Dielectric Properties of Co-Substituted Li-Ni-Zn Nanostructured Ferrites Prepared Through Chemical Route

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ABSTRACT
Mixed Co-Li-Ni-Zn ferrites having the general formula $Li_{0.5}Ni_{0.25-x/2}Co_{x/2}Zn_{0.5}Fe_2O_4$ (where x=0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared using auto combustion method. X-ray analysis reveals the polycrystalline nature of the samples. The lattice parameter and particle size increase with increase in Co content. The dielectric parameters were measured at room temperature in the frequency range 20Hz – 1MHz using a HP 4284 impedance analyzer. Plots of dielectric constant (έ) vs frequency show normal dielectric behavior of spinel ferrites. The frequency dependence of dielectric loss tangent (tan δ) is found to display a peak at certain frequency. The composition and freqency dependence of the dielectric constant and dielectric loss tangent is explained in terms of ferrous ion concentration. The low dielectric constant makes these ferrite materials useful in high frequency applications.

Keywords: Co-Li-Ni-Zn ferrites; chemical method; nanoparticles; dielectric constant; dielectric loss tangent.

1. INTRODUCTION
Spinel ferrites is an important class of electrical materials because of their high resistivity and low loss behavior, and hence vast technological applications over a wide range of frequencies. Ferrites are preferred in the field of electronics and telecommunication industry because of their novel electrical properties which make them useful in radiofrequency circuits, high quality factors, rod antennas, transformer core, read/write heads for high density digital tapes and other devices. Hence it is important to study their dielectric behavior at different frequencies.

The dielectric properties of ferrites are dependent on several factors, such as method of preparation, heat treatment, sintering conditions chemical composition, cation distribution and crystallite size[1-2]. During the last few years nanoscale spinel ferrites have drawn a major attention because of their technological applications in magnetic recording, magnetic fluids and catalyst. In nanocrstalline materials the physical properties are predominantly controlled by the grain boundaries than by the grains.

Polycrystalline ferrites are very good dielectric materials. The study of dielectric properties offers valuable information about the behavior of localized electric charge carriers and can explain the mechanism of electrical conduction and dielectric polarization. The substitution of small amount of magnetic or non-magnetic ions brings an important modification in the structural and transport properties of these materials.

Nanoferrites are usually prepared using various physical and chemical methods. The dielectric properties of nanosize nickel ferrites can be varied by addition of small traces of cobalt, manganese and copper, and also by deviation from stoichiometry.

Cobalt ferrite based nanomaterials are known to be the good candidates for magneto optical recording and high density storage [3-4] the present communication reports experimental results of dielectric properties of nanocrystalline ferrites $Li_{0.5}Ni_{0.25-x/2}\ Co_{x/2}\ Zn_{0.5}\ Fe_2O_4$

2. EXPERIMENTAL

2.1 Synthesis
Mixed Co-Li-Ni-Zn ferrites having the general formula $Li_{0.5}Ni_{0.25-x/2}\ Co_{x/2}\ Zn_{0.5}\ Fe_2O_4$ (Where x=0,0.1,0.2,0.3,0.4 and 0.5) were prepared using auto combustion method[6]. The powder was pre-sintered at 400^0C for 6 h and cooled slowly to room temperature. The pre-sintered samples were ground and pressed into disk shaped pellets of 10 mm diameter. A small quantity of polyvinyl alcohol was added to the powder as a binder. The samples were sintered again at 600^0C for 6h and slowly allowed to cool naturally.

2.2 X-ray diffraction studies
For the confirmation of spinel phase formation XRD studies were carried out using the XRD machine (Model Philips PW 3710) and CuKα radiation (λ=1.5418 Å).The average particle size was determined by using Scherrer formula assuming all the particles to be in spherical in shape [7].

$$t=0.9\lambda/\beta\cos\theta \qquad (1)$$

where t is the crystallite size, β is the line width at half maximum, λ the X-ray wavelength and θ is the Bragg angle.

The x-ray density of all prepared nanoparticles was calculated using the relation

$$dx= 8M/Na^3 \quad gm/cm^3 \qquad (2)$$

Where M is molecular weight, N the Avogadro's number and 'a' the lattice parameter.

2.3 Dielectric measurements
The dielectric measurements were carried out at room temperature using LCR Meter (Hewlett Packard 4284) over the frequency range 20 Hz to 1 MHz. The values of capacitance (C) and loss tangent (tan δ) were noted directly at different frequencies. The dielectric constnt (έ) was calculated using the relations

$$\acute{\varepsilon} = c \times t/\varepsilon_o A \qquad (3)$$

where c is the capacitance of the sample, t the thickness, A the surface area and ε_o the permittivity of free space.

