

# Effect on the B-H loop and complex permeability with nickel substitution on Li-Zn ferrite synthesized by the citrate precursor method

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**Abstract.**  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$  ferrites where  $0.02 \leq x \leq 0.1$  in steps of 0.02 have been synthesized by citrate precursor method. The samples were given final sintering at 1040°C after a pre-firing at a temperature of 650°C. Various characterizations using  $T_C$  set up, BH loop tracer were carried out on the sintered samples. The X-ray diffraction pattern confirmed the formation of spinel phase. Magnetic properties such as Curie temperature using  $T_C$  set up, BH loop parameter and complex permeability using BH loop tracer were studied. Experimental results show that the Curie temperature, saturation magnetization and initial permeability decreases with the increase in the  $\text{Ni}^{2+}$  concentration. The complex permeability measured as a function of frequency in the range of 20Hz-2MHz show dispersion. Possible mechanism contributing to the above process is being discussed.

## 1. Introduction

Ferrites had been studied by many workers because of the varied technological application. They are found to be used from microwave to radio frequency ranges, due to their characteristic magnetic properties [1-2]. The magnetic properties of ferrites depend upon various factors like the type of substitutions, synthesis method and the sintering temperature. Substituents play an important role in modifying the properties of basic lithium ferrites and various workers reported that Ni substitution enhances the densification which results in change in the magnetic properties [3-5]. Considering the synthesis method the chemical method known as the citrate precursor method gives samples at low temperature with high purity. However, the densification is less. On the other hand it is learnt that in magnetic applications, a high sintered density, high purity with lesser pores is in demand while fabricating a ceramic material. Therefore a double sintering process is subjected further which is expected to give more densification in addition to the effect of Ni substitution and hence a change in their various properties like Curie temp., BH loop properties complex permeability, dielectric constant, resistivity etc. The study of high curie temperature, high magnetization, permeability gives valuable information regarding the domain response paving way to technical application like microwave device, memory core application etc. Useful frequency range of ferrite is limited by the onset of resonance phenomena for which either the permeability begins to fall at a critical frequency or the losses rise sharply. Hence knowledge of frequency dependence of permeability and permeability loss is also necessary.



In the present work citrate precursor method has been used to prepare LiZnNi ferrite. The sample was further given double sintering and investigation is being carried out on the magnetic properties such as Curie temperature, BH loop parameter, complex permeability etc.

## 2. Experiment

### 2.1. Material synthesis

Nickel substituted lithium zinc ferrites with compositional formula  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$  where  $x=0.02 \leq x \leq 0.1$  in steps of 0.02 were prepared by the citrate precursor method. The starting chemicals used were lithium nitrate  $\text{LiNO}_3$  (Merck Germany), zinc nitrate hexahydrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck India), iron (III). $6\text{H}_2\text{O}$  nitrate nonahydrates  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck India), nickel(II) nitrate hexahydrate  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck India) and citric acid monohydrates  $\text{C}_6\text{H}_8\text{O}_7$ . Stoichiometric amount of lithium nitrate, zinc nitrate, iron nitrate, nickel nitrate and citric acid. were mixed to make a solution. The ratio of metal cations to citric acid is 1:1. The solution was mixed homogenously with the help of a magnetic stirrer using a magnetic agitator and the value of  $P_H$  was controlled at 7. The  $P_H$  controlled solution was refluxed at  $40^\circ\text{C}$  with continuous stirring for half an hour. It was then heated at  $100^\circ\text{C}$  to form a gel. Finally the dried gel ignite, undergoing a strong auto combustion process giving rise to the ash-synthesized product which is the typical spinel structured LiZnNi ferrite powder. These powder were mixed with polyvinyl alcohol as binder and pressed into torroids with 50 kilo Newton pressure. Final sintering was given to the pressed torropids at  $1040^\circ\text{C}$  after pre sintering at  $650^\circ\text{C}$ .

