

## FTIR Studies and Dielectric Properties of Cu Substituted Nano Crystalline Nickel-Zinc Ferrites Synthesized By Citrate-Gel Auto Combustion Technique

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**Abstract:** The nano crystalline Cu doped Ni-Zn ferrites having compositional formula  $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$  (where  $x=0.0, 0.2, 0.4, 0.6$  and  $0.8$ ) were synthesized successfully by Citrate-Gel Auto Combustion method at a low temperature ( $180^{\circ}C$ ). Analysis of the X-Ray diffraction pattern of all the samples confirmed the formation of single phase cubic final structure with an average crystallite size 24-73nm. In the present work, the effect of nano structured particle size and cu concentration on parameters such as bond length and vibration frequency are discussed with the help of FTIR data. The dielectric parameters such as dielectric constant, dielectric loss tangent, AC Conductivity of the samples were studied as the function of composition and frequency in the range 20Hz-2MHz at room temperature using Agilent E4980 precession, LCR meter.

**Keywords:** Citrate-gel auto combustion method, dielectric constant, ac conductivity, FTIR.

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### I. Introduction

Spinel ferrites are commercially important materials due to their excellent magnetic and electric properties [1]. Polycrystalline ferrites are very good dielectric materials and have many technological applications ranging from microwave to radio frequencies [2]. One important characteristic of ferrites is their high values of resistivity, low magnetic and dielectric losses [3] which makes them ideal for high frequency applications. Synthesis of nano-ferrites, especially spinel ferrites, characterized by a low size distribution is important due to their remarkable electrical and magnetic properties and wide practical applications in information storage systems, ferro-fluid technology, magneto caloric refrigeration and medical diagnostics [4-5]. Owing to the dielectric behavior, they are sometimes called multiferroics. They are commercially important because they can be used in, many devices such as Phase Shifter, high frequency transformer cores, switches, resonators, computers, TVs and mobile phones [6-7]. The electrical properties of ferrites depend upon several factors including the route of preparation, composition of constituents, grain structure or size and the amount and type of substitution[8].The properties of nano materials are remarkably different from that their bulk counter-part. The interest in Ferrite nano particles is due to their important physical and chemical properties and potential for various technological applications such has high density magnetic storage. Electronic and microwave devices, sensors, magnetically guides drug delivery etc. The transport properties of the nano-materials are predominantly controlled by the grain boundaries than by the grain itself [9]. Due to this reason, the magnetic materials have explored a wide range of applications and replacing conventional materials. The Conventional solid-state reaction route is widely used for the production of ferrite because of the low cost and suitability for the large scale production. The Citrate method is used to speed up the synthesis of complex materials. It is simple process, which offers a significant saving in time and energy consumption over the traditional methods. Nano size ferrites can be prepared by various methods including glass ceramic methods [10], Hydrothermal method [11], Ultrasonic cavitations approach [12], Reverse micelle technique [13], Mechanical milling [14], Radio frequency plasma torch [15], Sol-Gel method [16], Precursor techniques [17], and co-precipitation method [18].

### II. Experimental

#### 2.1 Synthesis:

Investigated ferrite samples was prepared by low temperature citrate-gel auto combustion method, which was already described in our earlier publication [19].

#### 2.2. Characterization

The structural characterization of the all prepared samples were carried out by x-ray diffraction (XRD) and confirms the well defined single phase spinel structure. XRD data were taken at room temperature using  $Cu-K_{\alpha}$

radiation. Fourier Transform Infra red (FTIR) spectra of prepared ferrite samples were recorded on the Bruker Equinox FTIR Spectrophotometer in the range of 200-600 $\text{cm}^{-1}$ , sample preparation included mixing ferrite powder with KBr (~10mg ferrite/~300mg KBr) because KBr is highly hygroscopic, it was dried before using and pellets were prepared under inert atmosphere. The dielectric parameters like dielectric constant ( $\epsilon'$ ), dielectric loss tangent ( $\tan \delta$ ) and ac conductivity ( $\sigma_{ac}$ ) are measured by using LCR meter at room temperature in the frequency range of 20 Hz to 2 MHz for all prepared samples.

### III. Results And Discussions

#### 3.1. Xrd Analysis

Figure 1 shows the XRD patterns for all the prepared samples of Cu doped Ni-Zn ferrites having chemical formula  $(\text{Ni}_{0.2}\text{Cu}_x\text{Zn}_{0.8-x})\text{Fe}_2\text{O}_4$ , (where  $x=0.0, 0.2, 0.4, 0.6$  and  $0.8$ ).The figure shows a typical cubic spinel structure. The diffraction peaks are broad because of the nanometer size of the crystallites.

