CHAPTER 1

INTRODUCTION TO MULTI LAYER CHIP INDUCTOR MATERIAL PROPERTIES

1.1 Introduction

The high demand for shrinkage of electronic products with complex functions raises the requirements both for miniaturization and performance on all components used [1,2]. Over the past few years, electronic devices such as cellular telephones, lap-tops, pagers, camcorders, etc., have been designed to accompany the benefits of smaller size, reduced weight, higher density and improved performance due to the development of surface mount components [3,4] using surface mount technology (SMT). Surface mount technology is a method of constructing electronic circuits in which the components are mounted directly onto the surface of printed circuit boards [5].

It is well known that an inductor is a passive electronic component that stores energy in the form of a magnetic field. Surface mount inductor has no wire leads at its ends and is mounted directly on the surface of printed circuit board through a metal pad at either end of the device. Since the inductor had to be wound with wire, it was difficult to reduce the size of the chip without exhibiting any deterioration of magnetic properties. In order to solve this problem, surface mounting devices such as multilayer chip inductors (MLCI) are fabricated by laminating ferrite and coating internal silver electrode layers alternately and co-firing them to form a monolithic structure [6,7]. MLCIs were developed in the 1980s by thick film printing and co-firing technologies using low temperature-sintered Ni-Cu-Zn ferrite and Ag [8]. Depending upon the inductance value, the ferrite multi-layer chip inductors are designed for energy storage applications at frequencies up to the hundreds of MHz.

Although very few ferrite systems like Ni [9], Ni-Cu-Zn, Mg-Cu-Zn, and Cu-Zn exist for MLCI applications, the extensive study of several researchers has revealed that Ni-Zn ferrites are the most universal ferrite materials to produce MLCIs useful for high frequency applications because of their high density and excellent soft magnetic properties coupled with high electrical resistivity. However, beyond 100 MHz, the ferrite is not suitable due to the generation of eddy current losses [10]. The permeability drops drastically at high frequency range due to domain wall resonance [11]. To improve the frequency of operation beyond 100 MHz, one has to improve the properties of ferrites considerably. The incorporation of several impurity elements to enhance the parameters in bulk systems has been proved to be futile. Thus, ferrites have been extensively used for five decades without major innovation despite significant power loss at elevated frequencies.

In the radio frequency range above 500 Hz to several GHz, the Ni-Zn ferrite based chip inductors cannot be used due to the limitation of the self resonant frequency of the material [12]. However, multilayer chip inductors for high-frequency circuit applications use sheets made of dielectric ceramics instead of ferrite. The use of a dielectric core was considered to be essential for high frequency operations since magnetic materials show degrading properties above 200 MHz due to Snoek limit [13]. To resolve the problem, it is highly desirable to improve the properties of ferrites at very high frequency. Most of the studies reported dealt with ferrites produced by conventional ceramic processes which are known to have certain inherent drawbacks due to high sintering temperatures resulting in non-reproducibility, high losses, low densities and deterioration in their magnetic properties [14]. The effective transfer of energy between circuits with maximum flux linkage and minimum flux leakage is possible only with high permeability materials. Bulk ferrites due to their high density and larger grain size yielding higher permeability have been under study for chip inductor applications. Because of the losses encountered at high frequency due to higher electrical conductivity and domain wall resonance, the bulk materials have to be replaced by fine grained ferrite materials [11, 15]. Fine grains facilitate the possibility of thin layers of ferrite which is highly favorable for realizing the better miniaturization of a MLCI [16]. So, concentration has been focused on producing higher magnetization and permeability for smaller grain size for increasing the permeability [17]. As most of the materials used for MLCI applications exhibit higher Curie temperatures there is need to develop ferrite materials having higher Curie temperatures which increase the device performance and reliability at the high temperatures [18].

