

Structural and Dielectric Characterization of Ni-Zn Nanoferrite by Sol-Gel Auto combustion Route

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Abstract: The nanoparticles of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (NZF) with stoichiometric proportion 'x' varying for 0, 0.5, 1. were synthesized by sol-gel auto combustion method; the x-ray diffraction analysis confirms that the system exhibits polycrystalline single phase cubic spinel structure. The particle size estimated using scherrer formula and is confirmed by scanning electron microscope (SEM) and transmission electron microscope (TEM). This reveals the formation of nanocrystalline ferrites. The dielectric constant of NZF is found to be less as compare to bulk sample, the migration of Fe^{3+} ion from octahedral site to tetrahedral site decreases the dielectric constant with increases zinc concentration. Conduction occurs due to charge libration and electron hopping this type of mechanism present in this compound.

Keywords: Ferrites, Dielectric constant, Dielectric loss.

I. Introduction

Nickel Zinc ferrites (NZF) play versatile role in the field of microwave devices because of their dielectric and low conductivity property. In nanocrystalline forms ferrites are technologically important materials not only in electric but also in their magnetic field.

Among the various types of spinel ferrite. Ni-Zn ferrite mostly knowing by their magnetic material for general use. Also they have many applications in low and high frequency devices and play a significant role in many technological applications such as microwave devices, power transformer in electronic, rod antenna as read/write heads for high speed digital tape etc[1-4]. Due to their high resistivity, low dielectric losses. Mechanical hardness and low eddy current loss when operating at high frequencies. NZF is a mixed spinel ferrite. Follows the spinel structure with formula.

$[\text{Fe}^{3+}_{1-x} \text{Zn}^{2+}_x]_{\text{tet}} [\text{Ni}^{2+}_{1-x} \text{Fe}^{3+}_{1+x}]_{\text{oct}} \text{O}_4$. $[\text{Fe}^{3+}_{1-x} \text{Zn}^{2+}_x]_{\text{tet}}$ means that the $[\text{Fe}^{3+}_{1-x} \text{Zn}^{2+}_x]_{\text{tet}}$ ions occupy the tetrahedral sites and $[\text{Ni}^{2+}_{1-x} \text{Fe}^{3+}_{1+x}]_{\text{oct}}$ ions occupy the octahedral site of lattice structure. The distribution of the various ions in tetrahedral and octahedral sites is different when the ferrites at different temperature with the particle size in nanometric scale. It is known that physical properties of the ferrites are very sensitive to the method of synthesis. The selection of appropriate method for synthesis is therefore the key to obtain good quality ferrites. For the synthesis of nanosize ferrite various methods have been used. Such as hydrothermal, chemical, coprecipitation sonochemical reaction, mechanical ball milling, sol-gel auto combustion etc. Among all these synthesis method, sol-gel auto combustion seems to be most convenient method because it posses high purity, chemical homogeneity, small and uniform particle size and controlled grain shape of the material. The dielectric behavior of the samples were analyzed and studied[6-10].

II. Experimental

Powder of nickel zinc nanoferrites having the formula $\text{Ni}_{1-x}\text{ZnFe}_2\text{O}_4$, $X=0, 0.5, 1$ were prepared by sol-gel auto combustion method. Using analytical grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as starting materials the stoichiometric proportions of above samples were dissolve in deionised water. The mixture of the solution was heated at 80°C on heating plate of magnetic stirrer until the solution transform in to gel was obtained. The gel of the solution which were ignited and burnt in microwave oven 600 watt on 7 min to obtain ash powder of NZF. the powder formed was heated slowly up to 800°C in a furnace for 4 hours after intermediate grinding in pistal mortar. the powder formed of the samples were pressed in to circular disc shaped pellets. Silver paste coating was done on the surface of the pellets to make the parallel plate capacitor geometry with ferrite material as the dielectric medium.