### 2.2. Characterizations

The phase identification of the sintered samples were performed using X-ray diffractometer (Phillips) with  $\text{CuK}_\alpha$  radiation ( $\lambda=1.5405 \text{ \AA}$ ). Curie temperature was measured using Soohoo's method [6]. Saturation magnetization, and coercivity was determined from BH hysteresis loops measured using BH loop tracer (Ferrites India). Complex initial permeability as a function of composition and frequency (20Hz- 2MHz) were carried out. Inductance (L) and the corresponding loss factor  $\tan\delta$  of the sintered toroids were measured in the frequency range of 20Hz – 2MHz using a precision LCR meter E4980A. The measured inductance was used to calculate the initial permeability  $\mu_i = L/L_o$  where L is the measured inductance and  $L_o$  is the air core inductance calculated using the relation,

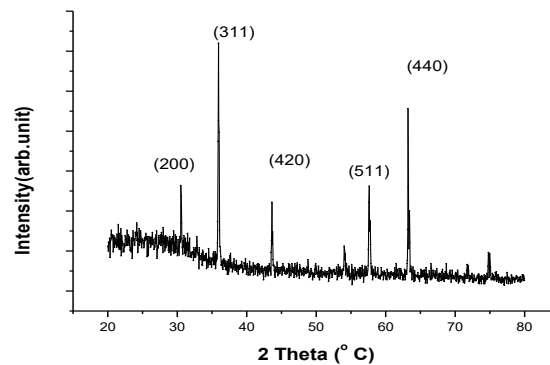
$$\mu_i' = \frac{L}{4.6N^2 \times 10^{-9} \frac{OD}{ID} \times h \times 10^{-3}} \quad (1)$$

where N is the number of turns of the coil ( $N=70$ ), h is the thickness, OD is the outer diameter and ID is the inner diameter of the toroidal specimen.

## 3. Results and discussion

XRD pattern was used to confirm the spinel phase structure of the  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$  ferrite sample (figure. 1,  $x=0.08$ ). The diffraction pattern shows peak which corresponds to the lattice plane of (220), (311), (420), (422), (511), (440) spinel structure of LiZnNi ferrite. All the peaks could be indexed to the standard pattern reported by the Joint Committee on Powder Diffraction Standards (JCPDS). There is no extra peak observed showing that there is no impurity present.

Magnetic studies such as Curie temperature, saturation magnetization, retentivity coercivity and complex permeability was carried out. Soohoo's method was used to determine the Curie temperature [6]. The variation of the Curie temperature ( $T_C$ ) with Ni concentration, show a decreasing trend (table 1).



**Figure 1.** XRD pattern for  $x=0.08$  of  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$ .

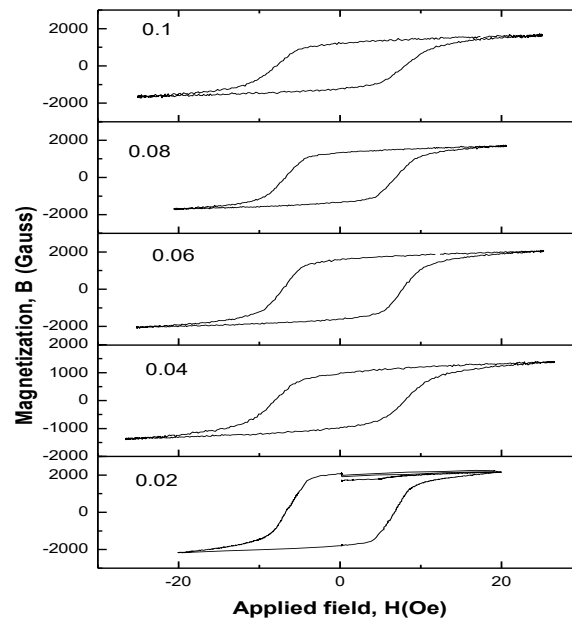
**Table 1.** Curie temp. B-H loop parameters and initial permeability of  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$

