1.1: INTRODUCTION

Ferrites being a magnetic material have been the subject of interest for the academician and technologist since 1945. The technical importance of ferrite lies in their high electrical resistivity, high saturation magnetization, high permeability, low eddy current and dielectric loss, chemically stable and low cost [1]. These remarkable properties of ferrites have made them useful in verity of applications. The use of ferrite has established in many branches of telecommunication, electronic engineering, and computers. Many efforts have been taken by various researchers in developing ferrite with new composition and desired properties useful in many applications [2, 3]. The important electrical and magnetic properties of ferrites can be modified by change in method of preparation, preparation conditions, preparative parameters, type and amount substituent [4, 5].

Synthesis of ferrites has been carried out in last decades mostly using ceramic technique. There are several advantages of Ceramic technique. From a commercial standpoint, the pre-fired material can be pressed into a useful shape and then fired, producing a finished product with minimal voids within the material. From the chemical viewpoint, this method provides a consistent product. There is minimal loss of cations in the reaction and so the ratio of cations in the product is controlled by the ratio in the reactant mixture. Because the cations are allowed to migrate to a thermodynamically favorably state, batch to batch variation of the cation lattice occupation is minimal. Sample prepared by ceramic method has larger particle size as compared to that prepared by other method. This inherent drawback affects the
quality of material. Ceramic technique requires more time, elevated temperature, long duration and possibility of mixing, impurities during grinding process. These drawbacks of the ceramic method are removed in wet-chemical method of synthesis. Large number of researchers have synthesized ferrites in nano-size form and investigated their structural, magnetic, electrical, dielectric and optical properties.

Ferrites are ferrimagnetic materials as proposed by L. Neel [6]. On the basis of crystal structure ferrites are grouped in three categories namely spinel ferrite, garnet and magneto-plumbite. Iron oxide is the main constituent of ferrite and hence these materials are useful in memory chips, permanent magnet and other magnetic applications. Crystal structure of ferrite possess two or more than two site in which cations are distributed over their interstitial sites verity of cations can be accommodated into the lattice site of ferrite bringing the wide variation in the properties of ferrites. The substitution of different cations in the lattice of the ferrite depends on ionic radii of the constituent ions. All these classes of ferrites are equally important from the point of view of their applications. Each has a unique crystal structure and distinct set of magnetic properties.

The three types of ferrites are classified by names of common minerals which have the crystal structure of the type magneto-plumbite, garnet and spinel. Magneto-plumbite ferrites are usually represented by $\text{MFe}_{12}\text{O}_{19}$ ($\text{M}=\text{Ba}, \text{Sr}, \text{Ca}$ etc.) and are important in permanent magnetic applications. Garnets have the formula $\text{R}_3\text{Fe}_5\text{O}_{12}$ ($\text{R}=\text{Yttrium or rare earth ions like Dy, Gd, La}$ etc.) and have applications in microwave systems. Spinel ferrite are represented by the chemical formula $\text{MFe}_2\text{O}_4$ ($\text{M}$ is the divalent cations like Co, Ni, Zn, Cd etc.). The crystal structure of spinel ferrite is based on cubic close packed anions.

Among the various types of ferrites, spinel ferrites have attracted the attention of scientist and academician because of their interesting electrical and magnetic properties and their utility in many applications ranging from microwave to radio frequency. The interesting physical and chemical properties of spinel ferrites arise
from the ability of these compounds to distribute the cations amongst the available tetrahedral and octahedral sites. The method of preparation also plays an important role in governing the properties of ferrites.

