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Effect of (Mg-Ti) substitution on the structure and Physical properties of Ni - Zn ferrite

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Abstract

Effect of the substitution by two ions together, (Ti-Mg) ions, on the structure, magnetic and electrical properties of Ni - Zn ferrite of chemical formula $Ni_{0.7}$ $Zn_{0.3}$ $(Mg\ Ti)_x$ $Fe_{2-x}O_4$ (x = 0, 0.1, 0.2, 0.3and 0.4) prepared by conventional ceramic method. These structure of the prepared samples was studied using X– ray diffraction pattern. It was found that as (Mg-Ti) ions concentration increases, the value of saturation magnetization, initial permeability and Curie temperature were decreased. It was also observed that the dc resistivity of the prepared samples increased with increasing (Mg-Ti) concentration and hence decreasing the dielectric loss of investigated samples. The present study indicated also that the samples of x = 0.1 and 0.2 show high resistivity and relatively high magnetic properties which can be exploited in a certain technical application.

1. Introduction

Ni-Zn ferrite is soft ferrite having low magnetic coercivity , high electrical resistivity , low dielectric loss, high Curie temperature and good magnetic properties but have relatively low initial permeability at high frequency make this ferrite an excellent core material for power transformers. Ni-Zn ferrite have a wide field of technological applications as transformer cores, rod antennas, high frequency inductors and read/ write heads for high – speed digital tape of disc readings [1] . The technological application of these material has been studied extensively[2-5]. The effect of (Ti), (Al) and (Mg) on the electric and magnetic properties of Ni-Zn ferrites was studied [6-8]. The micro structural and magnetic properties of $Ni_{0.7}$ $Zn_{0.3}$ Fe_2 O_4 ferrite, prepared by sol-gel auto-combustion method, has been investigated [9], It was found that, in the inverse spinel Ni-Zn ferrite, Zn ions prefer to occupy the tetrahedral sites while Ni ions occupy the octahedral sites. Earlier studies on mixed ferrites indicate that Ti^{4+} occupy octahedral (B)sites and Mg^{2+} occupy tetrahedral (A)sites[10, 11]. The aim of the present work is,

study the effect of (Mg-Ti) ions substitution on the structure, magnetic and electric properties of Ni-Zn ferrite.

2.Experimental Procedure:

Samples with chemical formula $Ni_{0.7}\ Zn_{0.3}\ Mg_x\ Ti_x\ Fe_{2-x}O_4$ (x = 0, 0.1, 0.2, 0.3 and 0.4) were prepared by using standard ceramic technique. High purity oxides were mixed together in stiochiometric ratio. The samples were grounded for 6h in a ball mill and the mixture of the samples were presintered at 900 ^oC for 9h using heating rate 8 ^oC/min. The presintered mixture was grounded again and pressed at room temperature into discs and triodes. Finally the samples were sintered at 1200 ^oC for 12h and then slowly cooled to room temperature. X - ray diffraction were formed using diffractometer of type X'pert Graphics and Identify with CuKα radiation.

The porosity percentage (P%) was calculated for all samples according to the relation P% =100 [1-(d/dx)%] where dx is the theoretical X - ray density and d is the bulk density of samples measured in toluene using Archimedes principle.

The magnetization M (Am^{-1}) was measured at room temperature as a function of the magnetization field H (Am^{-1}) ranged from zero to 3600 Am^{-1}.

The initial magnetic permeability (μ_i) was measured as a function of temperature at constant frequency (f = 10 KHZ) and low magnetizing current of I_p= 10 mA. The value of μ_i was calculated using Poltinnikov's formula

($V_s = K\ \mu_i$ where $K = 0.4\ \pi\ N_p N_s I_p A\omega/L$)

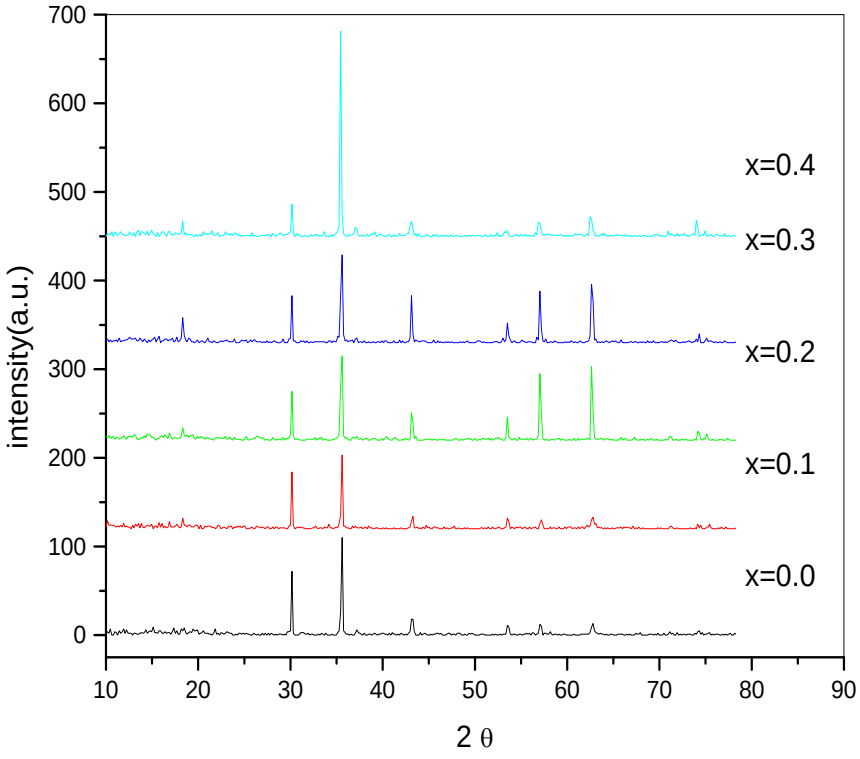
where V_s is the induced voltage in secondary coil N_p, N_s is the number of turns of primary and secondary coil ($N_p = N_s = 15$), A is the cross sectional area of sample, ω is angular frequency, L is the average path length of the magnetic flux.