XRD measurements of the samples were carried out by using Bruker AXE D8 advanced diffractometer with $\text{Cu-K}\alpha$ radiation at room temperature. TEM analysis is done using high resolution transmission

Where ‘C’ is the capacitance of the sample measured in farad. ‘D’ thickness of the pallet and ‘A’ be the flat surface area of pellet and ‘ ϵ_0 ’ is the constant of permittivity of free space and its value $\epsilon_0=8.854 \times 10^{-12}$ F/m. Dielectric loss is calculated using the relation $\tan\delta=D$ factor.

III. RESULTS AND DISCUSSION

The XRD pattern of the $Ni_{1-x}Zn_xFe_2O_4$ (with $x=0,0.5, 1$) it shows that the formation of single phase simple cubic structure of all the samples. The interplaner distances of two lattice point are calculated using Bragg’s diffraction law. The broad X-ray diffraction line indicates that the ferrite particles are in nanosize range. The crystalline size for all the samples has been calculated from the broadening line at high intensity peak corresponding (311) planes. which denote the spinel phase appearing at 34.89° & 35.12° The crystalline size were calculated for ($Ni_xZn_{1-x}Fe_2O_4$ with $X = 0.5,1$) using high intensity (311) peaks.

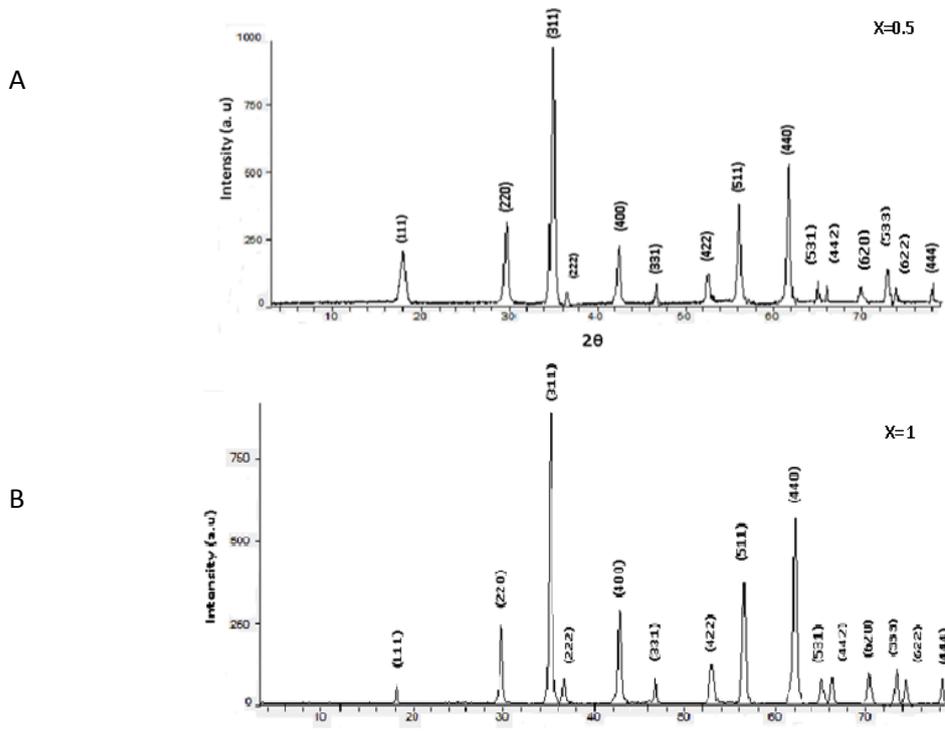


Fig.1. A & B) show 2θ pattern and brooding of high intensity peak for the system $Ni_{1-x}Zn_xFe_2O_4$, $x = 0.5, 1$.

