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Initial permeability studies of Mn substituted Mg-Zn ferrites synthesized by oxalate precursorsU.R.Ghodake^{1,2*}, N.D.Chaudhari³, R.C.Kambale⁴ and S.S.Suryawanshi¹¹ Department of Physics, Solapur University, Solapur - 413255, Maharashtra, INDIA.² Department of Electronics, Shri Shivaji Mahavidyalaya, Barshi - 413411, Maharashtra, INDIA.³ Department of Physics, Pratishtan Mahavidyalaya, Paithan-431107, Maharashtra, INDIA.⁴ Department of Physics, University of Pune, Ganeshkhind, Pune-411007, Maharashtra, INDIA.**Abstract**

Mn substituted Mg-Zn ferrites have been synthesized by employing a co-precipitation technique using oxalate precursors. Initial permeability is found to increase initially up to $x = 0.10$ and with further addition of Mn^{2+} content it decreases. The observed variation in initial permeability can be explained by considering the variation of saturation magnetization M_s , anisotropy constant K_1 , grain size D and density values. Thermal variation of initial permeability reveals that for higher Mn^{2+} content, μ_i - T curves become flat and it exhibits thermal hysteresis. The loss factor values are small which is due to the large density of the sample and due to the processing technique utilized.

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Keywords – Initial permeability; oxalate precursors; loss factor; Mn-Mg-Zn ferrites.**1. Introduction**

Ferrites are the important electronics ceramic materials; has gained lots of attention of many researchers worldwide due to their potential applicability in electronic, microwave, computer technology and biomedical devices [1]. Magnetic properties of ferrites find various technical applications such as magnetic refrigeration, detoxification of biological fluids, magnetically controlled transport of anti-cancer drugs, magnetic resonance imaging contrast enhancement, magnetic cell separation, magnetic devices, switching devices, recording tapes, hard

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disc recording media, read write head, active component of ferro fluids, color imaging , gas sensitive materials and catalytic materials, for high speed data transmission application and tumor thermotherapy [2-4].

The processing of ferrite materials and microstructure are major aspects to achieve better magnetic properties. Fine particles of magnetic materials exhibit interesting magnetic properties and recently fine particles of spinel ferrites synthesized by chemical route were shown to have magnetic properties markedly different from those prepared by the ceramic method [5-6]. Thus, the properties of ferrites are deeply influenced by chemical composition and microstructure which is very much sensitive to the processing technique of raw materials [7-8]. The selection of appropriate technique is therefore the key to obtain better magnetic properties. Initial permeability is known to be one of the most important and sensitive magnetic properties of ferrites. The permeability spectra of ferrites depend on various factors such as chemical compositions, sintering density and microstructure [9-10]. It is known that permeability of ferrite consist of two different mechanisms: spin rotation and domain wall motion. Domain wall motion is sensitive to both grain size and post sintering density whereas spin rotation depends only on the post sintering density of ferrites [11]. Here we report the synthesis technique and compositional, thermal variation of initial permeability and loss factor in Mn substituted Mg-Zn ferrite particles synthesized by using a simple method called oxalate precursors. The oxalate precursor for the synthesis of ferrite material is found to be convenient, since it yield a homogeneous product in short time .Oxalates are generally used due to their low solubility, low decomposition temperature and fine particle yield . The uniformity in the starting material favors the diffusion dependent formation of homogeneous spinel at low temperature.