The dc electrical resistivity (ρ) was measured as function of temperature by using two probe method. The surface of disc shaped samples were carefully polished to have uniformly smooth surfaces then coated with a thin layer of silver paste. The sample were placed between two electrodes inside a furnace to measure the resistivity as a function of temperature.

3. Result and Discussion

3.1. X - Ray Analysis

X-ray diffraction patterns (XRDP) at room temperature for all investigated ferrite samples are shown in Fig.(1)with composition $Ni_{0.7}Zn_{0.3}$ $(Mg\ Ti)_x$ $Fe_{2-2x}O_4$. Fig(1) shows that, all the prepared samples have a single phase cubic spinel structure. The interplaner spacing and experimental lattice parameter (a_{exp}) were calculated using Bragg's law and are plotted as a function of (Mg-Ti) concentration in Fig(2). It is clear from Fig(2) that, as (Mg- Ti) concentration increases the lattice parameter increases. The increase in lattice parameter with increasing (Mg - Ti) concentration could be explained on the basis of the ionic radii due to the replacement of ions with smaller ionic radius Fe^{3+} (0.64 Å) by (Mg-Ti) ions of larger ionic radii Mg^{2+}(0.65Å)and Ti^{4+} (0.68 Å).



Fig(1) : X –ray patterns of the investigated samples

The cation distribution of the prepared samples is assumed to be

$$(Zn_{0.3}Mg_xFe_{0.7-x})[Ni_{0.7}Ti_xFe_{1.3-x}]\,O_4$$

where the brackets ( ) and [ ] denote to A- and B-sites respectively, Zn ion preferentially occupy the tetrahedral sites, while Ni ions occupy the octahedral sites, Mg ions occupy the tetrahedral sites [10], Ti ions occupy the octahedral sites and Fe ions are distributed between A and B sites [11].

The theoretical lattice parameter is calculated using the equation

$$a_{th} = \frac{8}{3\sqrt{3}}[(r_A + R_o) + \sqrt{3}(r_B + R_o)]$$

where R_o is the radius of oxygen ion (1.32 Å), r_A and r_B are the ionic radii of tetrahedral and octahedral sites ,respectively [12]. The ionic radius of each site was calculated according to the following equations [13]

$$r_A = [(0.3)r_{Zn^{2+}} + (x)r_{Mg^{2+}} + (0.7-x)r_{Fe^{3+}}]$$

$$r_B = [(0.7)r_{Ni^{2+}} + (x)r_{Ti^{4+}} + (1.3-x)r_{Fe^{3+}}]/2$$

where $r_{Zn^{2+}}, r_{Mg^{2+}}, r_{Fe^{3+}}, r_{Ni^{2+}}$ and $r_{Ti^{4+}}$ are the ionic radii of Zn , Mg ,Fe,Ni, and Ti ions respectively.

The experimental values of lattice parameter are greater than those of the theoretical values, this can be attributed to the formation of Fe^{2+} ions, which have an ionic radius greater than Fe^{3+}. ions. The difference between experimental and theoretical radii decreases with increasing (Mg-Ti) concentration which indicates that the concentration of Fe^{2+} decreases as (Mg-Ti) concentration increase.