To overcome the drawbacks such as drop in permeability and generation of eddy current losses encountered at high frequencies in bulk ferrites, low temperature processing methods are needed [19]. The available literature on bulk ferrites has clearly established that higher electrical resistivity could be possible for a material containing suitable amount of impurity with vast number of fine grains and grain boundaries [20]. The contention imparts an idea to synthesize the ferrite material in the form of nanoparticles with innumerable grain boundaries by adopting new processing techniques like wet chemical methods. By increasing the resistivity of the ferrite material, the eddy current losses can be reduced and thereby operating frequency of the ferrite material can also be shifted to higher frequency region [21]. The process of obtaining fine nanoparticles of least size provides an ample scope for enhancing their magnetic properties through careful heat treatment. Sizeable improvement in saturation magnetization can be expected in nanomaterials by achieving characteristic length, a responsible parameter for exchange coupling to take place among the nanograins [22].

From the above understanding, it is clearly evident that the ferrite materials used in the fabrication of multi-layer chip inductor should have reasonable saturation magnetization, high initial permeability, high dc resistivity, and fine grains with low losses. As Ni-Zn ferrite has been reported to be the only core material suitable for high frequency multilayer chip inductor applications, attempts have been made to synthesize the Ni-Zn ferrite material in the form of nanoparticles to achieve modifications in the above said properties through proper substitutions.

In our laboratory, nanoparticles of several Ni-Zn ferrite compositions were prepared by sol-gel, co-precipitation, citrate gel, oxalate precursor and citrate precursor wet chemical methods and characterized by several techniques to understand structural, magnetic and electrical properties [23]. Among nickel zinc series family, the composition $Ni_{0.65}Zn_{0.35}Fe_2O_4$ processed by sol-gel method has been known to exhibit the highest saturation magnetization. Our team has succeeded in producing a uniform fine grained material with high saturation magnetization, very high resistivity, and high permeability with negligible loss suitable for high frequency core applications up to a frequency of 20 GHz.

1.2 Review of past work

Many attempts were made by a number of researchers [24] to synthesize the desired materials for MLCI applications. Superior magnetic and dielectric properties were observed in TiO_2 doped Ni-Cu-Zn ferrites widely used in the manufacturing of inductors and capacitors [25].

However, the composite was found to contain undesirable defects such as de lamination, cracks and camber.

Ni-Cu-Zn ferrites are known to be excellent soft magnetic materials in high frequency devices due to their low cost, high resistivity and low eddy current losses. These ferrites have been studied extensively for multiplayer chip inductor applications [**25-27**]. Very few reports are available up to now on RF integrated inductors made of ferrites and the observed Q factors are too low for high frequency performance [**28**].

In bulk iron deficient Ni-Cu-Zn ferrites, $Ni_{0.28}Cu_{0.10}Zn_{0.62}O(Fe_2O_3)1-x$, where x = 0.00, 0.02, 0.04, 0.06 and 0.08 processed by conventional method, it was noticed that the resonant frequency and Curie temperature increase initially with the increase in iron deficiency and decrease at x = 0.06. With increasing iron deficiency, the permeability was observed to increase significantly [**29**].

Below 80 K, the nanocrystalline $Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$ prepared using a chemical method exhibited superparamagnetism. The saturation magnetization was found to increase with the increasing particle size [**30**].

Very few have investigated the structural and electrical properties of Cu-substituted Ni-Zn ferrites and reported that the ac conductivity increases with increasing temperature of the sample and frequency of the applied field [**31**].

The magnetization, initial permeability and Curie temperature have been decreased where as dc resistivity increased with increasing Cr-concentration in Ni-Cu-Zn ferrite [**32**]. It was reported that the optimum bulk density, initial permeability and dc electrical resistivity can be obtained at copper concentration 0.2 [**33**].

In a study on $Ni_{0.7-x}Zn_{0.3}Cu_xFe_2O_4$, it has been reported that Cu occupies both A and B sites. Curie temperature and magnetization decrease with increasing copper concentration [**34**].

