Effect of M²⁺ substitution on properties of the system $Ni_x Zn_{1-x-y} M_y Fe_2O_4$

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ABSTRACT

The four types of ferrites have been prepared by co-precipitation technique(**Ni Zn Fe₂O₄,Mg Fe₂O₄,Mn Fe₂O₄, Cd Fe₂O₄**). The prepared ferrites were sintered at 800C°. Then using the these types of ferrite to prepared the final Synthesis $Ni_x Zn_{1-x-y} M_y Fe_2O_4$ wereM²⁺=(Mg,Mn,Cd)
with (X=0.3),(Y=0.4) to be six samples halve of these as pressed pellets (12.3 mm diameter, 5-4mm thickness)and later halve as triodes (R_{in}=9.85mm,R_{out}=19.4mm). All of them were sintered at (1100 °C) for (2 hr). (XRD) Technique was used to study the structure of matrix $Ni_x Zn_{1-x-y} M_y Fe_2O_4$, the apparent density , and porosity were calculated, The electrical characteristics for these samples included the measure of A.C current as the dielectric constant was calculated ($\acute{\epsilon}$) ,loses factor(tan δ) was measured at the same frequency range(20Hz - 3MHz)to calculate the imaginary part of dielectric constant and also the magnetic properties was measured by the same equipment, (*initial permeability* μ) was calculate after measuring the inductors(L), the VSM Technique was used to study hysterics lope behavior of these samples.

1. INTRODUCTION

Spinal ferrite possess unique electrical and magnetic properties for wide range of technological application .the general formula of spinal ferrite is represented by AB_2O_4 and it possesses 64 tetrahedral sites (A-sites) and 32 octahedral sites (B-sites)[1].
Manganese-Zinc Ferrites are the most common, and used in many more applications than the nickel-zinc ferrites. The MnZn category a large variety of materials is possible .The material selection is mainly a function of the application that needs to be accommodated. The application dictates the desirable material characteristics, which in turn determines the chemical composition of the ferrite material. Manganese zinc ferrite is primarily used for frequencies less than 2MHz . But Nickel-Zinc Ferrites this class of soft ferrites is characterized by its high material resistivity several orders of magnitude higher than MnZn ferrites. Because of its high resistivity Ni Zn ferrite is the material of choice for operating from l-2 MHz to several hundred megahertz. Also magnesioferrite ($MgFe_2O_4$) is one of the most interesting, because, due to its small magneto crystalline an isotropy .To cover such a wide frequency range and different applications, a large number of nickel-zinc materials have been developed over the years by mixing together, also Ni-Zn polycrystalline ferrites(NZF)are low-cost materials that are attractive for microwave device applications ,with spinel structure has a promising potential as high performance microwave devices owing to its high resistivity, mechanical hardness, high Curie temperature, chemical stability, and soft magnetic properties at high frequency. It is well known that the intrinsic parameters of these ferrites depend on the composition, Properties of ferrites are known to be sensitive to the processing technique[2]. The tailoring grain structure with electrical characterization such as that electrical resistivity decreasing with increasing of sintering temperature[3]. All these ferrites have been widely used in electronic applications such as transformers, choke coils, noise filters, and recording heads. By introduction of a relatively small amount of foreign ions, an important modification of both structure and magnetic properties can be obtained [3,4]. The electrical resistivity of ferrite at room temperature depending upon the chemical composition which lies between about 10^3- 10^8 Ohm-

cm. Low resistivity due to hopping of bonding electrons are caused by the simultaneous presence of Fe^{3+} and Fe^{2+} ions on crystallographically equivalent lattice sites. The resistivities of several ferrites are found to depend sensitively on firing conditions, temperature atmosphere and on the ions that substitute Fe^{3+} / Fe^{2+} ions. Ferrites with the properties as resistivity, low coercivity and low eddy currents are being used for a variety of high frequency applications. Substitution of divalent ion in to the spinel structure has been reported to lead to structural distortion. That induces strains in the material and to affect the electrical and magnetic properties significantly. There are several synthesis techniques such as solid-state reaction method, hydro- thermal method, precipitation/co-precipitation method and sol–gel auto- combustion method for the preparation of nanoferrites. Among these processes, co-precipitation has lately shown to be a very promising technique for the preparation of ultrafine ferrite particles of controlled size and morphology with a number of applications[5, 6]**.** Most of the work on the preparation of ferrite through hydrothermal processing has been carried out using (NaOH)   and the major impurity present [7].