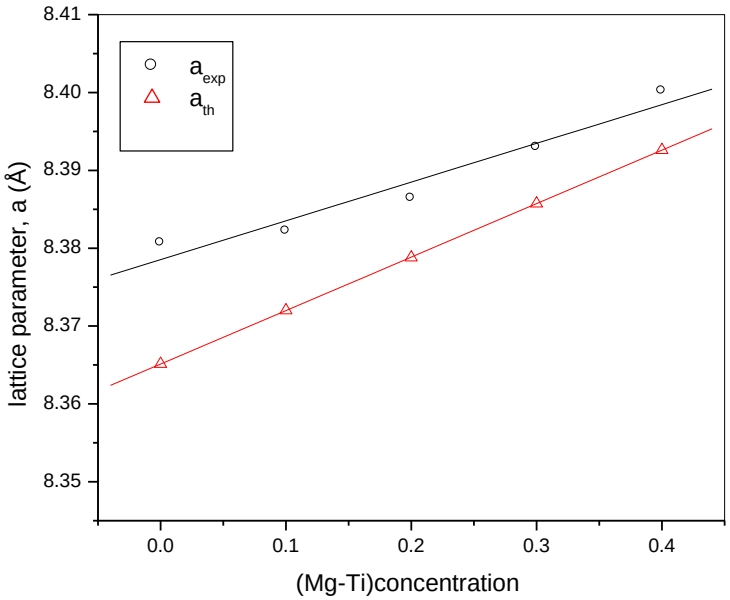


Fig. (2) : Variation of lattice parameter (a) with (Mg-Ti) -concentration

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The variations of porosity (P %) with (Mg-Ti) concentration (x) are shown in Fig.(3). It is obvious from Fig.(3)that, as (Mg-Ti) concentration increases the porosity increases. This behavior could be explained as follows: It is well known that the porosity of ceramic samples results from two sources intragranular porosity (P_{intra}) and intergranular porosity (P_{inter})[14]. so that the total porosity (P %) could be written as the sum of two types i.e.

$$P\% = P_{intra} + P_{inter}$$

It was reported that as (Ti) concentration increases in Ni-Zn ferrite the grain diameter increases and consequently the intergranular porosity increase [15,16].

Also the replacement of Fe^{3+} ions with (Mg-Ti) ions lead to an increase of intragrunlar porosity due to the ionic radius of Fe^{3+} ions is smaller than the ionic radius of Mg and Ti ions. Thus the value of the total porosity increase.

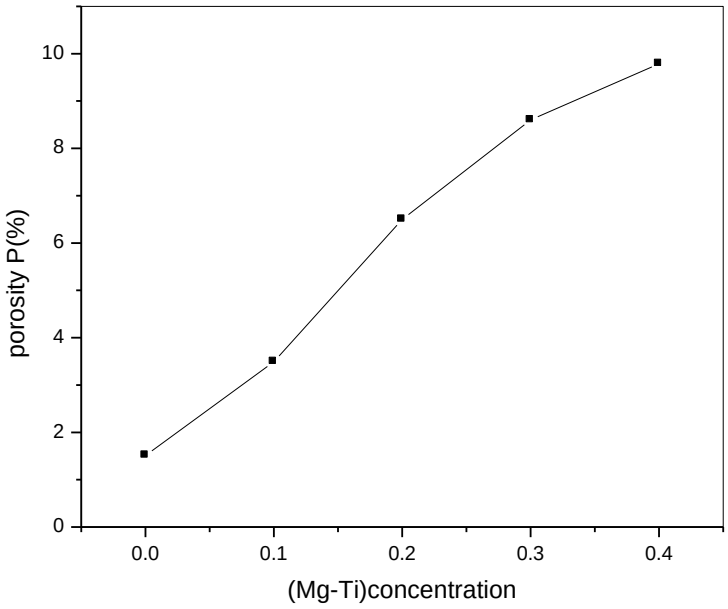

Fig. (3): Variation of porosity (P%) with (Mg-Ti) -concentration

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3.2.Magnetization and Relative Permeability

The variation of ac magnetization M (Am^{-1})with applied magnetic field H (Am^{-1}) for all investigated samples at room temperature is shown in Fig.(4). As a normal behavior, the magnetization increases with increasing applied magnetic field and attain its saturation value for higher fields.

The compositional dependence of ac magnetization (M) for the prepared samples at different value of the magnetic field is shown in Fig.(5). It is clear from the Fig.(5) that, as (Mg-Ti) concentration increases the magnetization (M) increases and attain it s maximum value at x = 0.1and then decreases.

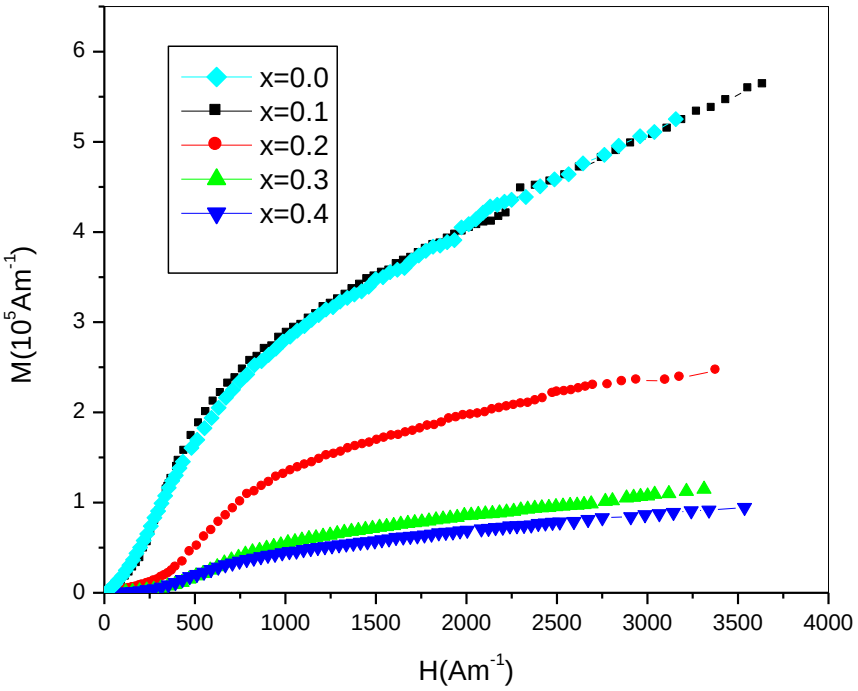


Fig. (4):Variation of the magnetization (M) versus the applied magnetic field (H)