Using Debye Scherrer formula

$$i.e. \quad D = 0.9\lambda/\beta\cos\theta \quad \text{-----}(2)$$

Where ‘ λ ’ is the X-ray wavelength(0.15418nm for Cu-K α , ‘ β ’ is full width of half maximum,’ θ ’ is the Bragg angle of the high peak (311) plane.

The values of particle size, lattice parameter, bulk density ‘ ρ_m ’ and the X-ray density. ‘ ρ_x ’ and porosity from X-ray data are given by table

Table 1.1.

sample	X-ray Density ρ_x (g/cm ³)	Bulk Density ρ_m (g/cm ³)	Porosity (p %)	Particle I size 'D'
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	5.1092	3.1412	38.51	21nm
$NiFe_2O_4$	5.1302	3.0687	38.18	22nm

And 'h' is the height of the sample.

The X-ray density of the prepared sample is calculated by the relation

$$\rho_x = 8M/Na^3 \quad \text{----- (4)}$$

Where 'M' is mol. weight of the sample.

'N' is the Avogadro's number (6.63×10^{-23})

'a' is lattice constant.

Porosity of the samples calculated by the formula

$$P\% = (1 - \rho_m / \rho_x) \quad \text{----- (5)}$$

Where, ρ_m is bulk density and

ρ_x is x-ray density

The lattice parameter for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and $NiFe_2O_4$ are found to be 8.5194 \AA and 8.4676 \AA this value which is nearly equal to JCPDS card no.520278. It is found that the lattice parameter decreases with increasing the Zn concentration of cations because the ionic radius of Ni^{2+} ions (0.69 \AA) is small than the ionic radius of Zn^{2+} cation (0.82 \AA) and hence the replacement of Ni by Zn in NZF causes a decrease in lattice constant obeying Vegards law. Hence the partial size in nano dimensions there is a change in cation distribution.

Transmission Electron Microscopy Analysis:

The particle size and morphology of $Ni_{1-x}Zn_xFe_2O_4$ with $x=0.5, 1$ is shown in the fig.2

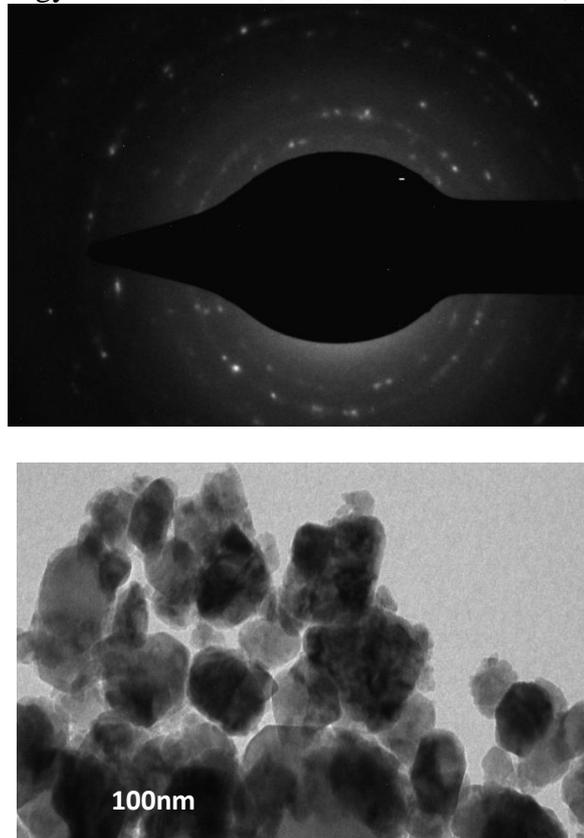


Fig.2 A typical TEM image of the as prepared $Ni_{1-x}Zn_xFe_2O_4$, $x=0.5, 1$

From the fig.2. We observed that circular diffraction ring are clearly visible indicating the nature of the sample is nanocrystalline and the average particle size is about 28nm. TEM analyzed revealed the particles are nearly spherical, the average size of the particle determine from TEM was found to be in close agreement with that obtained from XRD studied.