2. EXPERIMENTAL

The powders of Ni Zn - ferrites, Mg- ferrites ,Mn-Ferrite ,Cd-Ferrite were prepared using Co-precipitation The pH of the solution was adjusted to 7.5-8.5 using aqueous ammonia to avoid incorporation of sodium when using NaOH. The solution was uniformly heated at 80 ˚C with constant stirring to transform it into a gel and then filtered gel was obtained by dehydration process.. The prepared powder was then calcined at 800˚C.Four types of ferrite were synthesized which are Ni Zn - ferrites, Mn - ferrites , Mg- ferrites ,Cd- ferrites to formed final production with composition $Ni_x Zn_{1-x-y} M_y Fe_2O_4$ x=(0.3,) y=(0.4), by mixing every one with properly construction of(x and y)- value ,then it was pressed(5tons/Cm^2) as rings and (3tons/Cm^2)as pelts. the temperature of final sintering in this case was kept at1100 ˚C .The pellets samples were well polished to remove any roughness and the two surfaces of each pellet were coated with silver paste as contact material for electrical and dielectric measurements. Using *L.C.R type* **(micro test 6379),**dielectric measurement as a function of frequency in the range(20 Hz–3MHz) at room temperature. The real part of dielectric constant was calculated using the formula,

$$\varepsilon r = \frac{C\,d}{\varepsilon^{\circ} A}$$

(1)

where *C* is the capacitance measured of the pellet in pF, *d* the thickness of the pellet, *A* the cross-sectional area of the flat surface of the pellet and ε° the constant of permittivity for free space.
The imagery dielectric constant($\acute{\varepsilon}$) and loses factor(tan δ) was measured at the same frequency range(20Hz-3MHz)to calculate the imaginary part of dielectric constant using the formula,

$$\text{Tan}\delta = \varepsilon i\,/\,\varepsilon r$$

(2)

The magnetic properties was measured by the same equipment (initial permeability μ), which was calculated after measuring the inductors(L),using the formula, that

$$\mu i = \frac{L}{L^{\circ}};$$

(3)

L_o=4.6 N^2 d Log(r_{out}/r_{in})*10^{-9}
where r_{in} is the inner radius , r_{out} is the outer radius, and d is thickens of samples. L= the inductors of sample, N=the numbers of turns.

3.   RESULTS AND DISCUSSION

3.1. XRD Pattern

The phase identification and lattice constant determination were performed by x-ray diffraction pattern (XRD). Typical XRD pattern of ferrites sample is shown in Fig.(1),(2)and(3).
All the samples show good crystallization, with well-defined diffraction lines The structure can be indexed as a single-phase cubic spinel structure. It is obvious that the characteristic peaks for spinel ferrites appear in the samples as the main crystalline phase. The peaks (2 2 0), (3 1 1), (2 2 2), (4 0 0),(4 2 2), (5 1 1) and (4 4 0) correspond to spinal structure, The lattice parameter(a), and crystal Density were Calculated by the relation**,**