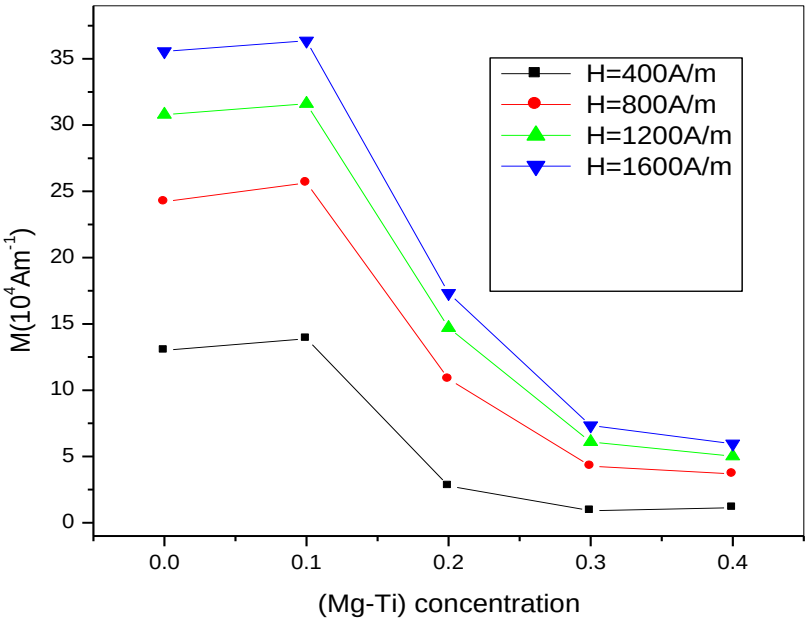


Fig. (5): Variation of magnetization (M) with (Mg-Ti) concentration

This behaviour could be explained as following: It is known that, for Ni-Zn and Cu-Zn ferrites

there is a canting angle (Yafet-Kittel angle (α_{YK})) between moments in B-site.

Such a canting angle is due to the negative B-B interaction [17-19] Thus, the total magnetization M could be expressed

$$M = M_B \cos\alpha_{YK} - M_A$$

where M_A and M_B are the magnetization of A and B-sites respectively [20]. M_A and M_B can be written with the known of magnetic moments for Ni^{2+} ($2\mu_B$), Zn^{2+} ($0\mu_B$), Mg^{2+} ($0\ \mu_B$), Ti^{4+} ($2\ \mu_B$) and Fe^{3+} ($5\mu_B$), Thus the total magnetization is calculated by the following equation

$$M = \mu_B (7.9+2x-5x) \cos\alpha_{YK} - (3.5-5x)\ \mu_B$$

In view of equation and according to the value of x, the increase of magnetization M up to x = 0.1 could be attributed to the increase of $\cos\alpha_{YK}$, decreasing of α_{YK}, due to the decrease of the negative B-B interaction leading to enhancing the parallelism of moments in B-site. For x > 0.1, a further replacement of Fe^{3+} ($5\ \mu_B$) ions by Ti^{4+} ions ($2\ \mu_B$) and Mg^{2+}($0\ \mu_B$) ions leads to a decreases of the magnetization due to the smaller values of the magnetic moments of Ti^{2+} and Mg^{2+}ions.

The variation of relative permeability (μ_r) with the applied magnetic field is shown in Fig. (6), where μ_r is given by the expression $\mu_r = \dfrac{B}{\mu_o H}$

In general the behavior of relative permeability (μ_r) could be divided into two regions. In the first region the relative permeability (μ_r) increases with magnetizing field until it reaches a maximum value. According to the above expression of relative permeability (μ_r), the increase of relative permeability (μ_r) could be related to the

ordering effect of the spins as a result of the applied field where a very rapid increase in the flux density (B) occurs for small values of H. In the second region the relative permeability (μ_r) decreases with increasing applied field H. In this region the alignment effect of the field continuous but with a small increase of B than that of the first region, accordingly the relative permeability decreases.

