

Effect of Li^{1+} substitution on Wall Permeability of Ni-Zn ferrites

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ABSTRACT: Li^{1+} substituted Ni-Zn ferrites have been synthesized by using oxalate precursors method and investigated for initial permeability measurements. With increasing Li^{1+} substitution in Ni-Zn ferrites, initial permeability goes on decreasing and explained by considering the variation of saturation magnetization, grain size and anisotropy constants. The magnitude of wall permeability is very large in comparison with rotational permeability. Sharp decrease near Curie temperature in μ_i -T curves indicates the single phase formation of spinel ferrites. Variation of loss factor with composition, temperature and frequency has been explained. Loss factor values are very small due to the processing techniques.

KEYWORDS: Ni-Zn ferrites, Oxalate precursors, Initial permeability, Loss factor

I. INTRODUCTION

Ni-Zn ferrites are extensively used in many electronic devices because of their high permeability at high frequency, high resistivity, chemical stability, mechanical hardness, reasonable cost and easily processable [1]. Magnetic properties of Ni-Zn ferrites are influenced by the chemical composition and microstructure which is very sensitive to the synthesis process. Hence selection of appropriate process is very important factor to obtain good quality with highly dense materials. Various manufacturing process such as ceramic method and chemical methods have been developed and used to synthesize the Ni-Zn ferrites. Ceramic method is one of most common and economical method employed for preparing the mixed ferrites. But this method requires very high temperature and milling process which may affect the uniform nature of particles and stoichiometry in the final product [2]. In order to overcome these difficulties arising out of ceramic method, chemical methods such as co-precipitation, sol-gel, combustion, hydrothermal etc have been employed for the production of more homogeneous and fine materials [3]. Many workers [4-9] have synthesized various ferrites using these chemical methods and studied their properties. Rezlescu et al [10-12] reports that with integration of some rare earth cations into Ni-Zn ferrites results in the modification of basic electrical and magnetic properties. They observed the formation of plateau in the temperature dependent initial permeability curve. The initial permeability is one of the most important and sensitive magnetic properties of spinel ferrites. It depends on chemical composition, density and microstructure [13-14]. It is known that, permeability of polycrystalline ferrite is due to two magnetizing mechanism: domain wall motion and spin rotation [15]. Domain wall motion is sensitive to both ferrite grain size and post sintering density while spin rotation depends only on post sintering density of ferrites [16]. In present work, the effect of Li^{1+} addition on wall permeability and loss factor of Ni-Zn ferrites synthesized by oxalate precursors have been investigated by studying their compositional, thermal and frequency variation.

II. EXPERIMENTAL

Different compositions of $\text{Ni}_{0.32}\text{Zn}_{0.68-2x}\text{Li}_x\text{Fe}_{2+x}\text{O}_4$ where $x = 0.00, 0.025, 0.05, 0.075, 0.10, 0.125, 0.15, 0.175, 0.20$ were synthesized as follows. The Ni-Zn-Fe oxalate complexes were prepared using the method suggested by Wickham [17] and later modified by M.Bremer et al [18] and Li oxalate was prepared using the method suggested by Dollimore et al [19]. For each composition Fe^{2+} acetate was synthesized separately by dissolving the required amount of AR grade iron metal powder with AR grade glacial acetic acid and distilled water in CO_2 atmosphere until the state of quantitative dissolution was reached. The respective acetates of Ni, Zn were dissolved in warm distilled water and all acetate's solutions thus prepared were added to hot oxalic acid solution to precipitate the required oxalate complex. The precipitate was filtered and washed with distilled water and dried. The Lithium oxalate solution prepared by saturating

a hot solution of oxalic acid with lithium carbonate was filtered and cooled. The resulting all solid solution oxalates were mixed and decomposed at 400°C for three hrs. The toroids of the dimension of 2 cm outer diameter and 1 cm inner diameter were prepared and sintered at 1050°C in air atmosphere. These ferrite compositions thus prepared were characterized using X-ray powder diffractometry. All ferrite compositions exhibit a single spinel phase. The compositional, thermal and frequency variations of initial permeability and loss factor measurements were carried out on a toroidal core.