Conc.(x)	Curie temp. (°C)	Sat. mag. (Gs)	Retentivity (Gs)	Coercivity (Oe)	Initial permeability
0.02(0.78%)	560	2162	1927	6.852	4.1
0.04(1.55%)	551	1160	842	7.420	3.8
0.06(2.32%)	543	1915	1571	7.112	3.7
0.08(3.09%)	530	1751	1466	6.824	2.7
0.1(3.85%)	527	1544	1155	7.917	2.2

This can be understood in terms of the magnetic super exchange interaction proposed by Neel which has a direct relation with the Curie temperature. According to this model the intersublattice AB super exchange interaction dominates over the intrasublattice AA and BB superexchange interactions. The strength of this A-B interaction is determined by the number of linkages  $\text{Fe}_A^{3+} - \text{O}^{2-} - \text{Fe}_B^{3+}$  per formula unit and the overall strength of this linkage determines the Curie temperature of the ferrite samples [7]. For the present series of ferrites the cationic expression is expressed as  $(\text{Zn}_{0.2}\text{Fe}_{0.8})[\text{Li}_{0.4-0.5x}\text{Ni}_x\text{Fe}_{1.6-0.5x}]\text{O}_4$ . The magnetic  $\text{Fe}^{3+}$  ions are being replaced by less magnetic  $\text{Ni}^{2+}$  ions and hence with progressive substitution of  $\text{Ni}^{2+}$  ion the number of active  $\text{Fe}_A^{3+} - \text{O}^{2-} - \text{Fe}_B^{3+}$  linkage decreases, thereby weakening the AB superexchange interaction. Hence the thermal energy required to offset the spin alignment decreases leading to decrease in the Curie temperature as was observed [7-8].

Figure 2 shows the BH hysteresis loop and table 1 gives the hysteresis loop parameter such as saturation magnetization, retentivity, coercivity of the samples. Experimental result shows a decrease in the saturation magnetization with the increases in  $\text{Ni}^{2+}$  concentration. These variation can be explained by considering the Neel's molecular field model and the cationic distribution as has been discussed earlier. According to Neels model AB superexchange interaction having the most favourable A-O-B angle of about  $125^\circ$  dominates over intrasublattice AA and BB interaction. Therefore the net magnetization is given by the vector sum of the magnetization of the two sublattices  $\mathbf{M}_A$  and  $\mathbf{M}_B$ . In the present ferrite samples  $\text{Ni}^{2+}$  ions have strong preference for the B site and  $\text{Fe}^{3+}$  ions partially occupy the A and B sites. The resultant magnetization,  $M$  is the difference of the magnetizations  $\mathbf{M}_B$  and  $\mathbf{M}_A$  of the B and A sublattices respectively. The cation distribution can be written as  $(\text{Zn}_{0.2}\text{Fe}_{0.8})_A[\text{Li}_{0.4-0.5x}\text{Fe}_{1.6-0.5x}\text{Ni}_x]_B\text{O}_4$  where parenthesis and square bracket represent tetrahedral (A) and

octahedral(B) sites respectively. As  $\text{Li}^{1+}$  and  $\text{Zn}^{2+}$  is non-magnetic it doesn't contribute so,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  only gives effect on net magnetisation. The magnetic moment of  $\text{Ni}^{2+}$  is  $2\mu_B$  and that of  $\text{Fe}^{3+}$  is  $5\mu_B$ , therefore, the net magnetisation becomes  $(8-2.5x+2)-4 = 6-2.5x$  [3,17-18]. Consequently,  $M_s$  values will decrease and was observed experimentally. However the drastic decrease for  $\text{Ni}=0.04$  needs investigation as saturation magnetization depend on several parameters.