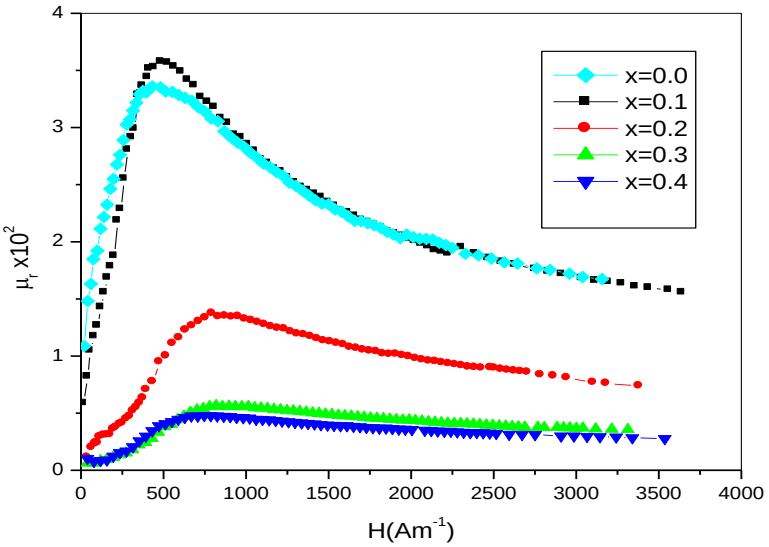
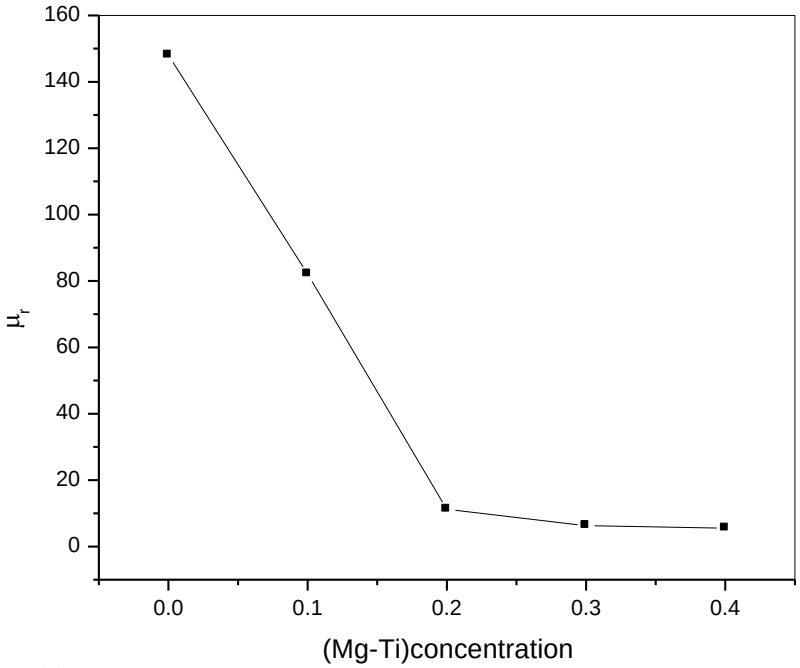


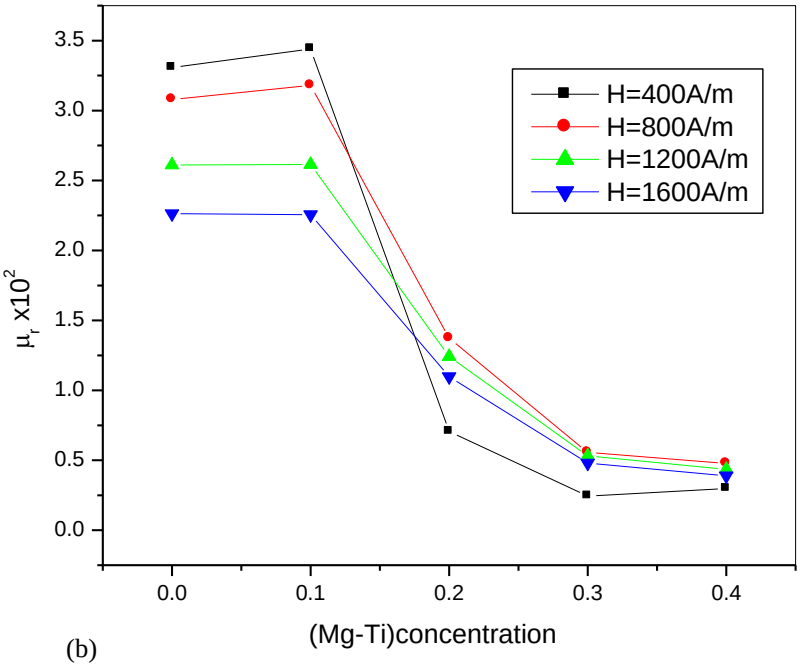
Fig.(6):Variation of the relative permeability (μ_r) with the applied magnetic field (H)

The compositional dependence of the relative permeability (peak value) at small magnetization field (H = 40 A/m)is shown in Fig.(7-a). Its clear from Fig.(7-a) that, as (Mg-Ti) concentration increases the relative permeability decreases due to replacement of the Fe^{3+} (5 μ_B) ions by Ti^{4+} (2 μ_B) and Mg^{2+} (0 μ_B) ions of smaller magnetic moments, leads to a decreases in the magnetization and hence the relative permeability should be decreases.

The compositional dependence of the relative permeability (peak value) at relatively higher magnetization field (H = 400-1600 A/m) is shown in Fig(7-b). Its clear from Fig(7-b) that, The relative permeability (μ_r) has a similar behavior of the magnetization (M) which explained before.