The imaginary part of dielectric constant (ε') was calculated using the relation

$$\varepsilon' = \varepsilon \tan \delta \quad (4)$$

where tan δ is dielectric loss

Dielectric loss tangent was calculated using the relation

$$\tan \delta = \varepsilon' / \varepsilon \quad (5)$$

From dielectric constant and dielectric loss, the ac conductivity σ_{ac}, of the ferrite samples can be calculated using the relation,

$$\sigma_{ac} = \omega \varepsilon \varepsilon_o \tan \delta \quad (6)$$

where ω is the angular frequency. σ_{ac} is temperature and frequency dependent and it is attributed to the dielectric relaxation caused by the localized electric charge carriers which obeys the power law,

$$\sigma ac (\omega T) = B \omega^{n} \quad (7)$$

where B and n are composition and temperature dependent parameters.

3. RESULTS AND DISCUSSION

3.1 X-ray analysis

The X-ray diffraction patterns of the samples are shown in Fig. 1. Analysis of x-ray diffraction patterns reveals that all the samples have a single-phase cubic spinel structure. The compositional variation of lattice parameter and particle size is given in Table-1. It can be observed that the particle size and lattice parameter increase with increasing Co concentration in the sample. In the present case Co^{2+} ion is bigger in radius (0.079 nm) as compared to the Ni^{2+} ion (0.069nm). Substitution of Co^{2+} ions results in an increase in lattice parameter. Similar results were reported earlier [8].The variation of lattice parameter with cobalt content is shown in Fig.2. The x-ray density goes on decreasing with Co content, and which is attributed to the increase in lattice constant and particle size.

3.2 Composition dependence of dielectric behavior

Fig. 3 shows the variation of real and imaginary parts of dielectric constant, dielectric loss tangent and ac conductivity with Co content at 10 KHz. It is seen that all the parameters decrease with Co^{2+} ion concentration up to x=0.2 and thereafter, they increases with further addition of cobalt. The specimen with x=0 exhibits highest value of dielectric constant. This high value can be explained on the basis of the fact that the sample has maximum number of ferrous ions which take part in the phenomenon of exchange (Fe^{2+}« »Fe^{3+}) giving rise to maximum dielectric polarization.

It is also pertinent to mention that the variation of ac electrical conductivity with composition parallels the variation of ferrous ion concentrations. Thus, it is the number of ferrous ions on octahedral sites that play a dominant role in the process of conduction as well as dielectric polarization.

Table 2 shows the compositional dependence of dielectric data for mixed Co-Li-Ni-Zn ferrites at room temperature for 10 KHz frequency.

Similar studies have also been carried out earlier e.g Ti-Ni-Zn ferrites [9-10], mixed Ni-Zn ferrite [11], Er-Mn-Zn ferrites [12], Ni-Cu-Mg-Zn ferrite [13]. Al-Co ferrites [14], Li-Mg-Zn ferrites [15].

3.3 Frequency dependence of dielectric constant

Fig. 4 displays the variation of dielectric constant (ε) as a function of frequency at room temperature. Samples having high d.c electrical resistivity acquire low value of dielectric constant and vice versa [16-17]. Generally, dielectric constant decreases with increasing frequency. The decrease of dielectric constant with Co ion substitution can be explained on the basis of the mechanism of polarization process in ferrites, which is similar to that in the conduction process.

A strong correlation between conduction mechanism and dielectric behavior of ferrites has been reported. The whole polarization in ferrites is mainly contributed by the space charge polarization, which is governed by the number of space charge carriers and the conductivity in materials [18] and the hopping exchange of the charges between two localized states and the resultant displacement of the charges with respect to the external field. The addition of cobalt ions reduces the iron ions on B- sites, which is mainly responsible for both space charge polarization and hopping exchange between the localized states. Therefore, increase of Co content causes a decrease in polarization which is accomplished by a decrease of dielectric constant, ε', of the composition. Koops[19] has proposed that the effect of grain boundaries is predominant at lower frequencies. The thinner the grain boundary, the higher the dielectric constant. The decrease in dielectric constant with increasing frequency is attributed to the fact that the electron exchange between Fe^{2+} and Fe^{3+} ions cannot follow the change of the external applied field beyond certain frequency [9]. The value of the dielectric constant is very high at lower frequencies and decreases with increasing frequencies. At lower frequencies the grain boundaries are more effective than grain electrical conduction. Similar low values of dielectric constant were found in Mn substituted Ni-Zn ferrites prepared by citrate method and Cd,Cr substituted Co ferrites.