III.RESULTS AND DISCUSSION

A. Compositional variation of μ_i :

The values of calculated initial permeability (μ_i), wall permeability (μ_w), rotational permeability (μ_{rk}), anisotropy constant (K_1), saturation magnetization (M_s) and average grain size (D_{av}) are given in Table 1. The initial permeability measurements on toroidal samples were taken using a LCR meter at 1 KHz from low field inductance measurements of coils with toroidal cores using the relation

$$\mu_i = \left[\frac{1}{0.0046N^2h \log \frac{d_2}{d_1}} \right]$$

Where L is the inductance, N is number of turns, d_2 is outer diameter, d_1 is inner diameter, h is the height and μ_i is initial permeability. Corrected initial permeability has been calculated using the relation given by Globus et al [20].

$$(\mu_i - 1)_c = (\mu_i - 1) \frac{d_x}{d_a}$$

Where $(\mu_i-1)_c$ is corrected initial permeability, (μ_i-1) is observed initial permeability, d_x is X- ray density, d_a is actual density of the ferrite sample.

Table 1: Data on Corrected initial permeability (μ_{ic}), wall permeability (μ_w), rotational permeability (μ_{rk}), anisotropy constant ($-K_1$) erg/cm³, saturation magnetization (M_s), average grain size (D_{av}) and loss factor (LF)

x	μ_{ic}	μ_w	μ_{rk}	$-K_1$	M_s	D_{av}	LF
0.00	1519	1339	181	1.8×10^3	45	0.73	0.000078
0.025	1049	924	126	3.8×10^3	52	1.82	0.000169
0.050	817	720	98	6.6×10^3	61	1.76	0.000177
0.075	586	516	71	1.0×10^4	64	1.52	0.000230
0.10	432	381	52	1.6×10^4	71	--	0.000442
0.125	290	235	36	2.3×10^4	73	---	0.000960
0.150	225	198	28	3.3×10^4	74	--	0.00130
0.175	125	110	16	6.2×10^4	75	--	0.00387
0.20	119	105	15	6.8×10^4	67	--	0.00483

It is observed that initial permeability decreases with increase of Li^{1+} in Ni-Zn ferrites. Initial permeability is dependent mainly on saturation magnetization and anisotropy constant which also depend on temperature and specific to given ferrite composition. The parameters of technological importance that govern μ_i are microstructure, stoichiometry and crystalline defects. From table 1, it is observed that on substitution of Li^{1+} in Ni-Zn ferrites, both saturation magnetization and anisotropy constant increases and grain size first increases up to $x = 0.025$ and then decreases with further higher concentration of Li^{1+} . Hence, it is concluded that decrease in initial permeability can be due to increase in anisotropy and decrease in grain size. The SEM photographs are shown in Fig.1. The increase in K_1 with Li^{1+} substitution suggests that more energy is required to turn the magnetization vector from an easy to hard direction. It is well known that anisotropy makes definite contribution to the quantity like magnetic susceptibility, frequency of ferromagnetic resonance, permeability and hysteresis [21]. This is due to the interactions between two

magnetic dipoles and is dependent on the arrangement of magnetic spins in the lattice and nature of the magnetic ions. The spin orbit interaction of magnetic ions involved makes a definite contribution to the anisotropy. As a result of this interaction, the spins align themselves in a direction perpendicular to the plane of the orbits, which is fixed with respect to crystal axes. Hence the magnetization along one of the crystal axes is preferred. These results in the increase of anisotropy energy thus K_1 increases. Therefore decrease of initial permeability can be attributed to increase in anisotropy constant K_1 . Thus K_1 plays a major role in decreasing μ_i .

It is well known that [22], ferrous ferrite has positive magnetostriction whereas nickel ferrite is negative, however it is difficult to substitute ferrous ions for nickel as both cations prefer B site and usually result in the substitution is the formation of two phase mixture of Fe_3O_4 and $NiFeO_4$ causing a reduction in permeability. In present system as Li^{1+} content increases, the Fe ion also increases. Hence it is expected that some Fe^{2+} ions are present and their percentage is also increasing. Hence, the presence of Fe^{2+} causes the initial permeability to decrease. Also lithium ferrite is known to lose substantial amount of lithium during the sintering above $1000^\circ C$, as a result, Fe^{2+} ions are formed [23].