2. Experimental

2.1 Material Synthesis and characteristics

The oxalates were prepared by a method suggested by Wickham [12] and subsequently modified by Bremer et al [13] for the preparation of manganese zinc ferrites. Iron acetate was prepared by adding glacial acetic acid to the required quantity of AR grade iron metal powder to make a solution with a slight excess of glacial acetic acid and heating it in a CO₂ atmosphere instead of in an N₂ atmosphere as employed by earlier workers [13]. Required quantities of warm magnesium acetate, zinc acetate, manganese acetate and the above synthesized iron acetate (total metal ion concentration = 0.45 M) were slowly added to ammonium oxalate solution (0.60 M) to precipitate the required oxalate to maintain the desired stoichiometry. In this way, different oxalate complexes of the general composition Zn_{0.4}Mg_{0.6-x}Mn_xFe₂(C₂O₄)_n·H₂O (where, x = 0.00, 0.01, 0.03, 0.05, 0.09, 0.10, 0.20, 0.25, and 30) were synthesized. The resulting co-precipitated oxalate complexes were decomposed in N₂ atmosphere at 500°C for 2 hours. The decomposed product was then pressed to toroid form of dimensions as 2 cm outer diameter and 1 cm inner diameter by applying pressure of 6 ton/inch² for 5 minutes . The green toroids thus prepared were sintered at 1100°C in N₂ atmosphere for 8 hours. The rate of heating was 100°C/h and rate of cooling was 60°C/h.

2.2 Initial Permeability

The initial permeability measurements of toroid samples were carried out using HP-4284 A precision LCR-Q meter in the range from room temperature up to 450 °C at 1 KHz from low field inductance measurements of coils with toroidal cores using the formula

$$\mu_i = L / [0.0046 N^2 h \log (d_2/d_1)] \quad (1)$$

Where L is the inductance in μH ; N is the number of turns; d₂ is the outer diameter; d₁ is the inner diameter; h is the height of core in cm; μ_i is the initial permeability.

3. Results and discussion

3.1 Compositional variation of initial permeability (μ_i)

The data on initial permeability (μ_i), saturation magnetization (M_s), grain size (D), magneto crystalline anisotropy constant (K_1) and density in % are given in Table 1.

Table 1. Data on initial permeability (μ_i), μ_{eff} , Saturation magnetization (M_s) (80 K), grain size (D), anisotropy Constant (K_1), and density in % for the ferrite system $\text{Zn}_{0.4}\text{Mg}_{0.6-x}\text{Mn}_x\text{Fe}_2\text{O}_4$.

x	μ_i	μ_{eff}	M_s (80K)	D (μm)	$-K_1 \times 10^4$ erg / cc.	Density in %
0.00	223	89	373	1.4	2.34	95.60
0.01	263	105	454	1.6	2.341	95.81
0.03	283	118	471	1.9	2.343	96.01
0.05	286	143	476	2.7	2.345	96.30
0.10	295	151	551	2.9	2.350	97.50
0.20	225	115	416	2.8	2.360	92.20
0.25	181	107	482	2.4	2.365	89.50
0.30	83	53	460	1.7	2.370	87.70

From table 1, it is seen that initial permeability increases with increase in Mn^{2+} content up to $x = 0.10$, thereafter it decreases with further addition of Mn^{2+} . The parameters which governs the initial permeability are microstructure, stoichiometry, internal stress and crystalline defects. In the present case the variation of initial permeability with Mn^{2+} content can be explained by considering the variation of M_s , D , and K_1 . It is interesting to note that P.J. Van der Zaag et al [14] have observed a grain size of the same order for Mg-Mn-Zn ferrite and have established that grains are monodomains and initial permeability is predominantly rotational and increases with grain size. It is therefore concluded that our system too is made of monodomains grain having rotational permeability. In such a case, the affecting non magnetic grain boundary (NMGB) model [15-16] to eliminate the grain size effect, the values of $\mu_{\text{eff}} = \mu_i D / (\mu_i \delta + D)$ are determined and are shown in table 1. From table 1, it is clear that, as Mn^{2+} content increases, magneto crystalline anisotropy K_1 and density both increases whereas saturation magnetization (M_s) is found to increase up to $x = 0.10$ then decreases with further addition of Mn^{2+} content. Hence the variations of K_1 , M_s , and % density have been considered for the variation of initial permeability

