu, Mg, Mn, Co or mixtures of these are substituted in different spinel ferrites. These substitutes have different sitting preferences for the two sites ('A' and 'B') in the spinel structure and can change many properties as an effect of modified cation distribution in the ferrite. On the basis of site distribution of M^{2+} ions and the strength of the exchange interaction among magnetic ions, the influence of M^{2+} substitutions on electromagnetic properties can be explained.

2.3. *Effect of Zn incorporation*

Zn^{2+} is used to improve electromagnetic properties as well as densification in the ferrite. It is substituted in spinel ferrite to improve magnetization [47]. It also lowers magnetostriction and anisotropy in ferrites [24]. Goev *et al.* [25] stated that initial permeability increased and hysteresis loss decreased with increasing Zn concentration in $Ni_{0.85-y}Cu_{0.15}Zn_yFe_2O_4$ ferrite. Both saturation and remancence magnetization had maximum at $y = 0.4$. An improved electromagnetic properties were obtained by Low et al. [48] at high Zn content of $Ni_{0.02}xCu_{0.02y}Zn_{0.02z}Fe_2O_4$; where $x+y+z= 50$. Ahmed et al. [49] investigated the influence of zinc ion substitution on densification in Ni-Zn ferrite. They found rapid densification with increased Zn^{2+} concentration. Sun *et al.* [50] reported the initial permeability and relative loss factor increased while the cut off frequency decreased with increasing Zn content in $Ni_{1-x}Zn_xFe_2O_4$ ferrite. Zn substituted $Cu_{1-x}Zn_xFe_2O_4$ ferrite had been prepared by Ajmal *et al*. [51]. They found that sintered density increased with increasing Zn concentration.

Both saturation magnetization and magnetic moment increased with increasing Zn concentration up to $x = 0.2$ and then decreased with further addition of Zn. Jadhav [52] worked on the structural and magnetic properties of Zn substituted Li-Cu ferrites having composition $Li_xCu_{0.4}Zn_{0.6-2x}Fe_{2+x}O_4$ and found that the magnetic moment increased with increasing zinc content up to $x = 0.15$ and then decreased with further addition of Zn. Shaikh *et al.* [53] investigated the electrical resistivity and Curie temperature of Zn substituted $Li_xMg_{0.4}Zn_{0.6-2x}Fe_{2+x}O_4$ ferrites and found that the resistivity initially decreased with Zn content up to 0.15 and then increased with further increasing Zn content. The

Curie temperature was also found to decrease linearly with the addition of Zn. At high level of Zn substitution, the 'A' site magnetic ion became so diluted that the coupling between the two lattices was lost and the saturation magnetization dropped. An additional consequence of the weakening magnetic interactions was that the spin coupling could more easily be moved out of alignment by thermal energy vibrations so that, the Curie temperature decreased with Zn substitution.

2.4. *Effect of Cu incorporation*

Cu is conventionally used in Ni-Cu-Zn ferrite to improve densification as well as electromagnetic properties [30]. The beneficial effect of copper ions on the densification of ferrite can be reasonably explained by possible sintering mechanisms that take place through a high atomic mobility of Cu ions at relatively low temperature. The increase of the lattice diffusion usually increases the diffusion path leading to an increase of the rate of cation inter diffusion in the solid solution, which is in agreement with the lattice diffusion mechanism proposed by Gupta and Coble [54, 55]. During sintering grain boundary diffusion [56] may play an important role in the grain growth because the activation energy for lattice diffusion is higher than that of for grain boundary. Nam *et al.* [57] investigated the effect of Cu substitution on the electromagnetic properties of $Ni_{0.5-x}Cu_xZn_{0.50}Fe_2O_4$ ferrite and found that electrical resistivity was maximum at $x = 0.2$. They also reported that saturation magnetization was maximum at $x = 0.2$ in $Ni_{0.2}Cu_xZn_{0.80-x}Fe_2O_4$ ferrite [35].