Some have worked on the stress insensitive ferrite and reported that the sensitivity of the magnetic property to the external stress in Ni-Cu-Zn ferrite can be examined from the relationship between stress and permeability. Many have worked on stress sensitivity of inductance in Ni-Cu-Zn ferrite and observed that stress sensitivity is more in the case of iron rich and stoichiometric iron samples while in the case of iron deficient samples the stress sensitivity has been found to be less [35, 36]. Studies have been carried out on the development of low temperature Ni-Cu-Zn ferrites and high performance for multilayer chip ferrites and reported that controlling of stress is essential for the high performance of MLCI [37].

In place of Ni-Cu-Zn ferrites, Mg-Cu-Zn ferrites were also prepared for the same purpose. Many researchers have carried out the initial permeability studies on high density Cu-Mg-Zn ferrite and reported that variation of initial permeability with composition was mainly affected by variation of magnetization and average particle size and showed that the initial permeability increased with increase of magnesium content [38]. Mg-Cu-Zn ferrites prepared by conventional ceramic method sintered at temperatures beyond 1050 ^{o}C [16, 39, 40] provided high magnetization and high quality factor but poses problems including low permeability, high losses, low densities and more power consumption.

Hu Jun et. al. [41] have observed that appropriate addition of sintering aids like V_2O_5 and reduction in the granularity of the raw materials particle decreased the sintering temperature of Ni-Zn ferrite from 1200 ^{0}C to 930 ^{0}C and obtained enhanced density with high initial permeability of 1700 in $(Ni_{0.17}Zn_{0.63}Cu_{0.20})\ Fe_{1.915}O_4$.

H. Saita et.al. [42] in an attempt to lower the sintering temperature, synthesized Ni-Cu-Zn ferrite to study the sintering behavior including densification and grain growth in a microwave field of 2.54 GHz. Densification was significantly promoted by microwave sintering and showed little effect on the activation energy for isothermal grain growth in Ni-Cu-Zn ferrite system. When compared to conventional sintering, the microwave sintering of Ni-Cu-Zn ferrite system sintered at 937 ^{0}C increased the initial permeability and quality factor to a small extent.

Yan et al. [43] prepared solid solution of Ni-Cu-Zn ferrites by the addition of V_2O_5 which promotes the grain growth. At 1MHz, domain wall motion plays a predominant role in the magnetizing process. Through addition of 10 mol% CuO and 0.20 mol% V_2O_5 the initial permeability reached 1417 at 1MHz. Kim *et al* also [44] have investigated the influence of addition of V_2O_5 and reported that the appropriate addition of sintering aids promotes the diffusion of ions and accelerates the solid reaction in the sintering process. Ni-Cu ferrites synthesized [45] by sol-gel technique exhibited non-collinear ferrimagnetic structure. *Navneet Singh et. al.* [46] prepared $Ni_{0.5}Li_{1.0-2x}Cu_xFe_2O_4$ $(0.0 \le x \le 0.5)$ by sol–gel auto-combustion method and observed that the saturation magnetization increases with addition of Cu^{2+}ions (up to x = 0.2) and decreases for higher amounts. Further decrease in resistivity and dielectric constants with increasing grain size has been noticed.

Materials having high initial permeability and high resistivity are most suitable for high frequency applications beyond 1 MHz. Low loss at high frequency is necessary in order to extend the application of Ni-Cu-Zn ferrite to high frequency devices. M.L.Rehman *et. al.* [**47**] synthesized $Ni_{0.20}Cu_{0.30}Zn_{0.50}Fe_2O_4$ by auto combustion method and noticed that the initial permeability increased with increasing sintering temperature up to 1200 ^{0}C due to the increasing grain size but decreased thereafter due to pores trapped in the grains. Also it was observed that f_r resonant frequency decreased with increasing sintering temperature.

In another study, *Xiang et. al.* [**48**] on $Ni_{0.50-x}Cu_xZn_{0.50}Fe_2O_4$ ($0.0 \leq x \leq 0.5$) nanofibres reported an increase in grain size along with increase in saturation magnetization initially and followed by a decrease for higher concentrations of copper. The room temperature VSM measurements carried out for the nanofibres and the same sample prepared by conventional method showed that the coercivity values were 9.7 and 11.6 kA/m respectively. The coercivitiy values as observed from the VSM data at 77 K were 23.6 and 15.4 kA/m for the nanofibres and the powders respectively. This difference has been attributed to the variation in morphology. Slama et. al. [**49**] synthesized $(Ni_{0.3}Zn_{0.7})_{1-x}Cu_xFe_2O_4$ by conventional method and reported that the saturation magnetization and Curie temperature increased with increasing copper content.