and μ_{eff} with Mn^{2+} content. The μ_{eff} although being largely dependent on density also appears to be modulated by the factors like K_1 and M_s . Thus K_1 , M_s and the density together influence the trend exhibited by μ_{eff} . It is seen that there is increasing trend in initial permeability with increase of Mn^{2+} content up to $x = 0.10$ which is due to increase in M_s , K_1 and density. For $x > 0.10$ the initial permeability decreases this can be attributed considering variation of M_s and K_1 . Both M_s and K_1 values increase with Mn^{2+} content. The increase in μ_{eff} is due to increase in M_s , density, while the decrease in initial permeability μ_{eff} is due to increase in K_1 and decrease in density, M_s . Thus μ_{eff} follows the trend with M_s and D . It is known that the thickness of grain boundary affect the value of initial permeability [17-18] have concluded that increase in μ_i (when both M_s and D decrease) can be attributed to decrease in thickness of non-magnetic grain boundary which in turn decrease the domain wall energy and allow the easy movement of domain wall. The higher the grain boundary higher will be domain wall energy which in turn leads to higher value of K_1 . Values of K_1 go on increasing with addition of Mn^{2+} indicating that domain wall energy increases, hence it constrains free and easy domain wall motion. This reduces the magnitude of initial permeability at higher concentration of Mn^{2+} .

3.2 Thermal variation of initial permeability (μ_i)

Thermal variation of μ_i gives the valuable information about domain nature [19], Curie temperature [20] and the factor contributing to permeability [21-22]. The parameters such as M_s , D , and K_1 are responsible for the thermal spectra of μ_i of the ferrites.

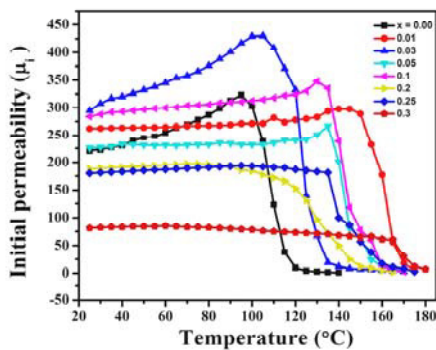


Figure 1 (a)

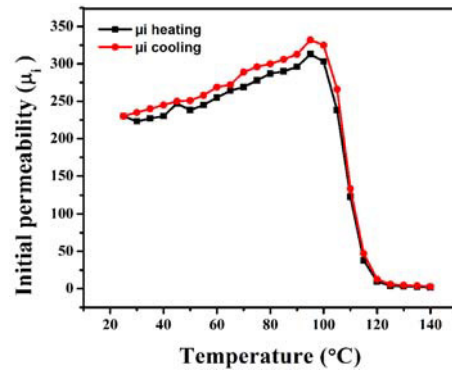


Figure 1 (b)

Figure 1 (a) Thermal variation of initial permeability (μ_i) for ferrite system $\text{Zn}_{0.4}\text{Mg}_{0.6-x}\text{Mn}_x\text{Fe}_2\text{O}_4$; (b) Thermal hysteresis in μ_i for the $\text{Zn}_{0.4}\text{Mg}_{0.6-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ Composition with $x = 0.00$.

Figure 1(a) shows the thermal variation of μ_i for the various compositions from room temperature to the Curie temperature (T_c). For compositions with $0 < x < 0.10$, the initial permeability increases slowly with temperature and exhibits a small peak near T_c . Near T_c , initial permeability falls rapidly and becomes zero at T_c . The sharp fall suggests the single phase formation of ferrite material, similar observations have been reported by various workers [18, 23]. The small increase in μ_i with temperature can be explained as the K_1 and M_s usually decrease with increase in temperature due to thermal agitation, which disturbs the alignment of magnetic moment [18]. But decrease in K_1 with temperature is much faster than M_s [24]. When K_1 goes through zero, initial permeability attains its maximum value and drops to zero above T_c . Both [25-26] have shown that the initial permeability (μ_i) is maximum at the temperature where the anisotropy constant K_1 changes sign. Thus it can be concluded that the peak in μ_i - T variation are due to change in sign of K_1 . For compositions with $0.2 < x < 0.3$, there