Shrotri *et al.* [58] reported the effect of Cu substitution on the electromagnetic properties of $Ni_{0.8-x}Cu_xZn_{0.2}Fe_2O_4$ ferrite and found that the bulk density, electrical resistivity and initial permeability increased considerably with the copper concentration up to $x = 0.2$. Saturation magnetization and Curie temperature decreased with Cu addition. Caltun et al. [59] also found improved electromagnetic properties at $x = 0.2$ and suggested that the specific amount of Cu substitution ($x = 0.2$) was favorable for the grain growth of $(NiZn)_{0.8-x}Cu_xZn_{0.2}Fe_2O_4$ ferrite.

Further, Rahman *et al*. [29] worked in the same composition range and stated that the partial substitution of Ni^{2+} with Cu^{2+} (up to $x = 0.25$) influenced the magnetic parameters due to the modification by cation re-distribution. It was found that the maximum coercivity dependent on average crystallite size. The saturation moment decreased linearly with the decrease in Ni^{2+} content replaced by Cu^{2+} ions at lower concentrations. At higher concentration deviation from this trend was found and magnetization increased with increasing Cu content.

The same property was found by Hsu *et al*. [28]. They reported that Cu substitution for Ni in Ni-Zn ferrite would enhance the densification of the ferrite and subsequently increased the permeability value as well as saturation magnetization value and decreased the coercivity of the sintered ferrite. Su *et al.* [23] stated that the presence of Cu ion up to 4 mol% activated the sintering process leading to increase in density and decrease in magnetocrystalline anisotropy constant of Ni-Cu-Zn ferrite.

Yan *et al*. [60] worked on the effect of CuO and V_2O_5 additions on the microstructure and relative permeability of low temperature fired Ni-Cu-Zn ferrite. They found high relative permeability value of ~1417 at 10 mol% CuO and 0.20 mol% V_2O_5 addition. Low *et al*. [48] reported that the increase in Cu content caused a decrease in the dissociation temperature and was beneficial to the electromagnetic properties of Ni-Cu-Zn ferrite as a result of grain growth and better densification. The range of critical CuO content was determined to be 12-20 mol%.

Dimri *et al*. [61] studied the effect of compositional variation on structural, dielectric and magnetic properties of the Cu substituted $Ni_{0.6-x}Cu_xZn_{0.4}Fe_2O_4$ ferrite. The results showed that the addition of copper promoted grain growth, resulting increase in grain size. However, Curie temperature was understandably lowered with the increase in Cu content. A saturation magnetization value of 92 emu/gm was obtained for the composition $x = 0.2$. Ferrite with Cu concentration of $x = 0.4$ showed the highest initial permeability.

Cu is also used in other ferrites as divalent cation for improving electromagnetic properties and for lowering the sintering temperature. Yue *et al*. [41] worked on the effect of copper on the electromagnetic properties of $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ ferrites and found that the density, grain size, permeability, Curie temperature increased, resistivity decreased with Cu content up to $x = 0.40$.

Rezlescu *et al*. [62] reported the effect of Cu substitution on the physical properties of $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ + 0.5MgO ferrites. They found that the density increased up to $x = 0.30$ whereas, resistivity increased up to $x = 0.10$ and permeability increased with Cu content as well. Rezlescu *et al*. [63] also reported that the sintered density and resistivity of $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ ferrite increased up to $x = 0.3$ whereas, permeability increased up to $x = 0.4$.

Hoque *et al*. [64] reported that the maximization of initial permeability and saturation magnetization at $x = 0.2$ in $Ni_{1-x}Cu_xFe_2O_4$ ferrite, which could be attributed to the maximum sintered density obtained for this composition. Haque *et al*. [65] worked on Cu substituted Mg-Zn ferrites. They found a remarkable increase in the bulk density with increasing Cu substitution for Mg. By incorporating CuO, the initial permeabilities of the samples increased. Saturation magnetization increased slightly with increasing copper content up to $x \leq 0.30$ and then it decreased for $x = 0.35$. Cu substitution is also used in hard ferrites for improving properties [66].

After a detailed study, Murbe *et al*. [67] found that $Ni_{0.35}Cu_{0.15}Zn_{0.5}Fe_2O_4$ provide effective sintering at low temperature ($T_s \leq 950\ ^0C$) and provide sufficient permeability and inductance.