$$Dx = \frac{8M}{Na^3} \tag{4}$$

then porosity p% will be Calculated by the formula,

$$.P = 1 - \frac{DB}{Dx} \times 100\% \tag{5}$$

where D_B is the bulk density , $D_{x.}$: the crystal density

Table (1)X-value for sample No. with some Parameter calculated by XRD test

M^{2+}-Type	Y-Value	X-Value	Lattice Parameter (a) Å	Crystal density D_x (g/Cm^3)	Bulk density D_B(g/Cm^3)	Porosity P%
Cd^{2+}	0.4	0.3	8.7	5.03	3.77	22%
Mg^{2+}	0.4	0.3	8.781	4.28	3.3	24%
Mn^{2+}	0.4	0.3	8.77	4.63	3.75	18%

the lattice parameter '*a*' as a function of M^{2+} content *y* is depicted in table (1). It is noticed that the most lattice parameter when the Magnesium content in the lattice. This variation can be explained on the basis of an ionic size difference of the component ions. The Mg^{2+} ions have a smallest ionic radius (0.24Å) than the Zn^{2+} ,$Ni^{2+} \approx$ (0.65 Å) ions [8]. The Mg^{2+} ions successively replace the Ni^{2+} & Zn^{2+} ions in B-site. The unit cell expands to accumulate the smallest ions. Thus addition of Mg^{2+} at the expense of the Ni^{2+} & Zn^{2+} in the ferrite is expected to decrease the lattice parameter while Cd^{2+} ion inter at the same pleas of Zn^{2+} ion in lattice .

3.2. Real & imaginary part of dielectric constant (ε_r ,ε_i) :

The dielectric behavior in ferrite can be explained based on the assumption that the mechanism of dielectric polarization is similar to that of conduction. Many scientists have established a strong correlation between the conduction mechanism and dielectric constant of ferrite [9,10].In the studies, they have explained the dielectric behavior based on a number of available Fe^{2+} ions. The electronic change such as $Fe^{2+} \leftrightarrow Fe^{3+}$ results in a local displacement of electron, which determines the polarization and thus the dielectric constant of ferrite .we observed that from Fig.(4) which shows the variation of the(ε_r)behavior with increasing frequency , Fig.(5) which shows the dielectric dispersion curves can be explained on the basis of Koop's two layer model and Maxwell-Wagner polarization theory. To interpret the frequency response of dielectric constant in ferrite and dielectric materials , Koop's [11] suggests a theory in which relatively good conduction grains and isolating grain boundary layers of ferrite material can be represent with the behavior of an

inhomogeneous dielectric structure. A assembly of space charge carriers in the inhomogeneous dielectric structure, is discussed by Maxwell and Wagner [9].Since an assembly of space charge carrier in the inhomogeneous dielectric structure described requires finite time to line up their axis parallel to an alternating electron field, the dielectric constant naturally decrease, if the frequency of reversal field increases, that

$$\tau = \frac{1}{2\pi\, f_{max}}$$ where τ: the relaxation time; f_{max}: the maximum frequency

3-3.A.C Conductivity

Figs (6) shows the variation of a.c conductivity behavior with frequency for $Ni_{0.3}Zn_{0.3}M_{0.4}Fe_2O_4$ systems at room temperature in the range of about (20 Hz-3MHz), with three of M^{2+} divalent type .According to Maxwell- Wagner theory, two layers forming dielectric structure. The first layer consist of ferrite grains of fairly well conducting (ferrous ions), which is separated by a thin layer of poorly conducting substances, which forms the grain boundary. These grain boundaries are more active at lower frequencies; hence, the hopping frequency of electron between Fe^{3+} and Fe^{2+} ions is less at lower frequencies. As the frequency of the applied field increases the conductive grains become more active by promoting the hopping of electron between Fe^{2+} and Fe^{3+} ions, thereby increasing the hopping frequency. Thus, we observe a slight increase in conductivity with frequency.

3-4. Vibrating Sample Magnetometer (VSM)

Figure 7 shows the magnetic hysteresis loops of $Ni_{0.3}Zn_{0.3}\,M_{0.4}\,Fe_2O_4$ samples taken by vibrating sample magnetometer at room temperature showing typical magnetic behavior having a non-zero coercivity and remanance. The value of magnetic saturisation, coercivity and remanance that Concluded was shown at table No.(2) . Low area hysteresis curve shows that the material formed is of soft magnetic material [12] .