is no peaking behaviour in μ_i -T variation, hence permeability is invariant up to T_c , near T_c permeability falls rapidly and becomes zero. Similar behaviour in μ_i -T variation have been reported by Sankpal et al (1998). From thermal variation of initial permeability for the composition $Zn_{0.4}Mg_{0.6-x}Mn_xFe_2O_4$ with $x = 0.00, 0.01, 0.03, 0.09, 0.10$ peaking behaviour is observed at T_c . The Hopkinson peak indicates the presence of SD grains. Hence it can be concluded that there is dominance of SD grains. However, for detail investigation the study of particle size distribution would have thrown light on an investigation. Initial permeability depends upon K_1 , M_s and D . As temperature increases both K_1 and M_s tend to decrease, the decrease in K_1 is more magnetic than the decrease in M_s . Hence μ_i tends to increase and finally becomes maximum at Curie temperature when $K_1 = 0$. It is also possible that there may be some SD type of particles formed during the sintering at elevated temperature. SD type of particles shows magnetic properties, which are sensitive to temperature variation. The variation in μ_i in our composition appears to be mainly due to variation of magneto crystalline anisotropy constant (K_1) and the grain size (D).

3.3 Thermal hysteresis of initial permeability (μ_i)

The initial permeability of polycrystalline ferrite exhibits thermal hysteresis when the temperature is cycled from above and below Curie temperature T_c . The thermal spectra of the initial permeability of polycrystalline ferrites can be classified into two categories [27].

- i) Ferrites exhibiting one peak in the permeability, named the Hopkinson peak, which is near T_c , followed by a steady decrease with decreasing temperature.
- ii) Ferrites exhibiting an additional peak at lower temperature, named the secondary peak.

Loaec [27] explained hysteresis by taking into account domain wall pinning a competition between intrinsic parameters M_s and K_1 around transition points. Few researchers [28, 29] have mentioned thermal hysteresis on the initial permeability by cycling the temperature and have proposed a partial explanation [30, 31] while others have not given any interpretation [29]. On the basis of observations on Mn-Zn ferrous ferrite, Loaec [27] classified hysteresis as

- (i) below secondary peak phenomenon is identical with that for Mn-Zn ferrite.
- (ii) Between secondary peak and Hopkinson peak phenomenon is reversed.

The secondary peak is lower and Hopkinson peak is higher during heating run between Hopkinson peaks T_c phenomenon is same as that of Mn - Zn ferrite. Hysteresis phenomenon shows fundamental character of Bloch wall mechanism in its magnetization and related to domain wall topography. The topography is sensitive to transition point. Around transition point hysteresis results from competition between intrinsic parameters on either side of transition. The thermal hysteresis of initial permeability has been exhibited by all the samples studied by us.

From the shapes of μ_i -T curves following conclusions have been drawn.

- 1] Two types of hysteresis are observed- first is below T_c and second one is between Hopkinson peak and T_c .
- 2] Permeability obtained during heating is lower than that obtained during cooling cycles, indicating the M_s and K_1 change differently with respect to temperature during cooling and heating.
- 3] The peak in μ_i -T variation during both heating and cooling cycle appears at same temperature indicating that K_1 changes its sign at the same temperature during heating and cooling.
- 4] All the compositions exhibit a pronounced peak before T_c .
- 5] The peak height during cooling cycle is more pronounced than that during heating cycle.

Table 2 represent initial permeability values during heating cycles, and during cooling cycles, as well as the difference between these values. i.e. $\Delta\mu_i$. $\Delta\mu_i = \mu_{ic} - \mu_{ih}$. Where μ_{ic} is the initial permeability value near Hopkinson peak during cooling cycle. μ_{ih} is the initial permeability value near Hopkinson peak during heating cycle. It observed that for $x = 0.10$, the value of $\Delta\mu_i$ is maximum and it increases as the content of Mn^{2+} increases for $0 < x < 0.1$ and for $x > 0.1$ it decreases.