2.5. *Effect of Mn incorporation*

Other interesting divalent cation is Mn^{2+}. Yue *et al*. [68] first worked on Mn substituted $Ni_{0.25-x}Mn_xCu_{0.25}Zn_{0.5}Fe_2O_4$ ferrites and found that the resonant frequency and the Curie temperature decreased with increasing Mn content whereas, the initial permeability increased up to $x = 0.06$. The same group reported [38] on effect of Mn substitution on

electromagnetic properties of $(Ni_{0.2}Cu_{0.2}Zn_{0.6})O.(Fe_{2-x}Mn_xO_3)_{0.98}$ ferrites. It was found that Mn content in formulations largely affected the grain size and electromagnetic properties of sintered Ni-Cu-Zn ferrites. With increasing Mn content, the initial permeability was significantly increased, while the electrical resistivity and quality factor decreased.

Further, Li *et al*. [69] investigated the effect of Mn doping on the magnetic properties and microstructure of the $(Ni_{0.2}Cu_{0.2}Zn_{0.6})_{1.03}(Fe_2O_3)_{0.97}+0.97xMnO_2$ ferrites. They found that the initial permeability increased with Mn-content, but Mn content more than 0.4 resulted in the formation of a second phase. The high Mn-content increased the grain size of Ni-Cu-Zn ferrites that reduced the fraction of grain boundary with high resistance thereby, lowering the resistivity. Chu *et al.* [70] studied the magnetic properties of low Mn-doped Ni-Cu-Zn ferrites. The results showed that with the increasing Mn^{2+} content up to $x = 0.02$, saturation magnetization (M_s) of the powder samples decreased. The real part of the permeability of the toroidal specimens increased up to $x = 0.01$.

Qi *et al.* [71] prepared Mn substituted $(Mg_{0.2}Cu_{0.2}Zn_{0.6}O)(Fe_{2-x}Mn_xO_3)_{0.97}$ ferrites. They found that Mn induced higher initial permeability and lowered grain size. It also decreased magnetostriction constant in Mg-Cu-Zn ferrites.

Bhaskar *et al*. [72] worked on Mn substituted $Mg_{0.456-x}Cu_{0.144}Mn_xZn_{0.4}Fe_2O_4$ ferrites. They found that the initial permeability and resistivity increased while magnetostriction constant decreased with Mn-content.

Bueno *et al*. [73] investigated the effect of Mn-substitution on the microstructure and magnetic properties of $Ni_{0.50-x}Zn_{0.50-x}Mn_{2x}Fe_2O_4$ ferrites. The results indicated that Mn-substitution increased induction magnetization (B_m) and remnant magnetization (B_r). The lattice parameter was found to increase with increasing Mn-substitution as well. The addition of Mn enhanced the material's densification.

2.6. *Incorporation of Co*

Co^{2+} is used to improve electromagnetic properties in ferrites. Groenou *et al.* [74] prepared Co-substituted $Ni_{0.78}Zn_{0.22}Fe_2O_4$ ferrite. The results showed that Co^{2+} was the anisotropic ion responsible for the magnetic response time. The Co^{3+} ions and presumable cation vacancies in association with Co^{3+} provide the means whereby, Co^{2+} was transported through the lattice. Byun *et al.* [75] investigated the electromagnetic properties of $(Ni_{0.2}Cu_{0.2}Zn_{0.6})_{1.02-x}Co_xFe_{1.98}O_4$ ferrites. The results showed that the grain size and sintered density changed a little. It also showed the concentration of cation vacancies increased with Co content and the increase in induced anisotropy results in the decrease of initial permeability. The magnetostriction of cobalt ferrite is many times higher than that of Ni-Zn ferrites.

Kulikowski *et al.* [76] worked on magnetostrictive properties of $Co_x(NiZn)_{1-x}Fe_2O_4$ ferrites and shown that the magnetostrictive effect of a core was the result of the effects of the sum of the magnetostrictions of all magnetic domains.

Xiang *et al*. [77] reported Co substituted $Mn_{0.4}Zn_{0.6-x}Co_xFe_2O_4$ ferrites. The results showed that the grain size, saturation magnetization and coercivity increased with

increasing Co-content. Rezlescu *et al.* [78] investigated Co-substituted $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrites and found that Co^{2+} ions increased the electrical resistivity due to the change in the valence state. Kaiser [79] investigated Ni substitution in $Cu_{0.8-x}Zn_{0.2}Ni_xFe_2O_4$ ferrites. The results revealed that the transition (metallic to semiconductor) temperature increased with an increasing Ni concentration.