In this work an effort was made to synthesize ferrite powder by a very simple process of co-precipitation which gained a reasonably incredible success, resulting good magnetic properties as shown by hysteresis curve.

### 3-5. Magnetic Permeability (μ_i)

Figs.8 shows variation the behavior of real part of permeability as a function of frequency. As its clear from figs.8 permeability decrease with increased frequency, that's due to the relation between magnetic inductance and frequency which act as the major caused in this decrease, whereas increasing frequency caused dipoles oscillations more aligned, that's cause inverse current, so that the inductance current decrease abruptly at low frequency, then changes become very small as its clear seem behavior for all samples.
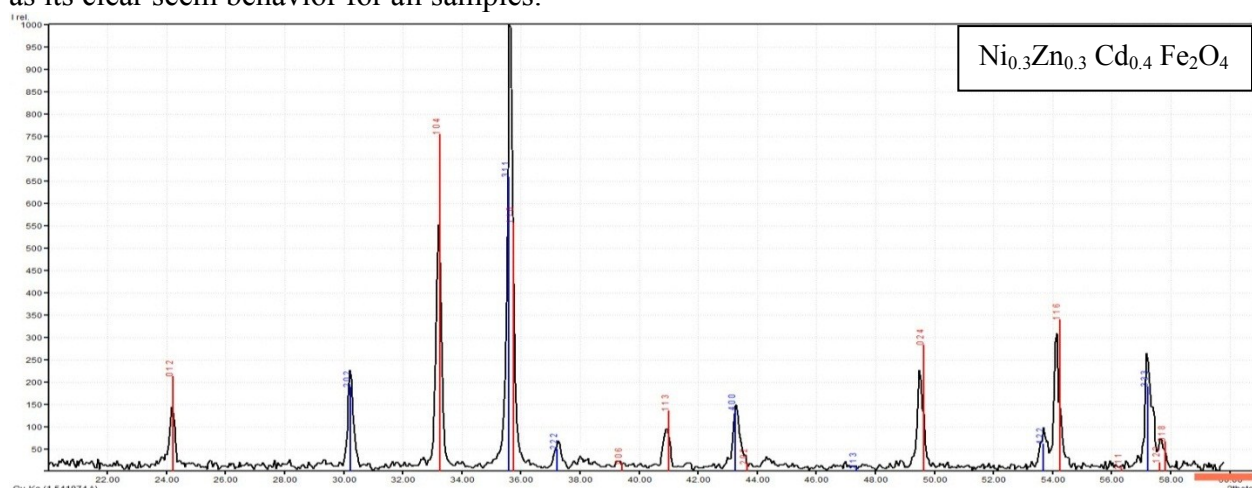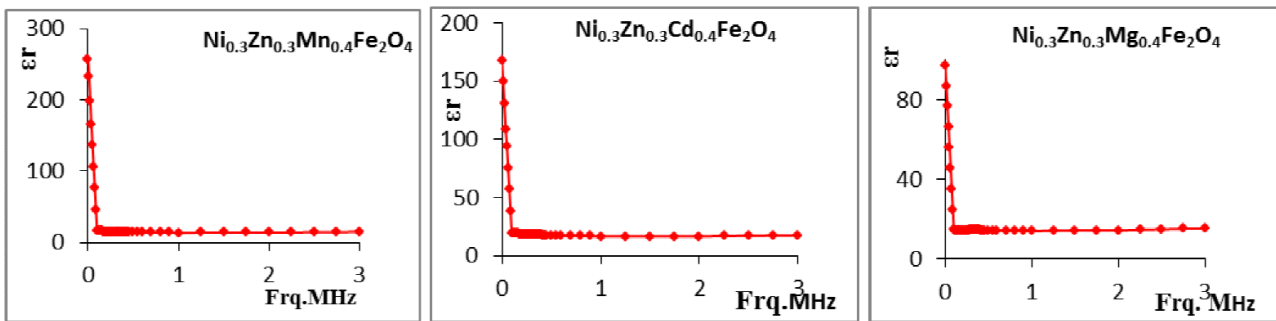