1.2 HISTORICAL BACKGROUND

The history of magnetism begins about 600 B.C. Magnetite, which has the chemical formula \( \text{Fe}_3\text{O}_4 \), and is an example of ferrite, was known to be Greeks at this time, and they are knew, too, of its peculiar properties of always setting in particular direction when freely suspended. However, they made no applications of the phenomenon and it is not until the middle of the 12th century A.D. [7]. Ferrites are compounds which contains ferric oxides and metal oxides exhibiting combined properties of electrical insulator and magnetic conductor. Certain ferrites have high electrical resistivities of the order of \( 10^9 \) ohm-cm. combined with high values of initial permeability and saturation magnetization. It is these properties which render ferrites invaluable in radio communication and television applications. The properties which have made ferrites so useful in radio and television frequencies also provide the key to their use at microwave frequencies.

Although ferrites were first prepared as long ago as 1859, the first systematic study on the relationships between chemical compositions and magnetic properties of various ferrites were only reported by Hilpert about one century ago in 1909 [8], who successfully prepared spinel ferrites using manganese, copper, cobalt, magnesium and zinc. After 20 years, Hilpert had done preparation of various ferrites and measurements of their saturation magnetization as well as curie temperature. The spinel ferrites are a large group of oxides that were first studied by Nishikawa (1915) [9] and Bragg (1915) [10]; they have the structure of the natural spinel \( \text{MgAl}_2\text{O}_4 \) [11]. Ferrites reached the stage of commercial importance in late 1930 through the efforts of Japan’s Kato and Takai [12]. In 1932, Kato and Takei discovered that a solid solution of magnetic and cobalt ferrite was strongly magnetized at = 300 °C and the solid solution had practical applications.
The active research on the preparation of ferrites for radio frequency usage did not start until 1933. The main pioneering work was performed by Dr. Snoek [13, 14] and his colleagues at Netherland. Anderson [15] and Van Vleck [16] develop the super-exchange theory. Yafet and Kittel [17] extended super-exchange theory by postulating the triangular spin arrangement of three sub-lattices. The work of Verway and Heilmann in 1947 [18] on the distribution of ions over the tetrahedral and octahedral sites in the spinel lattice has contributed to progress in the physics and chemistry of ferrites. After the Second World War the development of ferrites proceeded rapidly and by 1948 they were coming into wide spared use for radio and television purposes. Neel [19] of France explained the mechanism for the enhancement of magnetization by the addition of zinc ferrite successfully in 1948. Other French scientist also achieved great success in the fundamental studies of orthoferrite by Forestier and Guoit-Gaillain in 1950 [20] and of Garnet ferrite by Bertaut and Forrat [21] in 1956.

From the nineteen fifty, as radio and television spreads a ferrite, established a significant position in industry, and now ferrites are most essential materials in the electronic industry. Globus [22] developed a model which gives contribution of domain wall motion to permeability. M.T. Johnson [23] has developed a model to describe the grain size dependence of the rotational permeability. G. Rankis [24] has developed a modified model of initial magnetic permeability of polycrystalline ferrites. Polder [25] in 1949 first derived the ferrite permeability tensor, which laid the groundwork for the understanding of ferrite behavior at microwave frequencies.

Immediately after the work of Snoek and others, C. L. Hogan [26] has used ferrites in microwave compounds. In 1953, the first attempt was make to explain theoretically the behaviour of wave guides containing the ferrites. The microwave behaviour of ferrites has aroused the interest of others besides microwave engineers and applied mathematicians. Physicist has found studies of ferromagnetic resonance in ferrites and allied materials.
The first commercially available ferrite device the UNILINE manufactured by Cascade Research Corporation, California, USA appeared on the market in 1953. Since then the study of ferrites has been subject of many research workers.

Moreover, U.S. researchers in bio chemistry have explained the existence of magnetite in the bodies of pigeons by Walcott [27], honey bees by Gould [28] and bacteria by Frankel [29] which has brought about the dream for the ferrite industry in the future.

It is believed that the production of ferrites will increase year by year as their applications become more diverse. Reviewing ferrite history and accurately analyzing its present status will add greatly to further development in the future.