160
140
120
100
80
60
40
20
0
μ_r
0.0
0.1
0.2
0.3
0.4
(Mg-Ti)concentration

(a)



(b)

Fig. (7): Variation of relative permeability with different (Mg-Ti)-concentration
(a)at H=40A/m (b) at different value of H

3.3. Initial Magnetic Permeability (μ_i)

Initial magnetic permeability (μ_i) as a function of temperature for all samples $Ni_{0.7}Zn_{0.3}$ $(Mg\ Ti)_x$ $Fe_{2-2x}O_4$ was studied for (x = 0.0, 0.1, 0.2, 0.3 and 0.4) over the temperature range from room temperature to about 700k as shown in Fig(8). It was found that the curves are typical of multidomain grains showing a sudden drop in initial permeability (μ_i) at Curie temperature (T_c) [21]. The Curie temperature (T_c) of all samples is determined by drawing a tangent to the curve at the point of rapid decrase in initial permeability (μ_i). The intersection of the tangent with temperature axis determines Curie temperature T_c. The sharp decrease in initial magnetic permeability (μ_i) with temperature at Curie temperature (T_c) reflects the homogeneity of the samples [22]. It is clear from Fig(8)that, the initial magnetic permeability (μ_i) increases gradually with increasing the temperature and then drop at a certain temperature T_c.. The drop in the

initial magnetic permeability (μ_i) at Curie temperature(T_c) is due to the magnetic order phase transition from ferrimagnetic to paramagnetic state.

It was reported that the initial permeability can be calculated by approximate equation [23]

$$\mu_i \cong \left(M_s^2 \; D/\sqrt{K_1}\right)$$

where M_s, K_1 and D are saturation magnetization, the magneto crystalline anisotropy constant and the average grain diameter respectively. According to this equation, the initial permeability (μ_i) is directly proportional to M_s^2 and D and is inversely proportional to K_1which results from the presence of Fe^{2+}- ions which formed during the sintering process [24, 25].

The increase of the initial permeability (μ_i) with temperature can be explained in the view of the above equation, as the temperature increase the anisotropy field decreases and also the magnetization decreases with temperature, the anisotropy field seems to decrease much faster than the magnetization, then the initial permeability increase with temperature [26].

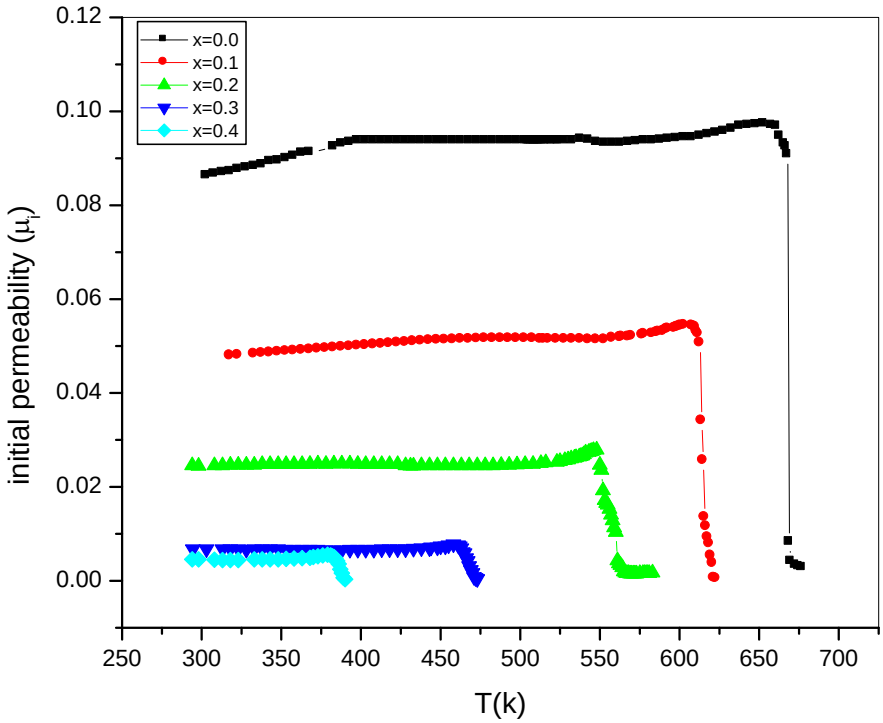


Fig.(8): Temperature dependence of initial permeability (μ_i) for different (Mg-Ti)-concentration

Figure (9) shows the composition dependence of the initial permeability (μ_i) at room temperature. Fig.(9) shows that, the initial permeability (μ_i) decreases with increasing (Mg-Ti) concentration. This behavior can be explained using above equation, as explained before as (Mg-Ti) concentration increases the grain diameter increases and saturation magnetization decreases, also as (Mg-Ti) concentration increases the concentration of Fe^{2+} decreases and consequently the anisotropy constant decreases. The effect of decreasing the saturation magnetization is dominate over the increase of grain diameter and the decreasing in the anisotropy constant which leads to a decreasing in the initial permeability of prepared samples.