2.7. *Incorporation of Mg*

Zhong *et al*. [80] reported the effects of NiO on microstructure and magnetic properties of $Zn_{0.32}Mn_{0.60x}Ni_xFe_{2.08}O_4$ ferrites. The results showed that Ni substitution could cause the lattice constant to decline, grain size to decrease, grain structure to be more compact and porosity to decrease.

Many researchers had worked on Mg substitution in different ferrite systems and found Mg substitution has a significant effect on the structural, electrical and magnetic properties. MgO is a very stable oxide that can be used in a large range of technological applications [81]. Mg containing composition is preferred to avoid the presence of divalent iron to obtain high resistivity. With increasing Mg content only octahedral Fe^{2+} ions are substituted by Mg^{2+} and it decreased with increasing Mg content [82].

In the iron-deficient ferrites, the dominant conduction mechanism is due to hole-hopping. At high concentration of Mg^{2+} ions, the conductivity is low due to the obstruction of Mg^{2+} ions to the hopping process between iron ions [83]. Mg is also preferred to increase the rate of densification and to avoid the tendency of discontinuous grain growth [84]. It is believed that increase of initial permeability can be obtained by decreasing magnetostriction constant. Magnetostriction constant of Mg-Cu-Zn ferrites is lower than that of Ni-Cu-Zn ferrites [85]. MgO has low dielectric loss and low dielectric constant. It is doped with ferroelectric material for high frequency device application [86]. So, Mg containing ferrites would obtain higher magnetic properties.

Bhosale *et al*. [87] investigated the effect of Mg in Mg-Cu-Zn ferrite and found that density increased and permeability decreased with Mg^{2+} content. But later they [88] reported the ferritization temperature of this system varies with increasing Mg^{2+}. It was also been found that lattice parameter decreased and density, initial permeability increased with increased Mg^{2+} content up to $x = 0.20$ in $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrites. Hiti [89] studied the effect of frequency, temperature and composition on the dielectric behavior of $Mg_xZn_{1-x}Fe_2O_4$ ferrites. The relaxation frequency was found to be shifted to higher values as the temperature increased.

2.8. *Inclusion of rare earth ions*

The rare earth substituted different ferrites are becoming the promising materials for different applications. Addition of small amount of rare earth ions to ferrite samples produces a change in their magnetic and electrical as well as structural properties depending upon the type and the amount of rare earth elements used.

Rare earth ions can be divided into two categories: one with the radius closes to Fe ions; while the other with ionic radius larger than Fe ions [90]. The difference in their ionic radii will lead to micro strains, which may cause domain wall motion resulting in deformation of the spinel structure [91]. It has been stated that the rare earth ions commonly reside at the octahedral sites by replacing Fe^{3+} ions and have limited solubility in the spinel lattice due to their large ionic radii [92].

Ferrimagnetism in ferrite is largely governed by Fe-Fe interaction (the spin coupling of the 3d electrons). If the rare earth ions enter the spinel lattice, the RE-Fe interactions also appears (4f-3d coupling), which can lead to changes in the magnetization and Curie temperature [93].

The rare earth oxides are good electrical insulators and have resistivities at room temperature greater than 106 Ω-cm [94]. Rare earth ion forms the orthoferrite phase ($REFeO_3$). The occupation of RE ions on 'B' sites impedes the motion of Fe^{2+} in the conduction process in ferrite, thus causing an increase in resistivity [50].

Many investigators have been carried out on the influence of different rare earth atoms (La, Sm, Gd, Nd, Dy, Tb, Ce, Th, Y, Eu) on the properties of ferrites. The results of these researches show that different rare earth atoms behave differently in spinel ferrite.

Rezlescu et al. [95] investigated the effect of Fe replacement by RE (Yb, Er, Sm, Tb, Gd, Dy and Ce) ions on the properties of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite. The results showed that the electrical resistivity of a ferrite increased by substituting a small quantity of Fe_2O_3 with RE_2O_3.