3.4 Dielectric loss factor

The dielectric loss factor is considered to be the most important part of the total core loss in ferrites [20]. Variation of ε' with frequency is shown in Fig. 5. The pattern of variation is seen to be similar to that of dielectric constant. The decrease in imaginary part of dielectric constant is pronounced more in comparison to real dielectric constant. The low dielectric values make these ferrites useful in higher frequency applications.

3.5 Variation of dielectric loss tangent (tan δ) with frequency

Fig. 6 shows variation of tan δ with frequency of present ferrites. The abnormal behavior is observed for the samples at lower frequencies. According to Rezlescu the observed relaxation peak may be due to the collective contribution of both p and n type carriers. The conduction mechanism in n-type ferrite is considered to be due to hopping of electrons between Fe^{2+} and Fe^{3+} and hole transfer between Co^{2+} and

Co^{3+} in octahedral sites. When the hopping frequency is nearly equal to the frequency of externally applied electric field, a maximum of loss tangent is observed. The decrease of tan δ with increasing frequency is attributed to the fact that the hopping frequency of charge carriers cannot follow the changes of the externally applied electric field beyond a certain frequency limit [21-22].

The condition for observing a maximum in dielectric losses of dielectric material is given by,

$$\omega\tau = 1 \qquad (8)$$

Where ω is the $2\pi f_{max}$ and τ is the relaxation time.

The relaxation time τ is related to jumping probability per unit time P, by the relation

$$\tau = \tfrac{1}{2} P \quad \text{or}$$

$$f_{max} \alpha P \qquad (9)$$

Above equation shows that f_{max} is proportional to the jumping or hopping probability. An increase of f_{max} with increasing Co content indicates that the hopping or jumping probability per unit time increases with cobalt content.

4. CONCLUSIONS

1. Mixed Co-Li-Ni-Zn ferrites were prepared by auto-combustion method.
2. The lattice constant and particle size increase with increase in Co content due to large ionic radius of Co^{2+} ions than Ni^{2+} ions.
3. Dielectric constant and loss decreases rapidly with increasing frequency. All the substituted samples have low dielectric constant than the basic composition without cobalt. The ac conductivity has been discussed in the light of ferrous ion concentration.
4. The electrical resistivity of ferrite decreases exponentially with temperature exhibiting the semiconducting behavior. Because of their high resistivity they have low eddy current losses.

5. ACKNOWLEDGEMENT

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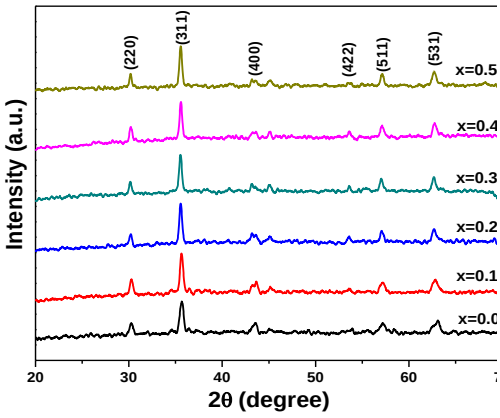

Fig. 1: X-ray diffraction patterns of -$Li_{0.5}Ni_{0.25-x/2}$ $Co_{x/2}$ $Zn_{0.5}$ Fe_2O_4 ferrite samples

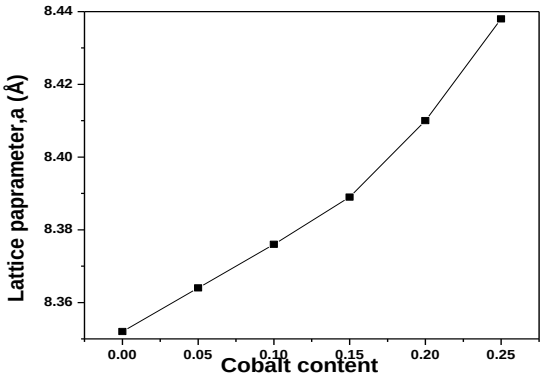

Fig.2: Variation of lattice parameter with cobalt content

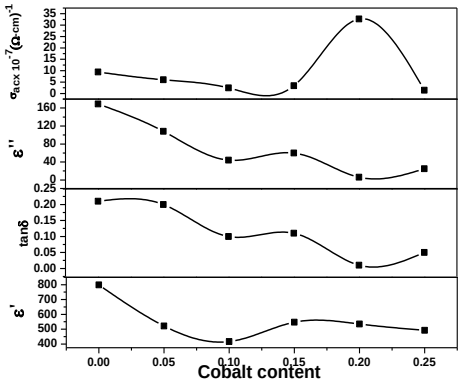

Fig. 3: Variation of dielectric parameters έ, έ',tan δ , σac with composition at 10 KHz