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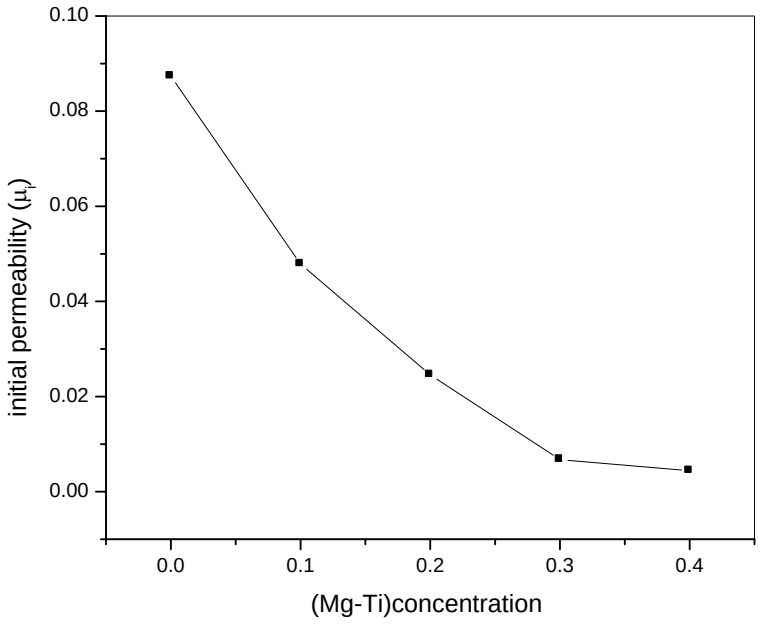

Fig. (Fig.(9): Variation of initial permeability(μ_i)with (Mg-Ti) concentration at room

3.3.1.Curie Temperature

Figure (10) shows the variation of Curie temperature T_c with (Mg-Ti) concentration .The cation distribution of $Ni_{0.7}Zn_{0.3}Mg_xTi_xFe_{2-2x}O_4$ was studied for (x = 0.0, 0.1, 0.2, 0.3 and 0.4), $(Zn_{0.3}Mg_xFe^{2+}_{0.7-x})[Ni_{0.7}Ti_xFe^{3+}_{1.3-x}]$

Its clear from Fig.(10) that, as (Mg-Ti) concentration increases the Curie temperature (T_c) of the prepared samples decreases. The decrease in Curie temperature (T_c) with concentration can be explained in the view of the cation distribution $(Zn_{0.3}Mg_xFe^{2+}_{0.7-x})[Ni_{0.7}Ti_xFe^{3+}_{1.3-x}]$, it's known that the curie temperature depends mainly on the A-B interaction. The strength of this interaction is affected by two factors, the magnitude of the magnetic moments of the ions occupying A and B sites and the distance between the moments on A and B sites. In the present study, the ferromagnetic Fe^{3+} ions (5 μ_B) are replaced by Mg ions(0 μ_B) and Ti ions (2 μ_B), a decrease in the density of magnetic ions and the magnetic moment of the sublattices was expected [27]. Also the increase in lattice parameter with (Mg-Ti) concentration means that the distance between the ions increase, which leads to a decrease in the A-B interaction.

These two factor contribute in the decreasing of the Curie temperature with increasing (Mg-Ti) concentration.

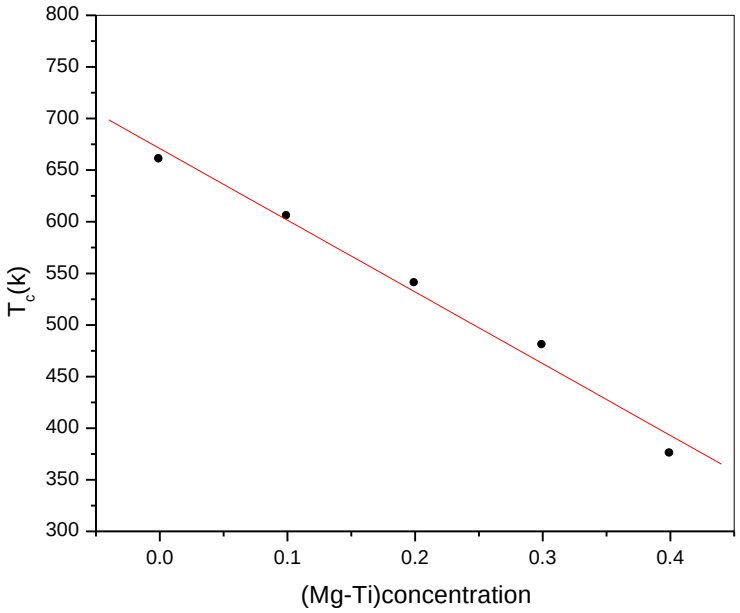

Fig.(10) : Variation of Curie temperature with (Mg-Ti) concentration

3.4. DC Electrical Resistivity :

The dc electrical resistivity of the prepared samples was studied at room temperature. The dependence of electrical resistivity (ρ) at room temperature on the (Mg-Ti) concentration is shown in Fig (10). It is clear that, the substitution of (Mg-Ti) ion leads to increase the resistivity of all investigated samples and hence decreasing the dielectric loss. this behavior could be explained in terms of two factors:

(1) As the (Mg-Ti) concentration increases the concentration of Fe^{2+}-ions decreases and so the hopping probability between Fe^{3+} and Fe^{2+} -ions decreases which leads to increase in the resitivity[9].