M.F.Akther Hossain *et. al.* [**50**] synthesized $Ni_{0.50-x}Cu_xZn_{0.50}Fe_2O_4$ x=0.0 to 0.25 in steps of 0.05 by auto combustion method and reported that bulk density, grain size and initial permeability increased upto a certain level of Cu^{2+} substitution but all these properties decreased with further increase in Cu^{2+} content. Initial permeability increased from 97 to 390 for the sample sintered at 1100 ^{0}**C**. The saturation magnetization M_s decreased with increase in Cu^{2+}content and attained a minimum value at x=0.15 and increased for further substitution of copper. Initially for lower concentrations of copper, Cu^{2+} enters into B site lowering the magnetic moment and for higher concentrations of copper the magnetic moment is increased as Cu^{2+}changes into Cu^{1+} which has a preference into A site. E.Usak [**51**] prepared $(Ni_{0.3}Zn_{0.7})_{1-x}Cu_xFe_2O_4$ and observed that copper substitution lowers the magnetic losses at particular concentration of Cu^{2+} when compared to the unsubstituted Ni-Zn ferrite and also increases the Curie temperature. However for higher values of Cu^{2+} ion concentration, due to the formation of secondary phases in the ferrite, such as $CuO/CuFe_2O_4$ the electrical and magnetic properties were deteriorated.

P.A Jadhav *et. al.* synthesized $Ni_{(0.7-x)}Cu_xZn_{0.3}Fe_2O_4$ (where x = 0, 0.2,0.4 and 0.6) by citrate precursor method [52] which exhibited high average grain size and consequently a corresponding decrease in dc resistivity. In a study by M.A.Gabal *et. al.*[53] on $Ni_{0.7-x}Cu_xZn_{0.3}Fe_2O_4$ system (x=0.0 to 0.6 in steps of 0.1), the saturation magnetization and coercivity were observed to decrease gradually from 48.4 to 37.8 and 76.8 to 33.1 respectively with increasing copper content. Curie temperature was also observed to decrease with increasing cooper content due to the weakening of AB interaction. A report by P. K. Roy on $Ni_{0.25}Cu_{0.2}Zn_{0.55}Sm_{0.05}Fe_{1.95}O_4$ [54] showed better initial permeability but poor frequency response of permeability.

Nam et al. [55] investigated the effect of copper substitution on the electromagnetic properties of Ni-Cu-Zn ferrites by preparing $(Ni_{0.5-x}Zn_{0.50}Cu_x)\ (Fe_2O_4)_{0.98}$ 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 $(Ni_{0.2}Cu_xZn_{0.80-x})\ Fe_2O_4$. *Dimri et al.* [56], in his studies about the effect of compositional variation on structural, dielectric and magnetic properties of the copper substituted Ni-Zn ferrite by synthesizing $(Ni_{0.6-x}Cu_xZn_{0.4})Fe_2O_4$, the results showed that the addition of copper promoted grain growth. However, Curie temperature was understandably lowered with the increase in Cu content.

A study by kin O. Low *et. al.* [57] on the electromagnetic properties of copper substituted Ni-Zn ferrites revealed that the sintering temperature was lowered to 950 ^{0}C, initial permeability increased initially with increasing copper up to 12 mol% and deteriorated thereafter. However electrical resistivity as high as 1000 KΩm was obtained at 4.5 mol% of CuO due to smaller grain sizes associated with lower content of copper and decreased to 1KΩm at about 28.5 mol% of CuO due to higher grain sizes associated with higher content of copper.

Zhenxing Yue et. al. [58] synthesized $Ni_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ by auto-combustion method of nitrate-citrate gel after carrying out room temperature Mossbauer spectral analysis of the sample reported about the coexistence of ferromagnetic particles with a small amount of paramagnetic particles due to very small size of the particles.