IV. DIELECTRIC PROPERTIES

The dielectric constant of the NZF samples has been studied for frequencies 100 Hz to 100 MHz Elhiti *et al.*[26] it is observed that the dielectric constant of the sample NZF decreases rapidly up to 5KHz and is nearly constant above this frequency as shown in the figure.3.

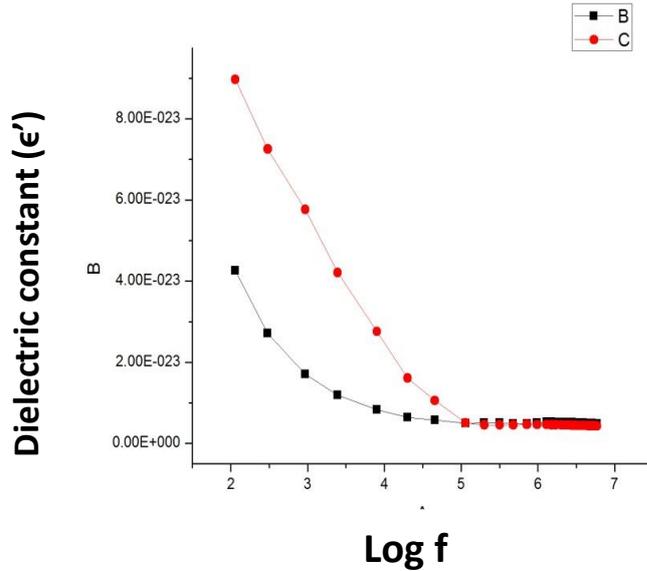


Fig.3.Variation of the dielectric constant with frequency of $Ni_{1-x}Zn_xFe_2O_4$ with $x=0.5, 1$ at room temperature.

It can be seen from the fig.3. That dielectric constant (ϵ') decreases with increasing frequency at room temperature. Even at different temperature. [28]

The dispersion of the dielectric constant can be observed even at lower frequency region is due to Maxwell-Wagner[28] this can be explained on the basis of hopping mechanism between Fe^{3+} and Fe^{2+} , Ni^{2+} and Ni^{3+} pair of ions. It is well known that ferrites with heterogeneous structure of the samples consist of well conducting grains separated by poorly conducting grains boundaries [16].the electron reach the grain boundary through hopping and if the resistance of the grain boundary is high enough electrons pile up at the grain boundaries and produce polarization.

However As the applied frequency increases slightly we observed that the electrons reverse their direction of motion more often due to this the probability of electron decreases to reach the grain boundary and as a result polarization decreases. Therefore the dielectric constant decreases with increasing frequency of the applied field. The variation of the dielectric constant with frequency 100Hz. it is clear that dielectric constant increases with increasing temperature at constant frequency even at different frequency.

The increase the value of dielectric constant with an increase in temperature is very large at lower frequency 100Hz. As shown fig.4.

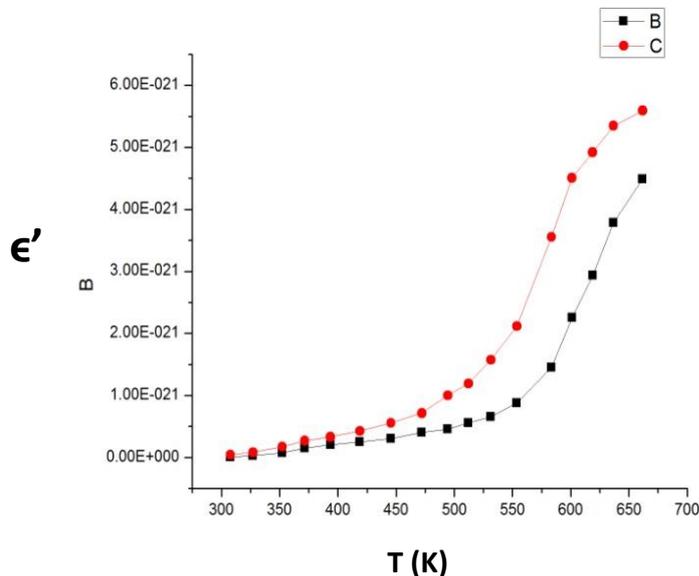


Fig.4. dielectric constant versus temperature curve at constant frequency for the sample $Ni_{1-x}Zn_xFe_2O_4$ with $X=0.5,1$