Table 2. Thermal hysteresis and initial permeability (during heating and cooling) data for Ferrite system $Zn_{0.4}Mg_{0.6-x}Mn_xFe_2O_4$

x	μ_{ih}	μ_{ic}	$\Delta\mu_i$
0.00	322	338	16
0.01	298	320	22
0.03	421	444	23
0.05	240	266	26
0.10	242	272	30
0.20	202	213	11
0.25	183	193	10
0.30	83	87	04

4. Loss factor (LF)

The ratio of the imaginary part of the permeability representing the losses in the material to the real part of the permeability is a measure of the inefficiency of the magnetic system .It is called the loss tangent. This loss factor (LF) parameter should be as low as possible. Loss tangent $\tan \delta = \mu' / \mu''$, the loss factor is defined as $LF = \tan \delta / \mu_i$.

From figure 2(a), it is found that LF is almost constant up to Curie temperature, while above T_c , the loss factor increases exponentially. The thermal variation of $\tan \delta$ seems to be responsible for increase in loss factor. In order to have low loss factor the ferrite must be operated below Curie temperature.

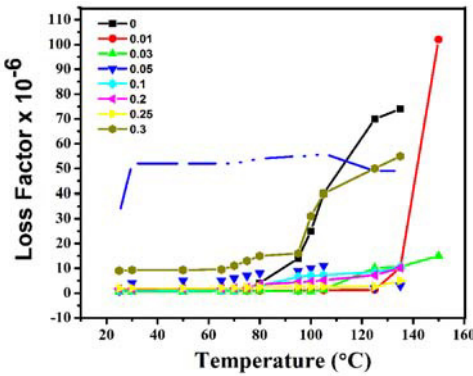


Figure 2(a)

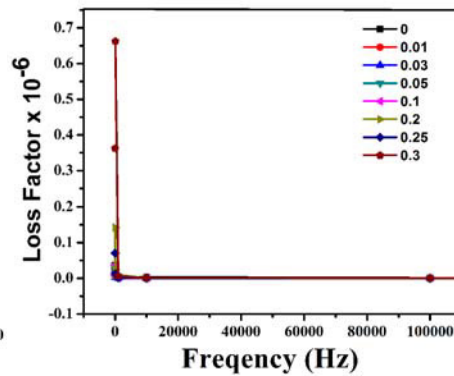


Figure 2(b)

Figure 2(a) Thermal variation of loss factor for ferrite system $Zn_{0.4}Mg_{0.6-x}Mn_xFe_2O_4$; (b) Frequency variation of loss factor for ferrite system $Zn_{0.4}Mg_{0.6-x}Mn_xFe_2O_4$.

In figure 2(b), the variation of loss factor with frequency in the range 20 Hz to 1 MHz is shown. It is observed that loss factor decreases with increase in frequency and attain a minimum value. The occurrence of high value of Loss factor at lower frequency is due to different types of wall relaxation processes [28]. It is assumed that the magnetic energy levels of a magnetic ion depend on the orientation of the magnetization for each orientation there exists equilibrium Boltzmann distribution. In the moving wall the magnetization change in directions and hence the energy levels, resulting in the change in redistribution that occurs in a finite relaxation time, causing the magnetization to lag behind the applied field. The maximum loss occurs at a frequency $\tau = 1/\omega$, which is proportional to the conductivity [32].

5. Conclusion

Various composition of Mn substituted Mg-Zn ferrites were synthesised by using oxalate precursor techniques. Initial permeability is found to increase upto Mn = 0.1 afterwards it decreases and explained using the variation of Ms, K₁ and D. It is concluded that the present ferrite system is made up of monodomain grains with rotational permeability. For higher concentration of Mn²⁺ in Mg-Zn ferrites, initial permeability – temperature curves becomes flat which exhibits a thermal hysteresis. The parameters such as Ms, K₁ and D are responsible for thermal variation of initial permeability. Thermal variation of loss factor reveals that loss factor is almost constant up to T_c and decreases with increase in frequency.

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