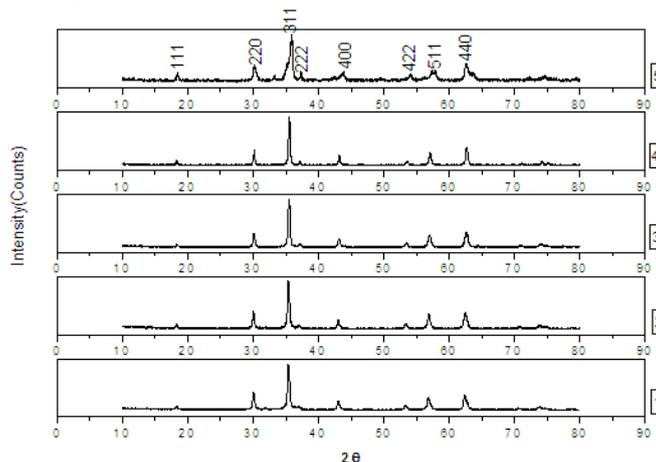


Fig 1 XRD pattern of Cu substituted Ni-Zn nanoferrites.

#### 3.2 FTIR Measurements

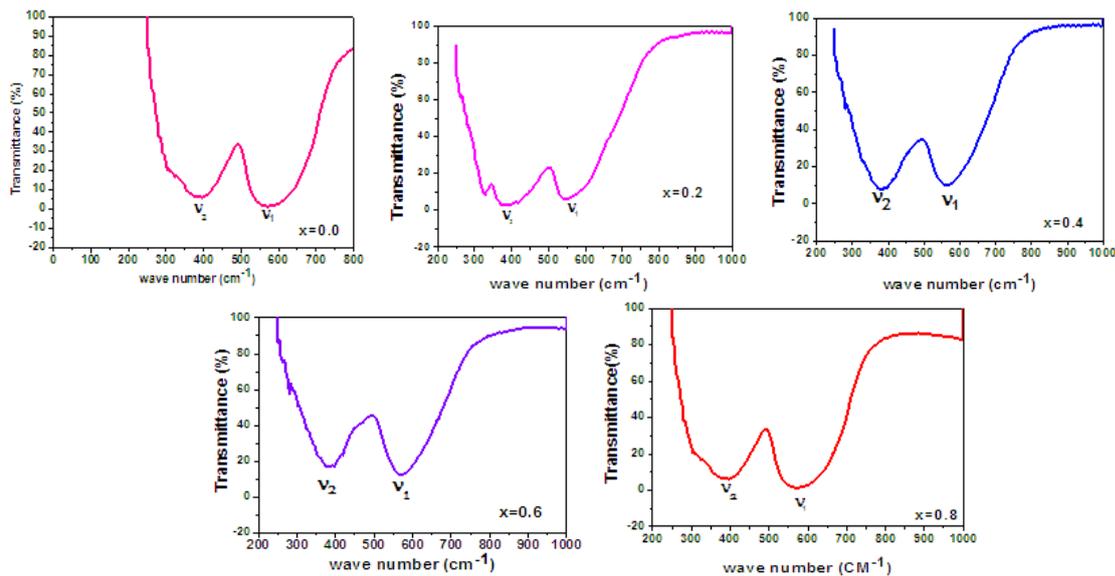


Figure (2) FTIR spectra of  $\text{Ni}_{0.2}\text{Cu}_x\text{Zn}_{0.8-x}\text{Fe}_2\text{O}_4$  ( $x=0.0$  to  $0.8$ ) ferrite nano-particles.

FTIR spectra of the as-synthesized ferrite nano-particles measured in the frequency range of 200 to 600  $\text{cm}^{-1}$  are shown in figure (2). Two prominent absorption bands ( $v_1$  and  $v_2$ ) around 400 and 600  $\text{cm}^{-1}$  are observed. These spectra represent characteristic features of ferro-spinels, and bands are attributed to the stretching vibrations due to interactions between the oxygen atom and the cations in tetrahedral and octahedral sites, respectively. The difference between  $v_1$  and  $v_2$  is due to the changes in bond length (Fe-O) at the octahedral and tetrahedral sites. The FTIR spectroscopic results are summarized in table 1. From the table it is clear that  $v_1$  is in the range of 556-575 and  $v_2$  in the range of 376-391 which confirm the cubic spinel structure of the investigated samples.