Therefore a dielectric constant increase with increasing temperature at lower frequency is observed. As shown in fig.4.

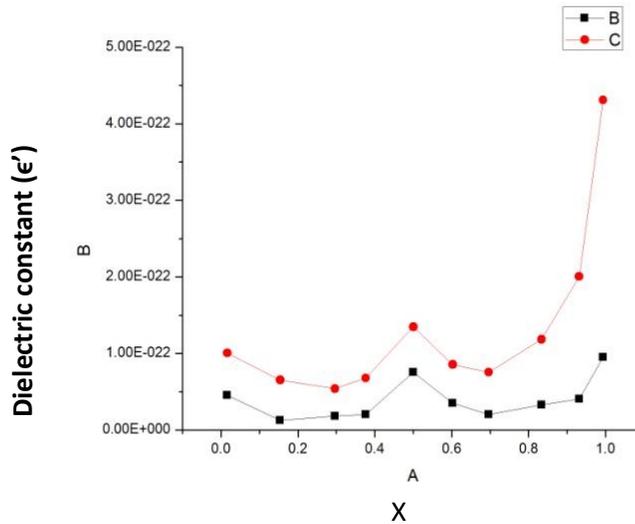


Fig.5. variation of the dielectric constant with composition of 1MHz at different temperature.

The variation of dielectric constant with X=0.5, 1 at which it has maximum value. Maxima is observed at room temperature for Zn composition X=0.5.

In Ni-Zn ferrites Zn occupies (A) sites and Ni occupies [B] sites while Fe occupies both (A) and [B] site. When Zn²⁺ is added in place of Ni²⁺ with increasing Zn composition X=0.5 some of the Fe³⁺ ions get converted in to Fe²⁺ ions so as to maintain the charge neutrality.

By addition of Zn concentration Ni converts Fe³⁺ to Fe²⁺ ions. This hopping mechanism between Fe³⁺ and Fe²⁺ ions thereby decreasing the resistance of the grain.

Hence Hopping mechanism increases the probability of electron reaching to the grain boundaries due to this polarization and dielectric constant increases which is observed for composition 0.5,1.

For further increase in composition of Zn. dielectric constant may be decreases due to less hopping mechanism between Fe³⁺ and Fe²⁺ ion [11-18].as shown in fig.5.

Variation of the dielectric loss (ε'') & tangent (tan δ):

Fig.6. shows the variation of dielectric loss (ε'') with frequency at room temperature as shown in fig.6. For x=0.5, 1