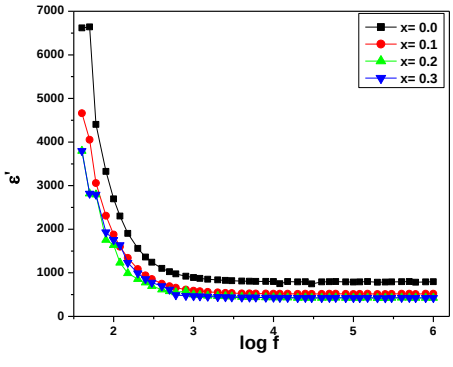

Fig. 4: Variation of dielectric constant with frequency

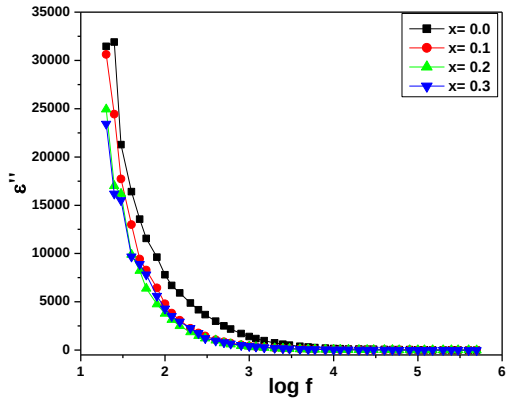

Fig.5: variation of dielectric loss factor with frequency

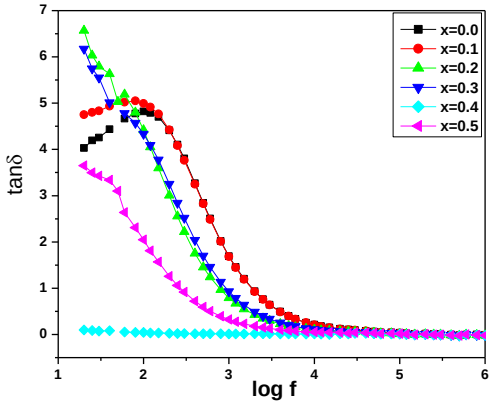

Fig. 6: Variation of dielectric loss tangent with frequency

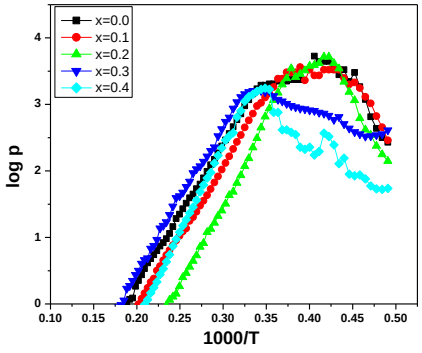

Fig.7: variation of dc resistivity with temperature

Table 1: Data on cobalt content, lattice parameters, particle size and x-ray density of $Li0.5Ni0.25_{-x/2}$ $Co_{x/2}$ $Zn_{0.5}$ Fe_2O_4 ferrite samples

Sample	Cobalt Content	at 10 KHz		
		έ	tan δ	έ’
x= 0	0.00	799	0.21	169
x=0.1	0.05	521	0.2	108
x=0.2	0.10	416	0.10	44
x=0.3	0.15	547	0.11	60
x=0.4	0.20	535	0.01	6
x=0.5	0.25	492	0.05	25

Table 2: Compositional dependence of dielectric parameters data of mixed Co-Li-Ni-Zn ferrites at 10 KHz

Sample	Co content	Lattice parameter a (Ǻ)	Particle size t,nm	density x-ray gm/cc
x= 0	0.00	8.352	17	5.167
x=0.1	0.05	8.364	21	5.145
x=0.2	0.10	8.376	23	5.123
x=0.3	0.15	8.389	24	5.100
x=0.4	0.20	8.410	24	5.035
x=0.5	0.25	8.438	23	5.018