(2) The increase of (Mg-Ti)-concentration leads to increase the intragranular porosity which in turn hinders the motion of charge carriers producing an increase of resistivity (ρ).

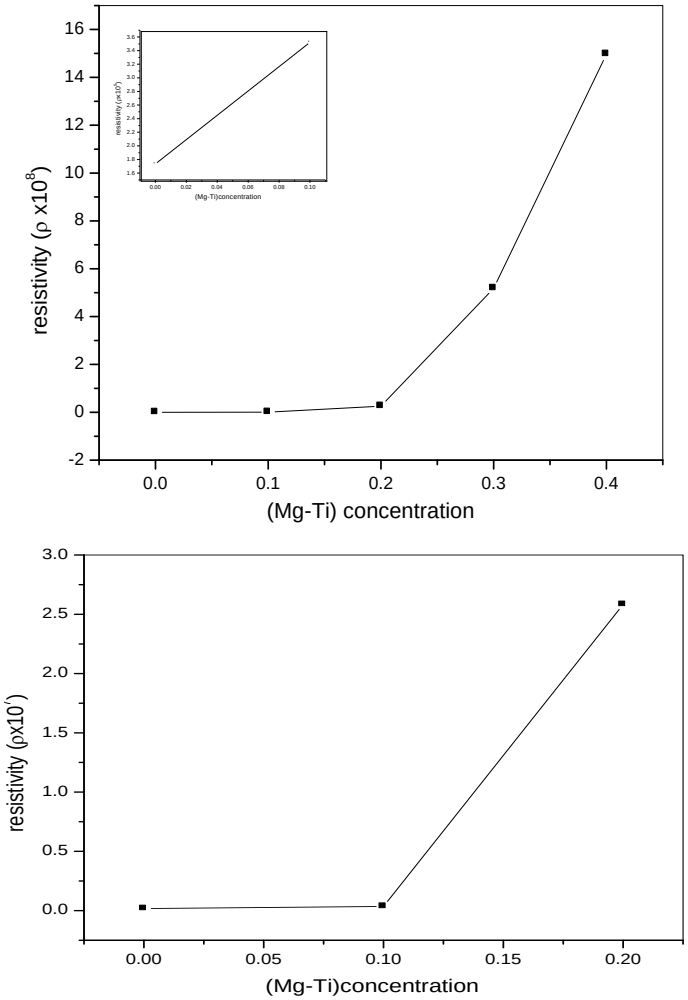

Fig. (10): Variation of resistivity with (Mg-Ti)-concentration at room temperature

4. Conclusions

1-The lattice parameter of Ni-Zn ferrite substituted by (Mg,Ti) ions increases with increasing Mg,Ti concentration. The increase in the lattice parameter is based on the larger ionic radius of Mg^{2+} and Ti^{4+} ions than Fe^{3+} ionic radius.

2- As (Mg-Ti) concentration increases, the value of saturation magnetization, initial permeability and Curie temperature were decrease, this decrease was explained on the basis of magnetic moment of ions.

3-The dc resistivity of prepared samples was found increased with increasing (Mg-Ti) concentration and hence decreasing the dielectric loss.

4- The sample $Ni_{0.7}Zn_{0.3}Mg_{0.1}Ti_{0.1}Fe_{1.8}O_4$ shows high resistivity (ρ = 3.5x10^5 Ω.cm),low dielectric loss, high Curie temperature(T_c = 605 k) and high magnetization.

5- Also the sample $Ni_{0.7}Zn_{0.3}Mg_{0.2}Ti_{0.2}Fe_{1.6}O_4$ shows a very high resistivity (ρ = 2.58x10^7 Ω.cm),low dielectric loss, relatively high Curie temperature(Tc = 540 k) and magnetization.

6- The samples of x = 0.1 and 0.2 show high resistivity and relatively high Curie temperature which can be exploited in a certain technical application.

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تاثير احلال كلا من التيتانيوم والمغنيسيوم على الخواص الفيزيائية للنيكل–زنك فريت

تاثير احلال كلا من التيتانيوم والمغنيسيوم على الخواص التركيبية والمغناطيسية والكهربية للنيكل–زنك فريت بالصيغة الكيمائية
$Ni_{0.7}\ Zn_{0.3}\ (Mg\ Ti)_x\ Fe_{2-x}O_4$ حيث (x تتغير من 0 الى 0.4 بتدرج قيمته 0.1)
التى اعدت بطريقة السيراميك المعتادة .وتمت دراسة الخواص التركيبية باستخدام حيود الاشعة السينية ووجد ان زيادة التركيز (Mg-Ti)
يؤدى الى انخفاض قيمة مغنطة التشبع والنفاذيةالاولية ودرجة الحرارة كورى .
ووجد ايضا ان زيادة التركيز (Mg-Ti) يؤدى الى زيادة المقاومة النوعية وبالتالى تقليل المفاقيد للعينات التى درست .واشارت هذه الدراسة ايضا الى ان عينة $x = 0.1, 0.2$ لها مقاومة عالية وخواص مغناطيسية مرتفعة نسبيا يمكن استغلالها فى تطبيق تقنية معينة.