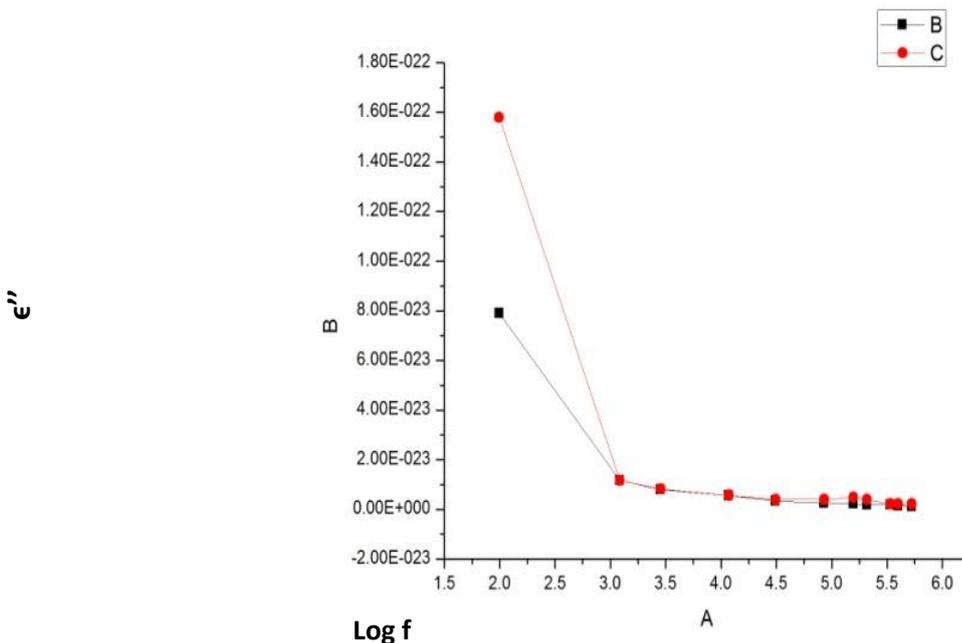


Fig.6.Variation of dielectric loss (ε'') with frequency of Ni_{1-x}Zn_xFe₂O₄ with X=0.5, 1 at constant room temperature

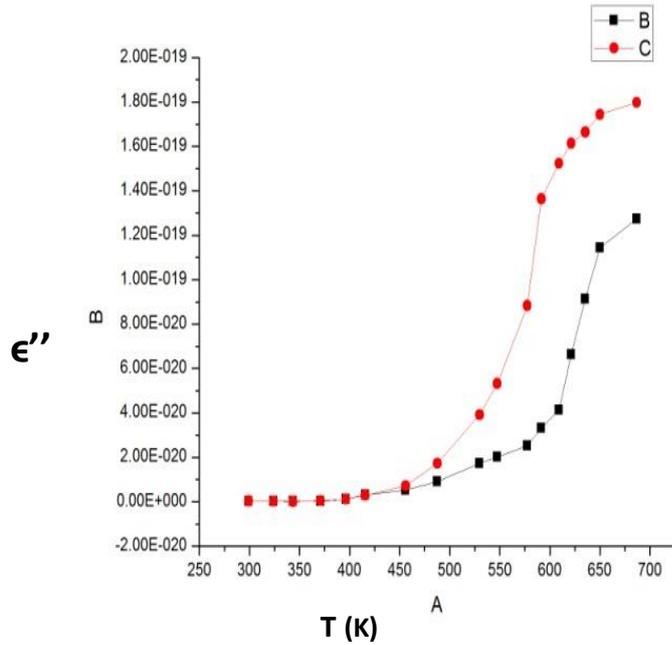


Fig.7. Variation of the dielectric loss (ϵ'') with constant frequency 100Hz for different temperature.

Variation of dielectric loss increases with increasing temperature at constant frequency 100Hz for the composition $X=0.5,1$ is as shown in fig.7. The dielectric loss decreases due to jumping frequency of electric charge carrier cannot follow the reverse when an external alternating field of the same frequency is applied beyond critical frequency. This type of variation observed for all the Compositions $X=0.5,1$ of system $Ni_{1-x}Zn_xFe_2O_4$ were studied [19-20]. Also the loss tangent increases with increases temperature with constant frequency for $X=0.5, 1$ shows identical behavior as shown in fig.8.