Fig(1)XRD test for $Ni_{0.3}Zn_{0.3}\,Cd_{0.4}\,Fe_2O_4$
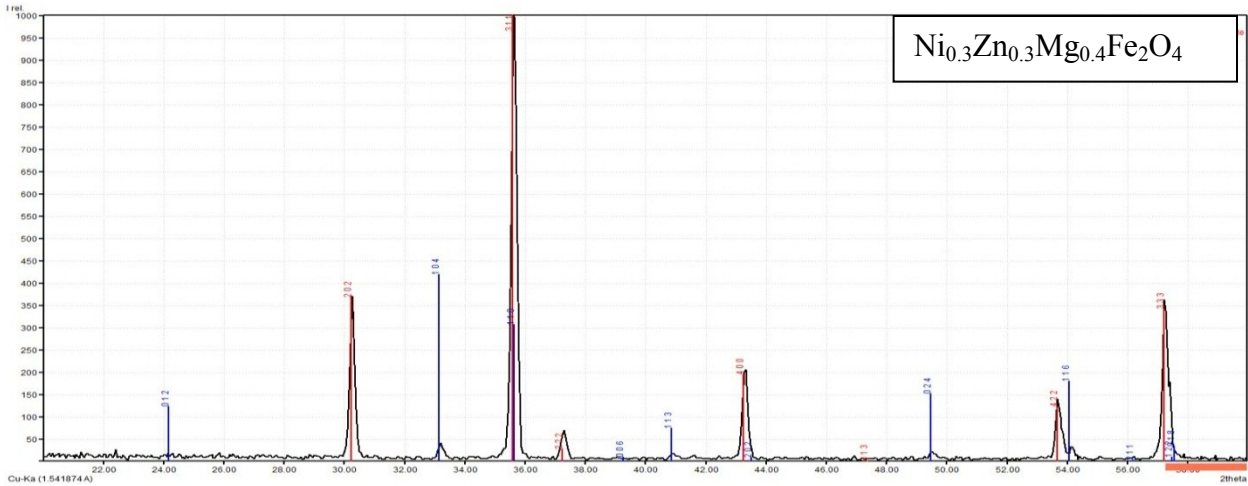
Fig(2)XRD test for Ni$_{0.3}$Zn$_{0.3}$Mg$_{0.4}$Fe$_2$O$_4$
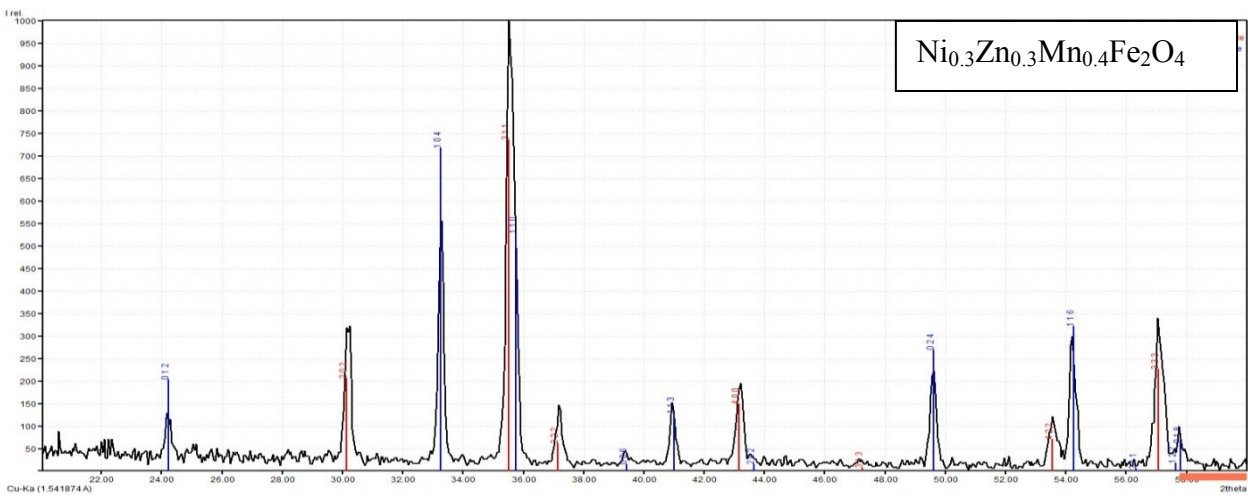
Fig(3)XRD test for Ni$_{0.3}$Zn$_{0.3}$Mn$_{0.4}$Fe$_2$O$_4$