1.3 APPLICATION OF FERRITES

Ferrites are the materials of great importance in technological applications on account of their combined electrical and magnetic properties. They can be classified on the basis of their crystal structure as well as best on their coercivity (Hc) values. For hard ferrites coercivity is greater than 1.5 KOe. For moderate ferrites Hc ranges between 100 Oe to 1.5 KOe. For soft ferrite Hc has to be very low (< 10 Oe).

Ferrites belonging to a magnesium ferrite family having inherent rectangular hysteresis loop characteristics were first to be identified for use in memory cores. Aluminium (Al) and Zinc (Zn) substituted magnetic ferrites are suitable for applications in microwave components. Magnesium ferrites have become important to industry, because of their applications in intermediate frequency transformer and antenna cores.

Nickel-Zinc ferrites are adequate for use in the high frequency band because of its high resistivity with sufficient low losses for microwave applications [30, 31]. Ni-Zn ferrites are widely used in electronic devices because of its environmental stability and high performance in the radio frequency region. A circulator is a representative microwave device in which the anisotropy property of ferrite is made used of to achieve nonreciprocal behaviour. The optical transmittance phenomenon
taking place in the visible range make Fe$_3$O$_4$ (ferrous ferrite) very promising compound in the development of new generation of materials for magneto optical media. Mn-Zn ferrites have been extensively used for transformers utilized for switching power supply because of the low core loss at high frequency. Mn-Zn ferrites posses the most appropriate properties and parameters and television related applications.

For the low and high frequency application, the most important technical properties are saturation magnetization, coercivity and initial permeability. The best combination of all these properties cannot be obtained for any specific applications by varying the composition or by adding the additives or by changing the preparation method one can control the properties for suitable application. The various applications of ferrites are illustrated in Table 1. The soft ferrites are mainly used in television in the form of Yoke. Soft ferrites can be used in magnetic recording head inductors and transformer cores, filter cores, magneto-strictive vibrator etc. For magnetic recording heads, beside low Hc high thermal stability one can requires low magneto-stiction and high frequency response.

Magnetic hardness is due to fine particles having shape and crystalline anisotropy. A large crystalline anisotropy is characteristic of hexaferrite. Hence a large coercivity is almost an inherent property of hexaferrite and other than that it is oxidation and corrosion resistant. Its temperature stability is not only good but is the cheapest among all the hard magnets. By virtue of its low cost and being suitable (BH)$_{\text{max}}$ for isotropic and anisotropic hexa-ferrites, it finds wide applications in motors, generators, loudspeakers, telephones, meter switches, magnetic separators, toys, flexible and rubber magnets, magnetic latch and magnetic levitation.

Rapidly growing of potentially large application of ferrite today, are used in modem digital computers. The rectangularity of Hysteresis loop and coercive forces are the important factors in these applications.
Table 1.1: Applications of Ferrites

Flow Chart of Applications of Ferrites

- Permanent
  - Motor
  - Loudspeakers
  - Rubber Magnet
- Magnetic Recording
  - Erase heads
- Computer
  - Power Transformer
- Microwave
  - Transformer Core
- Radio and Television
  - Delay Line
  - Flyback
- Telecommunication
  - Impedance
  - Electrolyte
- Miscellaneous
  - Ferrite Powder for Copying Machine
  - Electromagnetic
  - Magnetostriuctive
- Audio Tapes
  - Magnetic discote
  - Computer Tapes
- Magnetic Card
  - Video Tapes
  - Noise Absorber
  - Isolators
  - Circulator
- Ferrite Microwave
  - Low Temperature
  - High Stability Cores
- Rubber Ferrites
  - Low Accommodation
  - Low Loss Cores
- FT Cores
  - Rotary
- Magnetic Recording Heads
Microwave in the higher range are being increasingly utilized in wireless communication viz. radar, local area network, satellites communication, precise guidance system and remote sensing techniques.