Sun *et al.* [50] investigated the effects of rare earth ions on the properties of $(Ni_{0.5}Zn_{0.5})Fe_{1.98}RE_{0.02}O_4$ (RE = Y, Eu or Gd) nominal compositions. The partial substitution of Fe^{3+} with a small amount of RE ions increased the electrical resistivity and relative loss factor, whereas, it slightly decreased the Curie temperature. Results had shown that Y and Eu substitution tend to decrease μ_i while Gd did not reduce μ_i

Jacobo *et al*. [96] worked on $(Zn_{0.5}Ni_{0.5})RE_{0.02}Fe_{1.98}O_4$ ferrites, with RE = Y, Gd and Eu. The results showed a small increase in the hyperfine field parameters and a strong decrease of the total resonant area with respect to the pure Ni-Zn ferrite. Curie temperatures decreased and coercive fields increased with substitution. By adding much large ionic radii rare earth ions resulted in local distortion and disorder, enough to induce a softening of the network (s electron density).

Zhao *et al*. [97] reported the influence of Gd on magnetic properties of $(Ni_{0.7}Mn_{0.3})Gd_xFe_{2-x}O_4$ ferrites. It was found that the crystallite sizes decreased when Gd ions were doped into Ni-Mn ferrites. With Gd-substitution, when $x > 0.06$ all Gd ions could not enter into the ferrite lattice but resided at the grain boundary. The maximum content of Gd^{3+} ions in ferrite lattices was substituted when $x = 0.06$. The values of H_c and M_s were zero for all the samples calcined at 600°C. In addition, the H_c and M_s values of the samples calcined at 800°C were larger than those sintered at 850°C, with Gd contents less than 0.08. Whereas, when the Gd contents at $x = 0.08$ and $x = 0.10$, the H_c and M_s values of the samples increased with the calcination temperatures.

Zhao *et al.* [98] worked on the effect of substitution of Fe^{3+} by Nd^{3+} ions on structure and magnetic properties of $CoFe_{2-x}Nd_xO_4$ ferrites. It was stated that the value of saturation magnetization for Nd^{3+} doped samples was less than that of the pure cobalt ferrite whereas, the coercivity increased with Nd^{3+} content.

Rezlescu et al. [99] investigated the influence of rare earth ions like Yb, Er, Dy, Tb, Gd, Sm substitution on structure, magnetic and electrical properties of $(Li_{0.3}Zn_{0.4})Fe_{1.96}RE_{0.04}O_4$ ferrites. They found that RE_2O_3 facilitated the formation of secondary phases at grain boundary which suppressed the grain growth. The results also showed that the Curie point shifted to lower temperature and increased the electrical resistivity.

Ahmed *et al.* [100] reported the electrical properties of $(Mg_{1+x}Ti_x)RE_yFe_{2-2x-y}O_4$ ferrites doped with rare earth ions like Er, Ce and Nd. They found that the resistivity increased by introducing rare earth ions into ferrite structure.

Ahmed *et al.* [49] worked on $(Ni_{1-x}Zn_x)La_yFe_{2-y}O_4$ ferrite system and reported La^{3+} could not enter into the octahedral site but form small aggregates on the grain boundary.

Sun *et al.* [101] reported the effect of Fe substitution by La and Gd on the structure, magnetic, and dielectric properties of $(Ni_{0.5}Zn_{0.5}Fe_{2-x})RE_xO_4$ ferrites frequency, decrease the initial permeability and magnetic loss tangent (tanδ) which could be explained by a combination of low density, small grain size, secondary phase ($REFeO_3$) formation, and more lattice defects. The low tanδ values resulted mainly from the reduction in eddy current loss due to the higher electrical resistivity with increasing RE ion.

Ahmed *et al.* [93] reported the effect of rare earth ions on the structural, magnetic and electrical properties of $(Mn_{0.5}Zn_{0.5})RE_{0.05}Fe_{1.95}O_4$ ferrites where RE = Tb, La, Ce and Th. Rare earth ion formed orthoferrite ($REFeO_3$) phase and the formation of these secondary phases in ferrite during sintering process was governed by the type and the amount of RE^{3+} ion used. It was found that the molar magnetic susceptibilities for rare earth substituted samples were smaller than pure ferrite. The Curie temperature and electrical resistivity increased with increasing rare earth ions in Mn-Zn ferrites.