Fig(4) Variation of dielectric constant behavior with frequency for Ni$_{0.3}$Zn$_{0.3}$M$_{0.4}$Fe$_2$O$_4$system
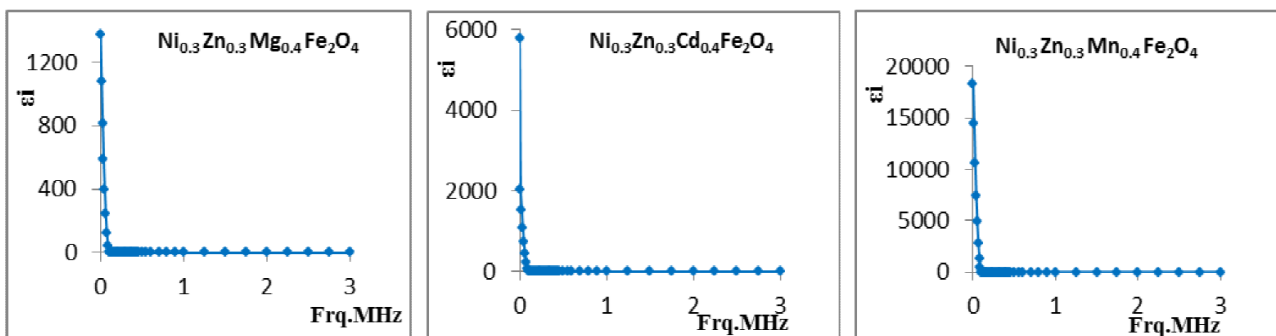
Fig (5)Variation of dielectric loss factor behavior versus frequency for Ni$_{0.3}$Zn$_{0.3}$M$_{0.4}$Fe$_2$O$_4$system