$(Mg_{0.5-x}Cu_xZn_{0.5})$ O $(Fe_2O_3)_{0.98}$ ferrites synthesized by Z. Yue [59] showed an increase in density, permeability and Curie temperature whereas resistivity decreased with copper content up to x = 0.40. *Haque et al.* [39] worked on copper substituted Mg-Zn ferrites. They found a remarkable increase in the bulk density with increasing copper substitution for magnesium. By incorporating CuO, the initial permeabilities have been found to be increased and saturation magnetization increased slightly with increasing copper content upto $x \leq 0.30$ and then decreased for x = 0.35.

A study has been carried out by S. F. Wang *et. al* on microstructure, density, ac resistivity, permeability, quality factor and magnetization of $Ni_{0.38}Cu_{0.12}Zn_{0.50}Fe_2O_4$ [60] by the addition of different wt% of $PbO:SiO_2$, $PbO:B_2O_3$ and Bi_2O_3 to lower the sintering temperature. Hua su et. al. [61] in his studies reported that with the addition of MoO_3 in Ni-Cu-Zn ferrite, the grain size and bulk density were increased and initial permeability reached its maximum at about 12 mole % of MoO_3 and thereafter it decreased.

Manganese substitution in Ni-Cu-Zn ferrites [62] remarkably affects the dependencies of magnetic and electric properties on frequency and temperature. With increasing MnO_2 content, the resonant frequency and the Curie temperature were observed to decrease, whereas the initial permeability increased first, took a maximum at 0.06 content of MnO_2 and then decreased. A decrease in DC electrical resistivity and activation energy is reported with increasing MnO_2 content.

Goev et. al. [63] stated that initial permeability was 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 remanent magnetization have been found to be maximum at y = 0.4. $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0 – 1.0) have been [64] prepared through the thermal decomposition of respective impregnated oxalates and found that the copper substitution greatly affected the magnetic properties. The saturation magnetization and the Curie temperature were found to decrease with increasing copper content whereas the coercivity was increased.

There are many reports about the segregation of copper in the form of CuO/ $CuFe_2O_4$ which are unwanted and deteriorated both the electrical and magnetic properties of Ni-Zn ferrites. In order to make the material suitable for MLCI applications, small grain sizes are preferable with high initial permeability, high electrical resistivity and high reliability. Recently it was shown that adding Bi_2O_3 to the Ni-Cu-Zn ferrite with SiO_2 could sinter the Ni-Cu-Zn ferrite densely while suppressing the grain growth, though Bi_2O_3 generally hastens the grain growth [65]. The effect of Al-substitution on the magnetic and electrical properties of different ferrites was studied by many authors [66-68]. They reported that the substitution of aluminum decreases the saturation magnetization (M_S), initial permeability (μ_i), Curie temperature, remanence ratio (M_R), and coercive field (H_c) whereas the anisotropy field and electrical conductivity were increased.

In another report, the substitution of Al^{3+} in Ni-Cu-Zn ferrite [69] has showed an increase in saturation magnetization up to an optimum concentration of x=0.05 followed by a decrease and the value of initial permeability was not observed to increase much. Mg-Cu-Zn ferrite is another competing system [44] on par with Ni-Cu-Zn ferrite towards MLCI applications. But there have been very few reports about this system. However in the reports there has been not much improvement in the initial permeability together with high Q which is a primary requirement for MLCI application.

There have been several reports on occupancy of copper in nickel zinc ferrites with controversial statements. Some **[70,71]** reported the preference of copper towards B-sites and some others [22, 50] reported the preference of copper at A-sites and a few reports on both the sites of the ferrite lattice. In addition to this there are [22] reports about the segregation of copper at grain boundaries. Existing controversies about the occupancy of copper in Ni-Zn ferrites made to be cleared in order to understand the magnetic and electrical properties of the ferrites.