Rezlescu *et al*. [42] worked on $(Mg_{0.5}Cu_{0.5})Fe_{2-x}RE_xO_4$ ferrites, in which RE = La, Gd, Y and $x = 0$ and 0.2, respectively. XRD analysis evidenced that the compounds containing Y^{3+} and La^{3+} ions are pluri-phasic whereas, the others are mono-phasic. The electrical resistivity decreased by La and Y incorporation and increased by Gd incorporation.

Costa *et al.* [102] investigated the effect of samarium on the microstructure, relative density and magnetic properties of $(Ni_{0.5}Zn_{0.5})Sm_xFe_{2-x}O_4$ ferrites. Results showed that the increased relative density and decreased average grain size with rare earth substitutions. It also showed the increase in coercive field and decrease in permeability with rare earth substitution. They also stated about the formation of secondary phase.

Sattar *et al.* [103] investigated Cu-Zn ferrites doped with rare earth ions like La, Sm, Nd, Gd, and Dy. They found that all samples were of high relative density and low porosity. The magnetization of the samples with Sm and La were higher than that of undoped.

On the other hand, samples with Gd and Dy had lower values of magnetization than that of the undoped ones. The magnetization values of the sample with Nd may be higher or lower than that of the undoped ones depending on the applied magnetizing field. The samples with La, Sm and Nd had higher values of μ_r than that of undoped samples while those with Gd and Dy had lower values of μ_r than that of the undoped ones. The most important result was that the relative permeability has increased by about 60%, 35.5% and 25%, in case of Sm, La and Nd, respectively.

Mahmoud *et al*. [104] studied the cation distribution and spin canting angles variation in $Cu_{0.5}Zn_{0.5}Fe_2O_4$ ferrites substituted with Sm and Nd using Mossbauer spectroscopy. They observed slight decrease in saturation magnetization M_s of the specimen doped with Nd and significant increase in M_s for the specimen doped with Sm.

2.9. *Use of sintering aids and additives*

The sintering temperature of ferrites can be lowered by using sintering aids [104]. These additives form liquid phase which either due to the melting of the additives or eutectic liquid phase formation between the additives and ferrites. Amount of liquid phase increases with increasing amount of sintering aids and results in increased densification.

Additives components may also play an important role in the contribution to the magnetic properties of the sintered ferrites. Excessive amount of sintering additives may deteriorate magnetic properties of ferrites.

Several researchers worked on different additives (V_2O_3, MoO_3, Bi_2O_3, WO_3, Glass and PbO) in different spinel ferrite systems to investigate the effect on lowering the sintering temperature and improving electromagnetic properties.

One of the most effective additives is V_2O_5. Hsu *et al*. [105] introduced V_2O_5 as sintering aids in Ni-Cu-Zn ferrite to reduce the sintering temperature. They found that V_2O_5 content up to 0.25 mol% improved the magnetic properties. However, a small amount of V^{5+} cations entered the crystal lattice of the ferrite and higher amount of V_2O_5 deteriorated the magnetic properties. 0.5 mol% of V_2O_5 was required to form the liquid phase for enhancing the densification of this composition at around 875°C.

Yan *et al.* [60] investigated the effect of CuO and V_2O_5 addition on the microstructure and relative permeability of Ni-Cu-Zn ferrite. They found that these additives contributed to the grain growth and densification of matrix in the sintering process. 10 mol% CuO and 0.20 mol% V_2O_5 compositions showed the highest initial permeability.

Lebourgeois *et al.* [106] worked on the effect of V_2O_5 on the densification of $Ni_{0.24}Cu_{0.2}Zn_{0.55}Co_{0.02}Fe_{1.99}O_4$ ferrite. They found that with small amount of V_2O_5 (0.6–1.2 wt %) as a sintering aid was enough for densification at around 850°C. EDAX analyses showed the presence of vanadium inside the ferrite grains. Magnetic properties were deteriorated with increasing the V_2O_5 content. The permeability decreased and the core losses increased for V_2O_5 content higher than 0.6 wt%. It was shown that V_2O_5

content 0.20-0.25 mol% (~0.15-0.20 wt%) improved electromagnetic properties in Ni-Cu-Zn ferrite.