The values of wall permeability and rotational permeability have been calculated using the formulae [24].

$$\mu_{rk} = 1 + \frac{2\pi M_s^2}{K_1} \qquad \mu_w = \mu_i - (\mu_{rk} - 1)$$

From Table 1, it is seen that the magnitude of wall permeability is very large in comparison with the rotational permeability in all the ferrite compositions. Hence it is concluded that the dominant contribution to initial permeability μ_i due to domain wall motion and the addition of Li^{1+} causes the hindrance to domain wall motion.

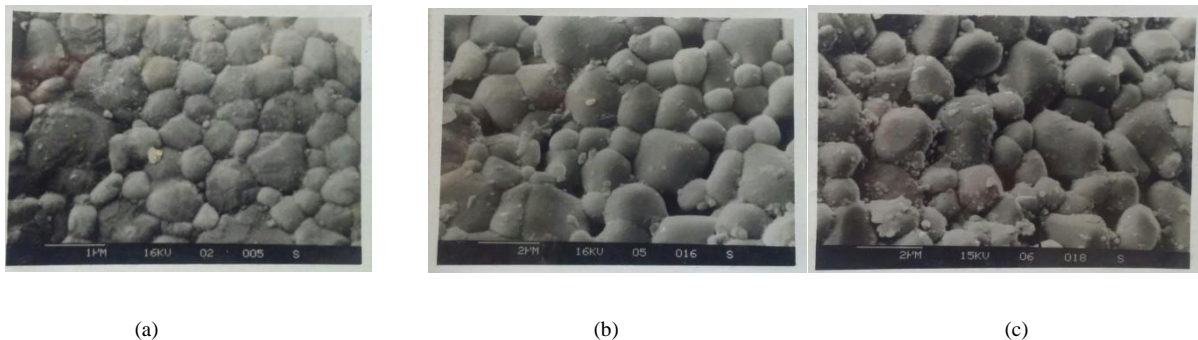


Fig. 1: SEM photographs for present ferrite system (a) $x= 0.00$, (b) $x=0.025$ (c) $x=0.050$

B. Thermal variation of μ_i :

Initial permeability is governed by both intrinsic parameters mainly saturation magnetization and anisotropy constant which depends on the temperature and are specific to the given composition and by technological parameters such as microstructure, grain size, stoichiometry, crystalline defects, all which are depending on sintering conditions. These parameters are responsible for the diversity of the thermal spectra of initial permeability. The behaviour of initial permeability as a function of temperature is one way to approach this mechanism and have been reported by many workers [25-29]. In many ferrite samples, μ_i increases with increase in temperature up to T_c . This is because the anisotropy field usually decrease with permeability much faster than M_s [26]. In present study, the variations of μ_i as a function of temperature in the range from room temperature up to Curie temperature have been shown in Fig. [2]. Following observations have been made

- 1] Initial permeability increases slowly with temperature and exhibits a small peak near T_c .
- 2] The peaking temperature increases with increasing Li^{1+} content.
- 3] As the Li^{1+} content increases, μ_i becomes nearly constant with temperature up to T_c .
- 4] Near T_c , μ_i falls rapidly and becomes zero. The sharp decrease indicates the single phase formation of ferrite materials.