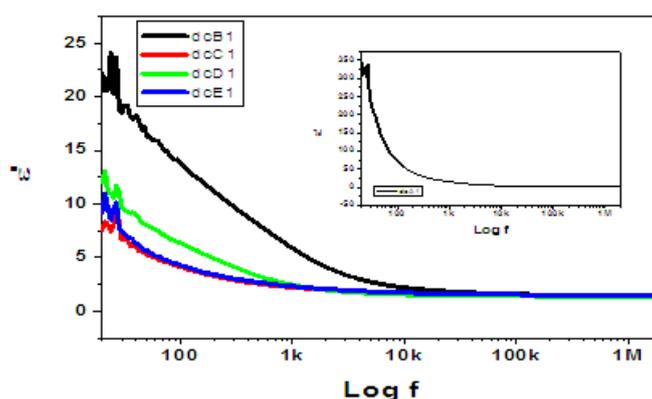
**Table1:** FTIR absorption bands in the investigated samples.

COMPOSITION	$\nu_1$	$\nu_2$
X=0.0	574	391
X=0.2	561	378
X=0.4	556	376
X=0.6	567	381
X=0.8	575	382

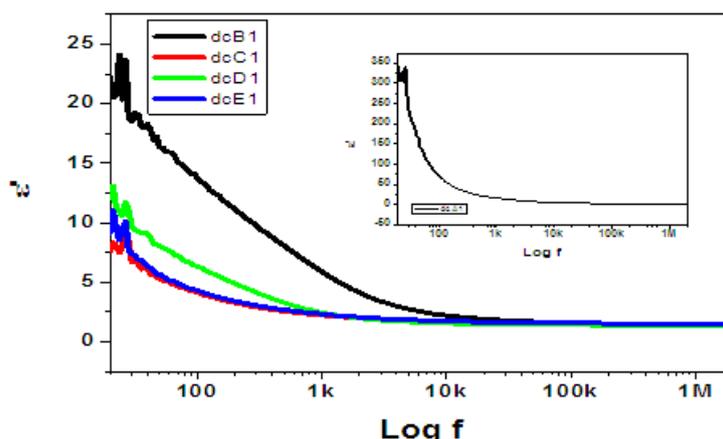
### 3.3 Dielectric Properties

#### 3.3.1 Variation of Dielectric constant with frequency

The dielectric properties of ferrites strongly depend on several factors, including the method of preparation, chemical composition and grain size. The frequency dependence of the real and imaginary part of dielectric constant ( $\epsilon'$  and  $\epsilon''$ ) for all the samples was studied at room temperature in the range of 20Hz to 2MHz. **Figure 3 and 4** depicts the variation of the real and imaginary part of the dielectric constant ( $\epsilon'$  and  $\epsilon''$ ) as a function of frequency for mixed ferrites  $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$  with different compositions ( $x= 0.0, 0.2, 0.4, 0.6,$  and  $0.8$ ). It is observed that all the samples have higher dielectric constant at lower frequency and there is a decreasing trend in value with increasing frequency which is a normal behavior of ferromagnetic materials.



**Figure (3)** Variation of real part of dielectric constant with frequency.



**Figure (4)** Variation of imaginary part of dielectric constant with frequency

The decrease in  $\epsilon'$  is sharp initially from 20Hz to 1000Hz (lower frequency) and then  $\epsilon'$  value decreases slowly with the increase in frequency and showed almost frequency independent behavior at high frequency regions[20] but X=0.0 composition was slowly decreasing due to non reacting of copper present in the composition.

**3.3.2. Dielectric Loss Tangent ( $\tan \delta$ ) with frequency:** Figure (5) shows the variation of dielectric loss tangent ( $\tan \delta$ ) with frequency (20Hz to 20MHz) at room temperature. The dielectric loss decreases with the increasing frequency which is a normal behavior of any ferrite material. The dielectric loss decreases is slow in the low-frequency region, and it shows an almost frequency independent behavior in the high-frequency region.