Mirzaee *et al.* [107] investigated the influence of V_2O_5 on the microstructure development and magnetic properties of $(Ni_{0.64}Zn_{0.36})Fe_2O_4$ ferrites. The results showed that the permeability, relative density and grain size initially increased up to 1.6 wt% and then decreased with further addition. The specific resistivity increased continuously. The Curie temperature and saturation magnetization showed peak values at 0.8 wt% and 1.2 wt% of V_2O_5, respectively. Mirzaee *et al.* [108] also worked on the influence of MoO_3 and V_2O_5 co-doping on the magnetic properties and microstructure of Ni-Zn ferrites. The results showed that 0.05 wt% of MoO_3 in addition to 0.2 wt% of V_2O_5 increased grain size and sintered density and also decreased power loss noticeably.

Another important sintering aid is MoO_3. Seo *et al*. [109] focused on the effect of MoO_3 addition on the sintering behavior and magnetic properties of $(Ni_{0.2}Cu_{0.2}Zn_{0.6})_{1.02}.(Fe_2O_3)_{0.98}$ ferrite. Results showed that MoO_3 addition reduced the sintering temperature and magnetic loss of Ni-Cu-Zn ferrite and it also increased the bulk density and initial permeability up to the additives content of 0.2 wt %.

Su *et al*. [23] was investigated on the amount of CuO contained in Ni-Zn ferrite and a small additive of MoO_3 added in $(Ni_{0.29}Cu_{0.08}Zn_{0.62})(Fe_2O_3)_{1.01}$ ferrite. Results showed that the initial permeability of the core increased but the Curie temperature decreased a little with 4 mol% CuO content. The highest initial permeability ≈2480 and relatively higher Curie temperature ≈118°C could be obtained at 0.12 wt% MoO_3 additive in Ni-Cu-Zn ferrite.

Gu et al. [110] reported the effect of MoO_3 and TiO_2 additions on the magnetic properties of Mn-Zn ferrite. It was found that the magnetic properties of Mn-Zn power ferrites fluctuate with the increase of MoO_3 content and could be considerably improved with suitable amount of MoO_3 addition. The sample doped with 600 ppm MoO_3 had a decreased power loss of 13.5%, and increased initial permeability of 7.2% than undoped samples.

A few authors also worked on WO_3 as sintering aid. Earlier, Park et al. [111] investigated the effect of WO_3 addition on the magnetic properties of Ni-Cu-Zn ferrites. The results showed that enhanced electrical and magnetic properties obtained from WO_3 addition upto 0.6 wt% into Ni-Cu-Zn ferrites. Later, Su et al. [112] reported that appropriate WO_3 additive could improve grain size of the specimen and removed closed pores.

Recently, Su *et al.* [113] studied the effects of WO_3 addition on properties of Ni-Cu-Zn ferrites. The results showed that to obtain a single-phase spinel ferrite WO_3 addition should be less than 0.28 wt%. With proper WO_3 addition, the average grain size and the initial permeability of the ferrites increased. The maximum initial permeability was observed at a WO_3 content of 0.16 wt%.

Lead oxide and glass also act as sintering aid in Ni-Cu-Zn ferrites. Earlier, Jean *et al*. [18] investigated the effect of PbO addition on the densification, microstructural

properties of Ni-Cu-Zn ferrites. Results showed that with a small amount of PbO (0.5-2 wt. %) in Ni-Cu-Zn ferrite increased the densification rate and final sintered density when the activation energy of densification was significantly reduced. However, interfacial reaction causes segregation of CuO onto the grain boundary and dissolution of PbO into the ferrite grains, yielding a reduction in initial permeability.

Later, Wang *et al*. [114] used PbO-SiO_2, PbO-B_2O_3 and Bi_2O_3 flux systems to lower the sintering temperature of $(Ni_{0.38}Cu_{0.12}Zn_{0.50})Fe_2O_4$ ferrite and found that the PbO-SiO_2 glass system to be the most effective additive to obstruct the grain boundary movement and prevent the exaggerated grain growth among these flux systems. Ferrites sintered with PbO-SiO_2 possess higher resistivity, higher Q and higher H_c compared with those obtained using other systems. The results also showed that the addition of Bi_2O_3 considerably deteriorated the quality factor of Ni-Cu-Zn ferrites, though benefited the densification and permeability. Thus, Bi_2O_3 is another most interesting sintering aid.