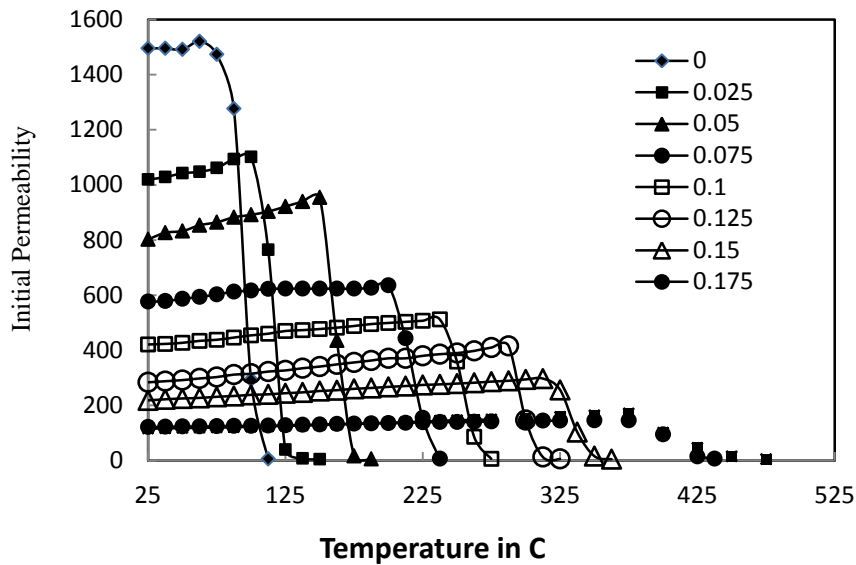


Fig. 2 Thermal Variation of Initial permeability for present ferrite system

Thermal variations of initial permeability can be explained by considering the compensating effect in M_s and K_1 with temperature. They usually decrease with increase in temperature due to thermal agitation which disturbs the alignment of magnetic moment [30]. But decrease of K_1 with temperature is faster than M_s . When K_1 reaches zero, μ_i attains its maximum value and then drops to zero. In ideal homogeneous ferrites, there will be only a temperature at which crystal anisotropy is exactly zero. K_1 when passes through zero, the permeability rises to a peak at this temperature. Thus the parameter K_1 modulates the behaviour of μ_i -T curves. It can be concluded that the small peak in μ_i -T curves is due to K_1 which changes its sign.

C. Frequency variation of μ_i :

Variation of initial permeability μ_i with frequency in the range from 20 KHz to 1 MHz for all ferrite compositions is presented in Fig.3. It is observed that μ_i is almost constant and increases sharply at higher frequency at 1 MHz except for little variation at low frequency. The major contribution to initial permeability is due to domain wall motion which is manifested here by the low frequency dispersion effect. The occurrence of dispersion and absorption at frequency in the region of 1 MHz was first established by Snoek, who attributed the phenomenon to spin resonance in the internal anisotropy field. Rado and his co-workers [31-34] believed that the absorption observed at higher frequency which is attributable to rotational resonance in the combined anisotropy -demagnetizing field. They attributed the lower frequency region to domain wall displacement which they believed to make the major contribution to the μ_i . In the present case, the dispersion at higher frequency is due to spin resonance in the anisotropy field and that at lower frequency to the major contribution of domain wall motion to initial permeability.

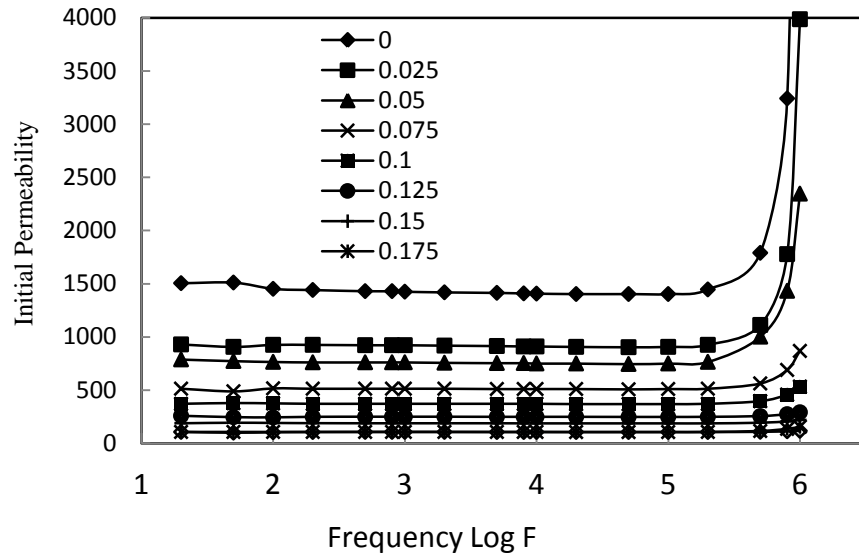


Fig. 3 Frequency (Log F) variation of Initial Permeability for present ferrite system

D. Compositional variation of loss factor:

Table 1, shows the values of loss factor. It is observed that the loss factor increases with increases in Li^{1+} content which is due to decrease in μ_i due to the formation of Fe^{2+} ions on addition of Li^{1+} .

E. Thermal variation of loss factor:

Fig.4 shows the thermal variation of loss factor for present ferrite system. It is seen that loss factor is in invariant with increasing temperature up to certain temperature afterwards it rapidly increases. This increase in loss factor is due to thermal randomization of domains. The increase in temperature weakens the exchange forces between the domains, due to this, domain orient in random manner, this result in phase transition from ferromagnetic to paramagnetic state at T_c . Hence the loss factor increases.