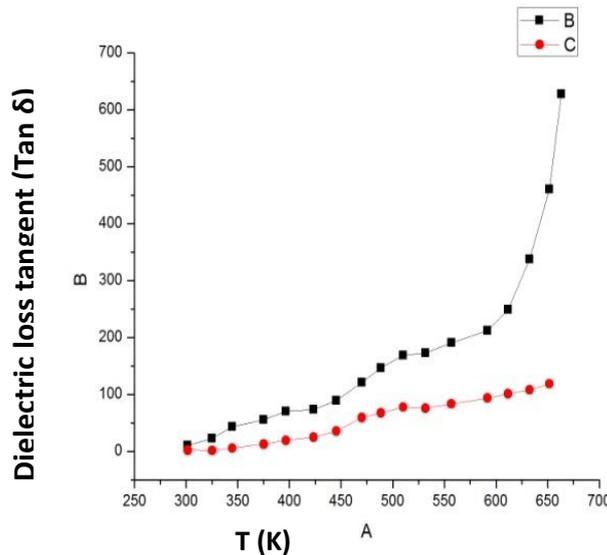


Fig.8. Variation of $\tan\delta$ with temperature of $Ni_{1-x}Zn_xFe_2O_4$ with $X=0.5,1$. at constant frequency.

According to Iwachi [21] there is observed strong correlation between the conduction mechanism and dielectric behavior of ferrites. Maximum value of dielectric loss tangent ($\tan\delta$) can be observed on the condition of the dielectric material which is given by

$$\omega\tau = 1 \text{-----(6)}$$

Where, $\omega=2\pi f_{\max}$ and ' τ ' is the relaxation time. Now, the τ relaxation time is related to the jumping probability per unit time p by the equation

$$\tau = p/2$$

Or $f_{\max} \propto p$ ----- (7)

Above equation (6) shows that f_{\max} is proportional to the jumping or hopping probability.

Now f_{\max} increases with increasing zinc content indicates that the hopping or jumping probability per

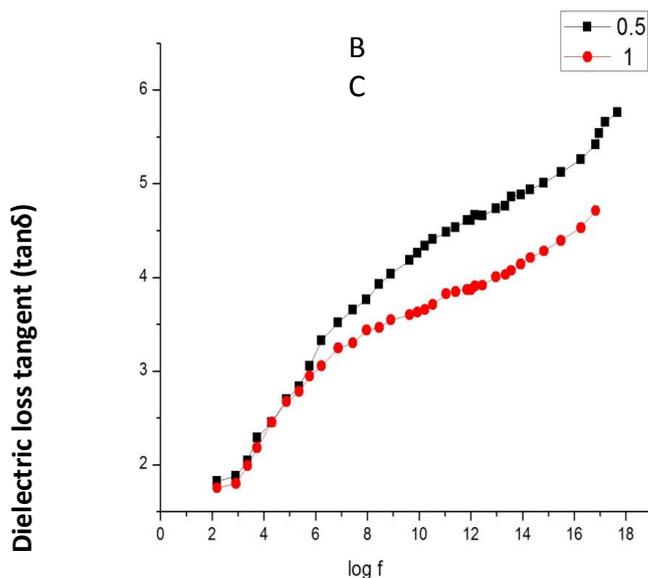


Fig.9.Variation of $\tan\delta$ with frequency of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $X=0.5,1$.at constant temperature.

The variation of dielectric loss tangent ($\tan\delta$) with frequency is shown in fig.9.the dielectric loss tangent ($\tan\delta$) increases with increasing frequency for the composition $X=0.5,1$ this type of nature was observed in case of other ferrite[21-25].

V. CONCLUSION

The Ni-Zn nanoferrite powder are prepared by sol-gel auto-combustion method. The formation of simple cubic spinel structure investigated by XRD studies. the particle size of the samples are found to be 21nm and 22nm by Scherer formula. Which is in close agreement with TEM result? And the X-ray density increases with increasing zinc content and Porosity decreases with increasing zinc content. The dielectric constant (ϵ') and dielectric loss (ϵ'') of the prepared NZF decreases with increasing frequency and increases with increasing temperature. we concluded that the dielectric constant increases up to 0.5 and decreases with further concentration of Zn concentration. And the dielectric loss tangent ($\tan\delta$) increases with increasing temperature and frequency.

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