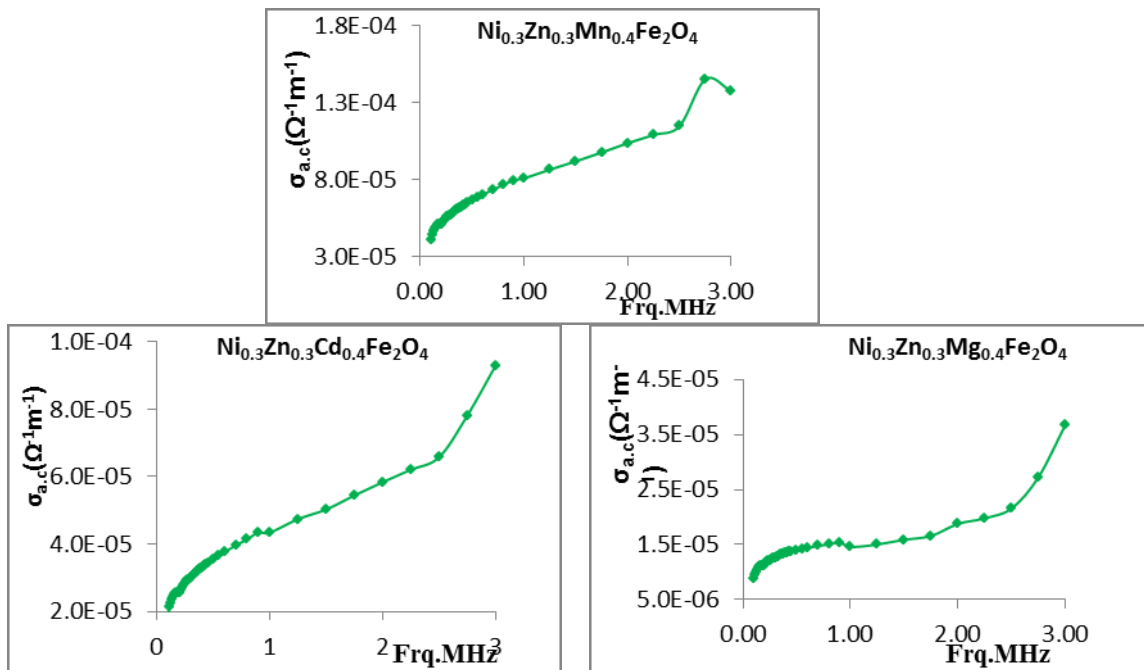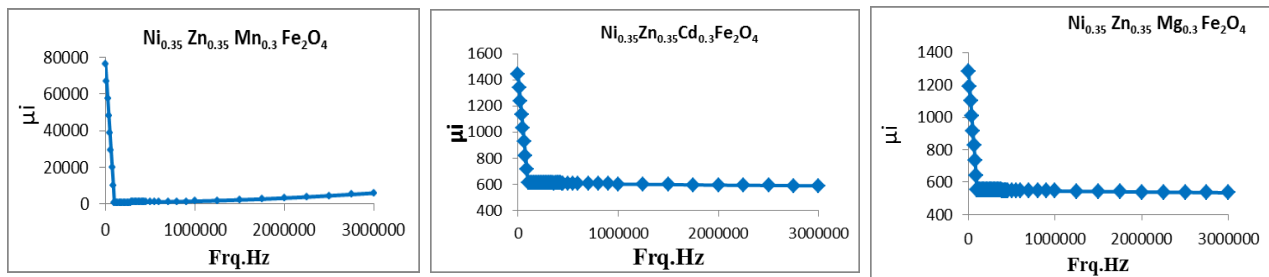
Fig(6) Variation of (AC)conductivity ($\sigma_{a.c}$) behavior with frequency for $Ni_{0.3}Zn_{0.3}M_{0.4}Fe_2O_4$ system
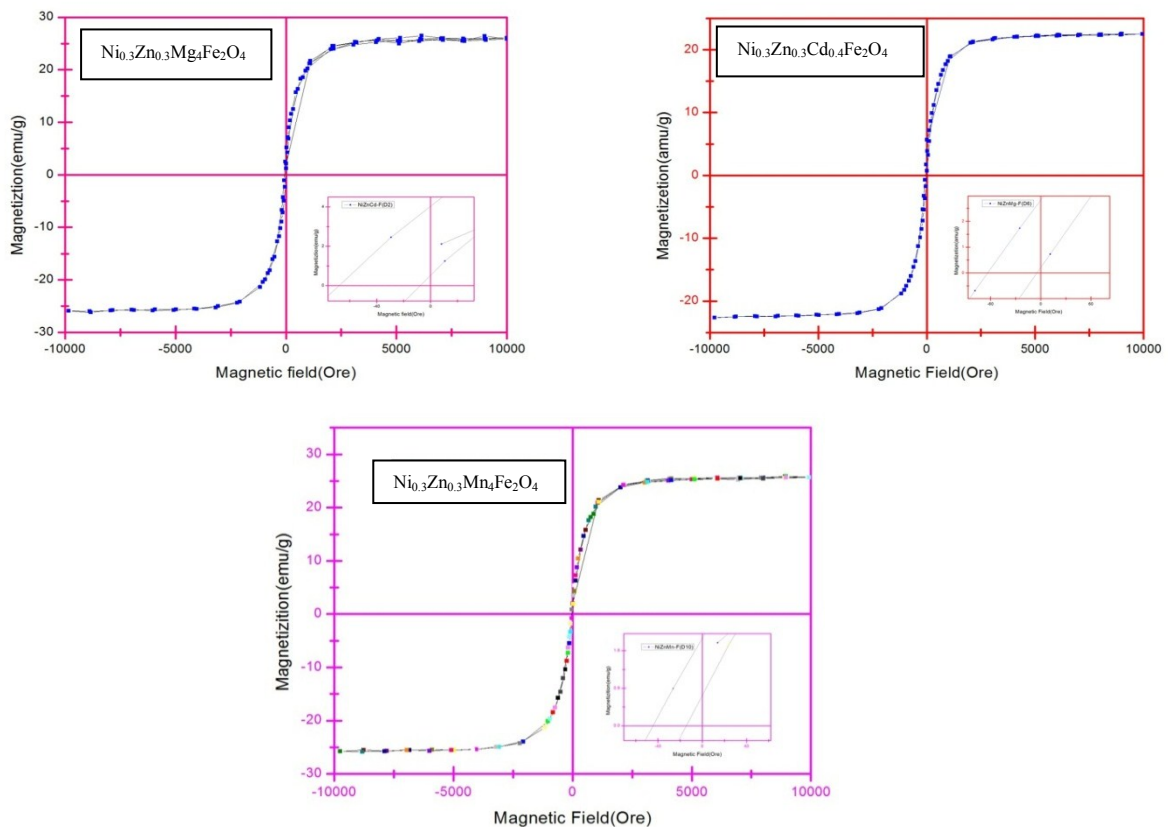
Fig(7) Variation of(VSM)for $Ni_{0.3}Zn_{0.3}M_{0.4}Fe_2O_4$ system