Microwave absorbers are also in high demand for defense use. Application of microwave absorbing coating on the exterior surface of military aircraft and vehicles helps avoid detection by radar. The M-type hexaferrites due to their large tunable anisotropy field are extensively exploited in the recent years in higher gigahertz range [32]. Recently, ferrites were considered as one of the most versatile magnetic materials for multiplayer chip inductor (MLCI) applications and surface mount devices (SMDs) due to their high electrical resistivity and permeability [33]. The ferrite material system exhibits super-paramagnetic behaviour, display little or no remanence and coercivity while keeping a very high saturation magnetization have potential applications in biomedicine [34], magnetic drug delivery and cell sorting systems [35, 36].

1.4 LITERATURE REVIEW

Spinel ferrites exhibiting twin property of electrical insulator and magnetic conductors have been widely studied by several researchers. The modification in their properties has been brought by substituting various divalent, trivalent and tetravalent ions in place of ferric ions. The synthesis methods and synthesis parameters plays a crucial role in controlling properties of spinel ferrite.

Among the spinel ferrites Ni-Zn, Mg-Zn and Mn-Zn ferrites with various substituents have found enormous applications and therefore they have been extensively studied by many groups [37-39]. Ni-Zn ferrites are one of the versatile, low cost, magnetic materials and can be used in low and high frequency applications. The properties of Ni-Zn spinel ferrite can be tailor-made for suitable applications by substituting them with different metal ions such as Co$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Cu$^{2+}$ etc. Ni-Zn spinel ferrites successfully with good quality can be prepared at high sintering temperature (> 1200°C). To reduce the high sintering temperature, cations like Cu$^{2+}$
can be incorporated into the structure Ni-Zn. The substitution Cu\(^{2+}\) ions favors in lowering sintering temperature and high densification [40]. Recently, with development of surface mount technology (SMT) and multilayer chip devices NiCuZn ferrites has been extensively studying and widely used to fabricate chip conductors and EMI filters [41]. NiCuZn spinel ferrite has been widely used in inductive multilayer devices due to their high electrical resistivity and good magnetic properties [42].

In the literature effect of sintering temperature on structural and magnetic properties of NiCuZn and MgCuZn ferrites have reported by M. Penchal Reddy et.al. [43], Mariana Usakova et.al. [44] have reported the influence of Cu\(^{2+}\) ions on the structural and magnetic properties of NiZn ferrites they showed that Cu\(^{2+}\) as positively influence the thermal stability of NiCuZn ferrites and simultaneously maintain good magnetic properties. J. Murbe and J. Topfer et.al. [45] have studied NiCuZn ferrite and observed the effect of sintering behaviour and permeability. Phase formation grain growth and magnetic properties of NiCuZn ferrite has been studied by K. Sun et. al. [46] NiCuZn ferrite in nanocrystalline form has been prepared and investigated for its structural and magnetic properties by many workers [47-49].

1.5 AIM OF THE PRESENT WORK

The aim of the present work is to synthesize NiCuZn spinel ferrite with chemical composition Ni\(_{0.37-0.02x}\)Cu\(_{0.02x}\)Zn\(_{0.63}\)Fe\(_2\)O\(_4\) (for x = 0, 1, 2, 3, 4 and 5) for its possible applications in multilayer chip conductors by ceramic technique. In the literature such composition of NiCuZn is not reported to our knowledge. NiZn spinel ferrite with Ni\(_{0.37}\)Zn\(_{0.63}\)Fe\(_2\)O\(_4\) chemical formula shows higher resistivity and good magnetic properties. The substitution of copper (Cu\(^{2+}\)) ions in NiZn may reduce the sintering temperature. In the literature emphasis is given on structural and magnetic properties of NiCuZn ferrites. Initial permeability, electrical and dielectric studies on NiCuZn spinel ferrite is rarely studied [50, 51]. In view of this in the present work the structural, infrared, electrical, dielectric, magnetic and permeability studies were carried out for various Cu\(^{2+}\) concentration x.
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