1.3 Aim of work

The success of our team in providing a core material useful for high frequency applications prompted the author to carry out a systematic investigation to understand the influence of copper in a well established composition $Ni_{0.65}Zn_{0.35}Fe_2O_4$. This composition has been known to produce the highest saturation magnetization, high initial permeability and high dc resistivity among the bulk Ni-Zn ferrite family. The selected best composition has been subjected to sol-gel synthesis in different polymer matrices, *viz.* polyvinyl alcohol (PVA) and polyethylene glycol (PEG) with a view of further enhancing magnetization, reducing particle size, grain size and increasing resistivity without affecting the permeability. There have been very few reports available on the influence of chelating agents on the control of particle size **[72]**. It is well known that initial permeability is highly sensitive to microstructure which in turn depends on method of processing. There has been no report available in the literature in the direction of achieving the high initial permeability. By substituting copper in place of nickel it would be possible to enhance the initial permeability to a higher value. Careful annealing process is essential to obtain the least possible crystallite size, a crucial parameter in obtaining the desired characteristics. The presence of smaller grains leads to provide innumerable grain boundaries which would generally improve the resistivity of the material. A compromise over the desired characteristics can be decided by the optimal copper content. Moreover, copper substitution in nickel zinc ferrite acts as a sintering aid [**19**] and helps to improve the sintering density at relatively low temperatures without degrading the magnetic and dielectric properties.

No systematic investigation correlating all the structural, magnetic and electrical properties is available in the literature. Also, systematic influence of chelating agents and organized heat treatment on the selected system were not found in the literature.

The established characteristics of MLCI are high density, high magnetization, high permeability, high resistivity, high Curie temperature, fine grains, low dielectric constant, low magnetostriction, low coercivity and low losses. With the attainment of high electrical resistivity and high saturation magnetization, high permeability, high Curie temperature, fine grains, low coercivity, low dielectric properties and quality factor, it would be certainly possible to operate the processed material for high frequency MLCI applications.

1.4 Measurement techniques employed

Several techniques have been adapted to procure vast information in the direction of understanding the variations related to the several parameters useful for the development of multilayer chip inductors. X-ray diffraction measurements give information related to the spinel structure and crystallite size. Transmission electron micrographs support the information about crystallite size, particle size and its size distribution. FTIR studies provide the information regarding the site occupancy of copper ions in the ferrite lattice. Vibration sample magnetometer studies offer information regarding saturation magnetization and coercive force. The process of annealing provides optimal temperature on the basis of obtaining high saturation magnetization. FESEM observations offer extensive information in understanding the microstructure of Ni-Cu-Zn ferrites. DC resistivity, initial permeability and frequency dependence of permeability have been investigated to check the applicability of the material for high frequency operation. To have a clear view about the magnetic interactions among iron ions in the spinel lattice, Mossbauer spectroscopic studies have also been carried out.

1.5 Thesis outline

The thesis comprises of 5 chapters and the chapter-wise break up is given as follows. First chapter provides an overview of developing a ferrite material with superior characteristics to stand as a good MLCI material. It presents a detailed review about the necessity of preparation of ferrite nanoparticles with smaller crystallite size, smaller grain size and the influence of different sintering aids on density and initial permeability.

The experimental techniques and theoretical background needed for carrying out the present investigation has been given in chapter 2. The importance of the starting composition and its method of preparation have been discussed in chapter 3. The variations taking place in crystallite size, particle size, saturation magnetization in basic nickel zinc ferrite with annealing temperature have been dealt with in detail.

In chapter 4, the influence of copper has been studied on several parameters like lattice constant, crystallite, particle, grain sizes, saturation magnetization and initial permeability in Ni-Zn ferrites. Further, the frequency dependence of initial permeability, magnetic loss tangent, importance of quality factor and details about the site occupancy of copper ions in the Ni-Zn ferrite have been discussed.

Chapter 5 presents the analysis of Mossbauer spectra in providing an accurate estimation about the valence state of iron ions, their environment, magnetic exchange interactions among the cations and their distribution in copper substituted nickel zinc ferrites. The proposed cation distribution has been justified with the help of X-ray diffraction and magnetization studies.

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