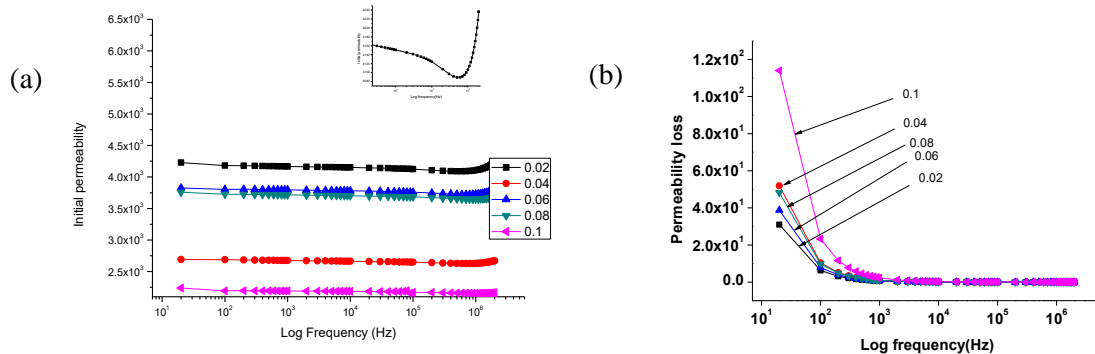
**Figure 2.** B-H loop for  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$ .

The variation of the value of retentivity with increasing Ni concentration also decreases which can be explained in relation to grain size which is known to be inversely proportional to retentivity. It was reported in our earlier work for single sintered LiZn Ni ferrite samples that Ni substitution increases the grain size. [10]. However properties of hysteresis parameters are dependent on the various microstructural properties like grain size, porosity, nature of pores etc. which are largely controlled by sintering process. Hence it is difficult to attribute to a single factor and a detail investigation is required.

Investigation on the variation of initial permeability as a function of concentration and frequency is carried out. The complex permeability is given by,  $\mu = \mu'_i - j\mu''_i$  where  $\mu'_i$  is the real part of permeability known as initial permeability and  $\mu''_i$  is the imaginary part of initial permeability known as permeability loss. The initial permeability shows a decrease with increasing  $\text{Ni}^{2+}$  ion concentration (table 1). The permeability mechanism can be explained in terms of domain wall displacement and rotation of spins in each domain and is found to be dependent on square of the saturation magnetization, ionic distribution, microstructure like grain size, density, such as magneto anisotropy etc. [9-12]. In the present study the saturation magnetization decreases with addition of Ni and the observed overall decreased in the value of initial permeability is expected.

The frequency variation of initial permeability showed dispersion at low frequency, (figure.3a) and becomes nearly constant at higher frequencies. At low frequency, changes of the magnetization direction occur by the motion of domain walls, so that a domain oriented in the direction of the applied field grows at the expense of its neighbours, which are oriented in different direction. As the frequency increases the domain wall is unable to move sufficiently rapidly to follow the alternating field. The overall magnetization vector does not follow the applied field hence accounting for the low value of permeability. The occurrence of resonance at still higher frequency was reported by other workers which was not observed in the present investigation as frequency ranges of the LCR meter being 20Hz

– 2MHz [13]. However the frequency limit up to which the material can be used in a device is given by resonance frequency. This gives us knowledge that the sample can be used for high frequency application.



**Figure 3.** (a) Variation of initial permeability with frequency for  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$   
(b) Variation of permeability loss with frequency for  $\text{Li}_{0.4-0.5x}\text{Zn}_{0.2}\text{Ni}_x\text{Fe}_{2.4-0.5x}\text{O}_4$ .

Figure 3(b) shows the permeability loss as a function of frequency. It shows dispersion and at higher frequencies the value becomes small and nearly constant. The loss observed may be due to a lag of the motion of the domain walls which may be attributed to the imperfections in the crystal structure.

#### 4. Conclusion

Ni substituted LiZn ferrite was synthesized by citrate precursor method. XRD confirms the spinel phase structure of the sample. Experimental results show a decrease in Curie temperature, saturation magnetization, retentivity, initial permeability with the increase in  $\text{Ni}^{2+}$  concentration. Frequency variation of initial permeability and permeability loss show dispersion. It is expected that resonance for real part of complex permeability known as initial permeability might be occurring at higher frequency beyond 2 MHz suggesting the sample may find application in higher frequency.

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