Table (2)Show the magnetic parameter which calculated from hysterics lope diagram

Samples parameter	$Ni_{0.3}Zn_{0.3}Mn_{0.4}Fe_2O_4$	$Ni_{0.3}Zn_{0.3}Cd_{0.4}Fe_2O_4$	$Ni_{0.3}Zn_{0.3}Mg_{0.4}Fe_2O_4$
σ_s	25.672	26.103	22.24
σ_r	2.078	4.05	2.76
H_c	15	30.1	29.56

Fig(8) Variation of for initial permeability $Ni_{0.3}Zn_{0.3}M_{0.4}Fe_2O_4$ system

4. CONCLUSION

For all samples the dielectric constant values affected where increases and decreases by change the proportion n of added Y-value and the type of added M^{2+} as well as change frequency applied, also not affected by behavioral fixed dielectric dispersion curves Change added lineage, but the change in values match as an increase or decrease to a large extent with changes that occur in the real dielectric constant ,as in the previous point of the three types of ions M^{2+} Added in all the frequencies used. Despite the high values of dielectric constant (ε_r) models, but they are excluded from use as insulation industry capacitor due to lack of ability to maintain storage of cargo for a long time, because of the ownership dielectric dispersion factor was high (tanδ, ε_i), but can be used to electromagnetic radiation, especially if This factor agree with high dispersion factor magnetic (Power losses density). So this compatibility and harmonization coincides with the spectrum of electromagnetic frequencies and by the fact that the specific electromagnetic wave will interact with material absorbed her magnetic and electric dimension factor do not have the materials in the nature of these rare qualities, as ferrites materials.

Affected heavily magnetization measurements and hysterics loop   which include saturation magnetization and coercive force and residual magnetization in terms of value, but should remain its behavior as soft ferrite. Magnetic permeability values the addition of manganese is the highest in all frequencies applied and this is consistent and previous research.

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