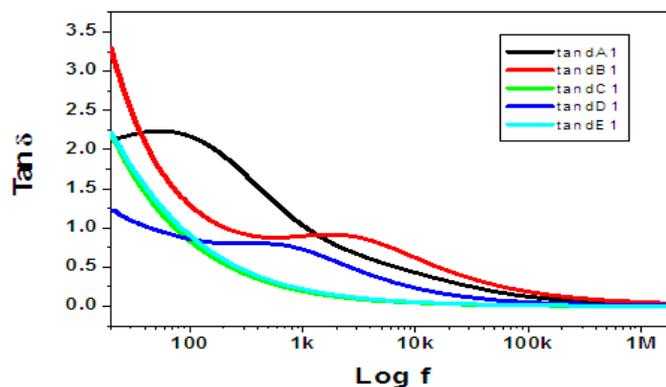


Figure (5): Variation of dielectric loss tangent with frequency

In the high-frequency region, which corresponds to low resistivity (due to grains), small energy is required for electron transfer between the two Fe ions at the octahedral site. Moreover, the dielectric loss factor also depends on a number of factors, such as Stoichiometry,  $\text{Fe}^{2+}$  content, and structural homogeneity, which in turn depend upon the composition and sintering temperature of the sample (21-22). It is possible that in the case of composition  $x=0.0$  to  $0.8$  the hopping frequencies between appropriate magnitude to absorb a loss maximum at 21-25Hz respectively.

### 3.3.3. AC Conductivity:

Conductivity is the physical property of a material which characterizes the conducting power inside the material. The electrical conductivity in ferrites is mainly due to the hopping of electrons between the ions of the same element present in more than one valence state. **Figure.6** shows the variation of the AC conductivity ( $\sigma_{AC}$ ) of  $\text{Ni}_{0.2}\text{Cu}_x\text{Zn}_{0.8-x}\text{Fe}_2\text{O}_4$  ferrites of all compositions as a function of frequency in the range of 20Hz to 2MHz at room temperature.

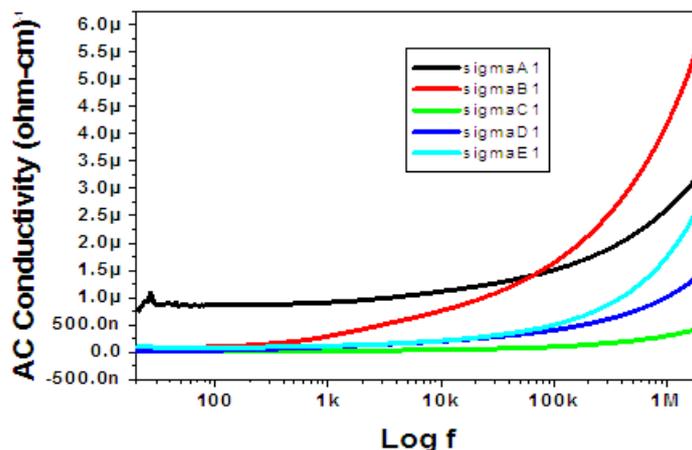


Figure (6): Variation of ac conductivity with frequency.

At low frequency range the AC conductivity was nearly independent of the frequency and showed an increasing trend with increase in frequency for all the samples. This behavior is akin to Maxwell-Wagner type. The dielectric structure of ferrites is given by Koops phenomenological theory and Maxwell-Wagner theory [23-24]. At lower frequencies the conductivity was found low due to the grain boundaries that are more active which acts as hindrance for mobility of charge carriers and hence the hopping of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is less at lower frequencies. As the frequency of applied field is increased, the conductive grains become more active thereby promoting the hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions and also responsible for creating charge carriers from different centers. These charge carriers take part in the conduction phenomenon thereby increasing the AC conductivity. The linear increase in conductivity was observed with frequency that confirms the polaron type of conduction. The frequency dependent conduction is attributed to small polarons [25]. At higher frequency where conductivity increases greatly with frequency, the transport is dominated by contributions from hopping infinite clusters. Finally, low values of conductivity around room temperature indicate that the studied compositions may be good candidates for the microwave applications that require negligible eddy currents [26].

#### IV. Conclusions

- ❖ X-ray diffraction of the pattern of the preparation of prepared samples conforms the formation of single phase cubic spinel structure.
- ❖ Ferrites composition of  $(\text{Ni}_{0.2}\text{Cu}_x\text{Zn}_{0.8-x})\text{Fe}_2\text{O}_4$  with an average crystallite size between 24 to 72 nm were synthesized through citrate Gel-Auto combustion method.
- ❖ The FTIR spectrum exhibited  $V_1$  and  $V_2$  fundamental bands, corresponding to octahedral and tetrahedral sites in the ferrite structure.

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