Hsu *et al*. [115] reported Bi_2O_3 and lead glass as sintering aids for Ni-Cu-Zn ferrite. Results showed that both additives formed liquid phases in the grain boundaries during the sintering process to enhance the densification. But Bi_2O_3 exhibited better effect than the lead glass to lower the sintering temperature.

Wang *et al.* [116] worked on the mixing of $(Ni_{0.38}Cu_{0.12}Zn_{0.50}).Fe_2O_4$ powders with Bi_2O_3 using the solid-state mixing as well as wet chemical coating processes such as ammonia precipitation coating, urea precipitation coating, and solution coating. Ferrites prepared from the wet chemical coating processes could be densified at a lower sintering temperature without significant impact on the micro structural evolution compared with that prepared by solid-state mixing. In addition, samples prepared from the wet chemical coating process have a higher B_r and B_m and a lower H_c compared with that from the solid-state mixing process. Considering both effects of sintering temperature and sintered density (>95% theoretical density), ferrites with 1.5 wt% Bi_2O_3 addition by ammonia precipitation coating process followed by sintering at around 900°C could provide the best permeability and quality factor.

Jeong *et al.* [117] investigated the effect of Bi_2O_3 addition on the microstructure and electromagnetic properties of Ni-Cu-Zn ferrites. The grain size and bulk density gradually increased with the increase in Bi_2O_3 content. Above 0.5 wt% Bi_2O_3, abnormal grain growth was observed. Specimen with 0.25 wt% of Bi_2O_3 showed the highest initial permeability with good quality factor and a uniform microstructure.

Su *et al.* [112] investigated the effects of mixed Bi_2O_3–WO_3 additives. The results showed that appropriate additives of mixed Bi_2O_3–WO_3 could enhance densification of the specimens, improve the initial permeability and the Q-factor of Ni-Cu-Zn ferrites. The maximum initial permeability was achieved with 1.5 wt. % Bi_2O_3 and 0.3 wt. % WO_3 additives.

Kawano *et al*. [118] fabricated Bi, Si oxides-doped Ni-Cu-Zn ferrite composite materials. Analysis showed that the composite materials has mainly Ni-Cu-Zn ferrite and

$Bi_4(SiO_4)_3$ phases. The optimum percentage of Bi_2O_3 content to improve the electromagnetic properties in Ni-Cu-Zn ferrite is 0.25 wt. %.

Kong *et al.* [119] reported the effects of concentration of Bi_2O_3 on $MgFe_{1.98}O_4$ ferrite. It was found that 3 wt. % Bi_2O_3 could result in fully sintered ferrite. Low concentration of Bi_2O_3 increased the static permeability of the ferrite owing to the improved densification and grain growth, while too high concentration led to decrease in permeability owing to the incorporation of the non-magnetic component (Bi_2O_3) and retarded grain growth.

Murbe *et al.* [67] found that the addition of Bi_2O_3 further enhances the densification and has dramatic influences of the microstructure and permeability. With the addition of 0.35-0.5 wt. % Bi_2O_3 a bimodal microstructure with large (25-30µm) grains surrounded by small-grained (1-2 µm) regions is observed.

Saha *et al.* [120] revealed that sintering temperature could be reduced by 150^0C when 0.8 wt. % of Bi_2O_3 is added to Ni-Cu-Zn ferrites. The results also showed that the addition of Bi_2O_3 considerably benefited the densification and permeability.

3. Conclusion

Ni-Cu-Zn ferrite system is an established well-known ferrite material to be used in various electromagnetic devices due to their high resistivity, high permeability and comparatively low magnetic losses. Extensive research on Ni-Cu-Zn ferrite shows better performance with $Ni_{0.35}Cu_{0.15}Zn_{0.50}Fe_2O_4$. It shows better electrical, structural and magnetic properties. Small amount of Bi_2O_3 addition can reduce sintering temperature considerably and thus providing advantage in view of energy saving and increase of productivity by reducing the sintering time in the manufacture of ferrites. It has also been found that the addition of Bi_2O_3 to Ni-Zn ferrites increases the initial permeability and improves the magnetic loss factor.

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