F. Frequency variation of loss factor:

Fig. 5 shows variation of loss factor with log F in the range 20 Hz to 1 MHz. It is observed that the loss factor decreases as the frequency increases and attain the minimum value in the frequency range 50 KHz to 100 KHz. At higher frequency it slightly increases which may be attributed to the phenomenon of domain wall relaxation which involves the hindrance of domain wall motion of small grains by those of large grains where the later type of grains occur in small number[35]. The high value of LF at lower frequency is due to different type of wall relaxation process [36].

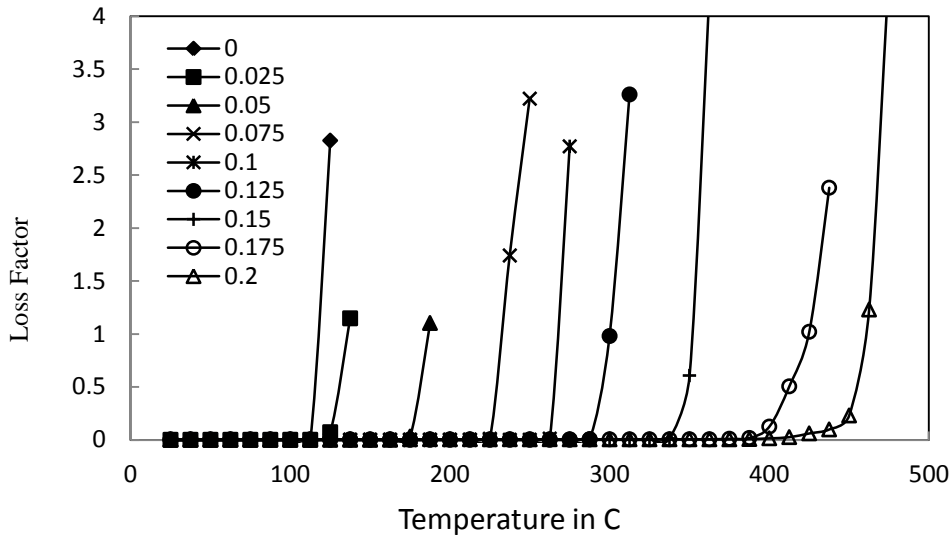


Fig.4. Variation of Loss Factor with temperature for present ferrite system

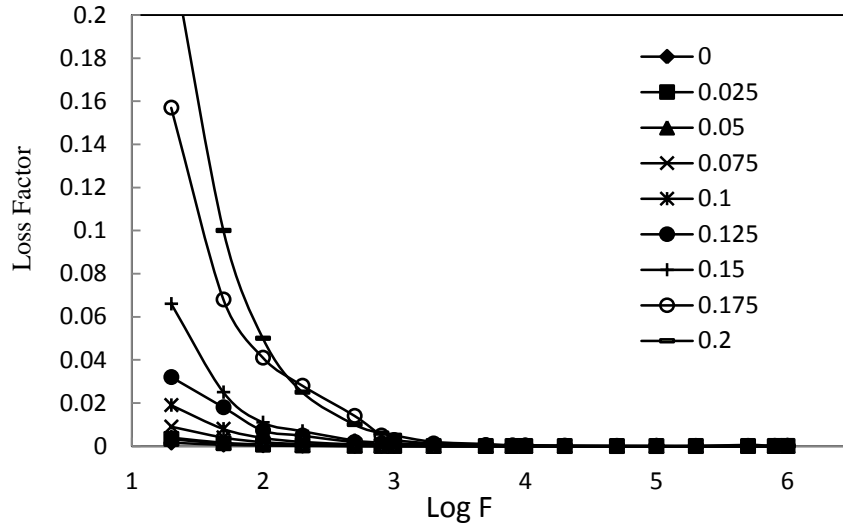


Fig. 5 Variation of loss factor with Log F for present ferrite system

IV. CONCLUSION

Various compositions of $Ni_{0.32}Zn_{0.68-2x}Li_xFe_{2+x}O_4$ ferrites have been synthesized by employing oxalate precursors method. Initial permeability decreases with increasing Li^{1+} content. The magnitude of wall permeability is very large in comparison with rotational permeability. Thermal variation of initial permeability indicates that the peak height decreases with increase in Li^{1+} content. Loss factor shows increasing trend with addition of Li^{1+} .

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