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The Effect of Zn^{+2} Substitution on Properties of the System ($M_xCo_{1-x}Fe_2O_4$)

[1]Nahedh H. Alwash and [2]Raheem abed Jeber
[1]Department of Physics, College of Science, Al-Muthana University, Sanawah, Iraq
[2]Department of Physics, College of Education,University of Al-Qadisiyah, Al Diwaniyah, Iraq

Abstract: The (co-precipitation) method is used to prepare two types of ferrite ($CoFe_2O_4$, $ZnFe_2O_4$). Precursor materials ($ZnCl_2$ $CoCl_2.6H_2O$), mixed with iron chloride ($FeCl_3$). The prepared powder of ferrites were primary sintered at 800°C for 2 h XRD technique were used to study the structure of two types ferrite prepare. Then using these types of ferrite to prepare finely synthesis ($Zn_xCo_{1-x}Fe_2O_4$) with (x = 0.2, 0.4, 0.6, 0.8) to be 8 samples halve of these were pressed as pellets (12.3 mm diameter, 5-4 mm thickness) then later halve as triodes (R_{in} = 9.85 mm, R_{out} = 19.4 mm) by hydraulic press at pressure (3-5 tons), all of them were sintered at (1100°C) for 2 h. Bulks densities were measured, DC measurements were used to determine electrical resistivity (ρ), AC measurements real part and of dielectric constant, initial permeability (ε_r', μ_i) were calculated, the study is show that, the x increase lead to decrease the density. Electrical resistivity has minimum value for x = 0.4. Real part of dielectric constant decrease sharply with increasing frequency to reach 100 kHz then the decrease is reducing.

Key words: Co-precipitation, ferrites, permittivity, initial permeability, measurements, pressure

INTRODUCTION

These ferrites have been widely used in electronic applications such as transformers, choke coils, noise filters and recording heads. Spinal ferrites have been regarded as more superior magnetic materials than pure metal due to their high resistivity, higher efficiency and lower cost. By introduction of a relatively small amount of Foreign ions an important modification of both structure and magnetic properties can be obtained (Verma *et al*., 2000; Rezlescu *et al*., 1992). Cobalt ferrites in bulk exhibit inverse spinal structure with one half of Fe^{3+} ions in the A sites and the remaining half of Fe^{3+} ions occupying the B sites along with Co^{2+} ions. The magnetic properties of bulk $CoFe_2O_4$ ferrite are found to be sensitive to the distribution of the transition metal ions among the cationic sites in the spinal structure (Rezlescu *et al*., 1992). Properties of ferrites are known to be sensitive to the processing technique (Paulsen *et al*., 2003; Alwash *et al*., 2016). A small deviation in the compositional stoichiometry of the ferrite affects its properties greatly. 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 (Tung *et al*., 2003). There are several methods of preparation of fine powder including hydrothermal synthesis, precipitation/co-precipitation, sol-gel processes, etc. 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 (Tung *et al*., 2003). Most of the work on the preparation of ferrite through hydrothermal processing has been carried out using (NaOH) and the major impurity present (Verma *et al*., 1999). The aim of this reserch was to evaluate the influence of the various Zn ions on the ceramic parameters of a Co-ferrite the dielectric and magnetic properties.

MATERIALS AND METHODS

Preparation soft ferrite: The powders of two types ferrites (Co and Zn-ferrites) was done by co-precipitation. Using high-purity $CoCl_2.6H_2O$, $ZnC_4H6O_4.2H_2O$ and $FeCl_3$ as starting materials.

Each one dissolved in 400 mL distil water, ferrites have been synthesized using aqueous ammonia to avoid incorporation of sodium. Control of synthesis parameters has resulted in the production of ferrite particles having a meta stable cation distribution as revealed from micro structural and magnetic studies. The pH of the solution was adjusted to 7-9 using ammonia solution. 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 dried gel was combusted with the evolution of large amount of gases and it resulted in the formation of loose powder. The solution filtered, washes with deionized water several time and dried at

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Corresponding Author: Nahedh H. Alwash, Department of Physics, College of Science, Al-Muthana University, Sanawah, Iraq

200°C for 24 h. The precipitated particles grinded using agate mortar and pestle, these particles were subsequently sintered at 800°C for 4 h then cool to room temperature, the mixture grinded again for 4 h to have very fine particles of $CoFe_2O_4$. Same steps were done to obtain $ZnFe_2O_4$. The crystallite structures of the prepared samples were studied by using, Philips PW 1710 X-ray diffractometer with a Cu-Kα radiation source (λ = 1.5405 A), two types of ferrite were synthesized which are of Co and Zn-ferrites to formed final production with composition ($M_xCo_{1-x}Fe_2O_4$), x = (0.2, 0.4, 0.6, 0.8) by mixing every one with properly construction of x-value, then it was pressed (5 tons/cm^2) as rings (Rn) and (3 tons/cm^2) as pelt (Dn). The temperature of final sintering in this case was kept at 1100°C. The bulk density have been calculated for pellet samples then 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 LCR type (micro test 6379), dielectric measurement as a function of frequency at the range (20 Hz-3 MHz) at room temperature. The real part of dielectric constant was calculated using the equation (Abbas *et al*., 2007) (Eq. 1):

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A} \qquad (1)$$

Where:

ε_o = The 8.85×10^{-12} F/m (dielectric constant of vacuum)
A = The plate area of samples (m^2)
d = Thickness of samples (m)
C_P = Parallel electrical capacitance (F)

Also, the magnetic properties was measured by the same equipment (initial permeability μ_i) was calculate after measuring the inductors (L) then by using the Eq. 1 (Hussien, 2011):

$$\mu_i = \frac{L}{L_o} \qquad (2)$$

Where:

L_o = The 4.6×10^{-9} N^2 d Log (r_{out}/r_{in})
r = The inner radius and rout is the outer radius
d = Thickens of samples
L = The inductors of sample
N = The numbers of turns

RESULTS AND DISCUSSION

Structural characteristic: Typical XRD pattern of ferrites sample $CoFe_2O_4$ and $ZnFe_2O_4$ sintered at temperature 800°C is shown in Fig. 1 and 2, good crystallization with well-defined diffraction lines the structure can be indexed as a single-phase cubic spinal structure. It is obvious that the characteristic peaks for spinel ferrites appear in the samples as the main crystalline phase. Density of samples sintered at 1100°C determined from the relationship (Verma *et al*., 2000):

$$D = m/v$$

Where:

D = Density of samples (g.cm^{-3})
m = Mass of samples (g)
v = Volume of samples (cm^3)

It's clear from Fig. 3, the density of samples increase with increase percentage $ZnFe_2O_4$ in the system $Zn_xCo_{1-x}Fe_2O_4$ that's due to the atomic weight of zinc ions (Zn^{+2}) higher than the atomic weight of cobalt ions (Co^{+2}), so, the increase in percentage (Zn^{+2}) leads to increase density.

Electrical measurements

AC measurements

Permittivity spectra: Real part of dielectric constant calculated using the Eq. 1. Values of C_P measured using LCR meter device at range frequencies (20 HZ-3 MHZ). All measurements taken at room temperature. Figure 4 shows variation in real part of dielectric constant as a function of frequency at range (20 HZ-100 kHZ) and for every samples variation at range (20 HZ-3 MHZ) represented in Fig. 5-7 observe the behaviors real part of dielectric constant (ε_r) a small variations at high frequencies for all samples.

DC measurements: Electrical resistivity was calculated using Eq. 3:

$$\rho = \frac{RA}{d} \qquad (3)$$

Where:

R = The resistance measured by high resistance meter device (Ω)
A = The samples area (m^2)
d = Thickness of samples (m)

All measurements taken at room temperature (Fig. 7). The relation between electrical resistivity versus x-value is an inverse proportionality between resistivity and dielectric constant and the maximum value of ε_r' were at x = 0.4 which corresponding with minimum value of resistivity. Figure 4 shows frequency dependence of $Zn_xCo_{1-x}Fe_2O_4$ permittivity. The decrease of the permittivity with an increase of frequency is a normal dielectric behavior of ferrites. The positive ions Co^{+2}, Zn^{+2} and Fe^{+3} at their respective positions form the electric dipoles with the surrounding negative O^{-2} ions,

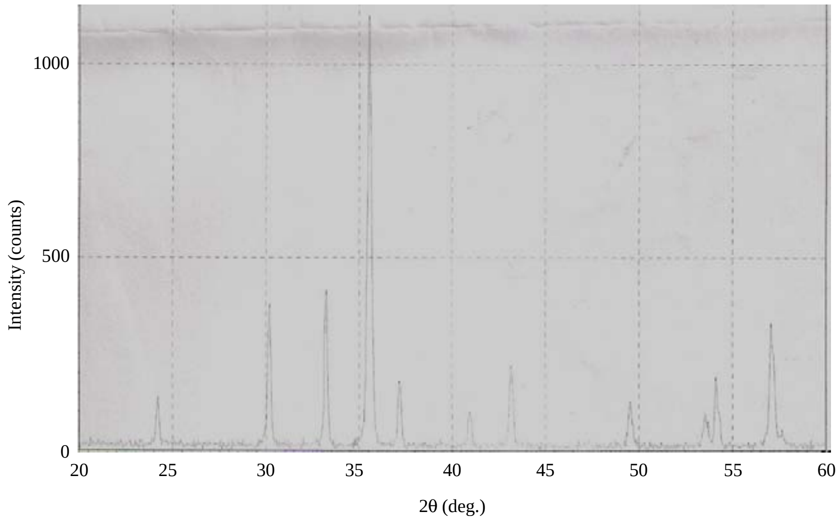

Fig. 1: XRD pattern of $CoFe_2O_4$ treated at 800°C

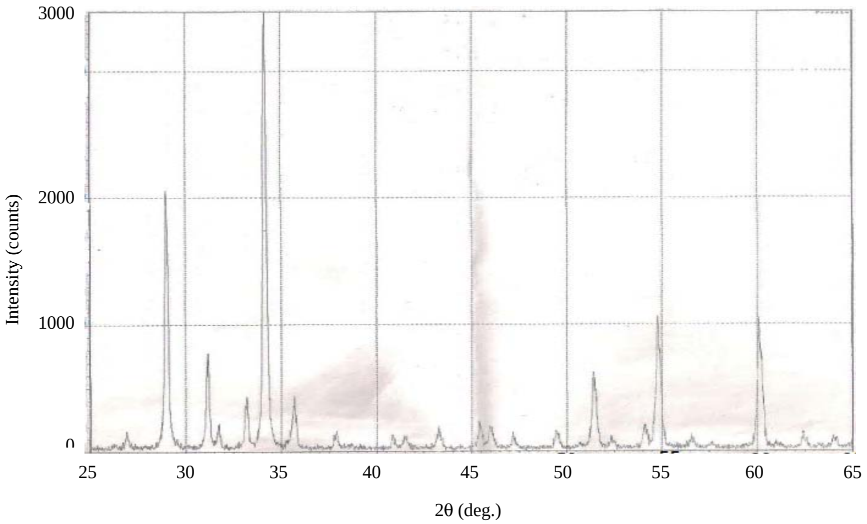

Fig. 2: XRD pattern of $ZnFe_2O_4$ treated at 800°C

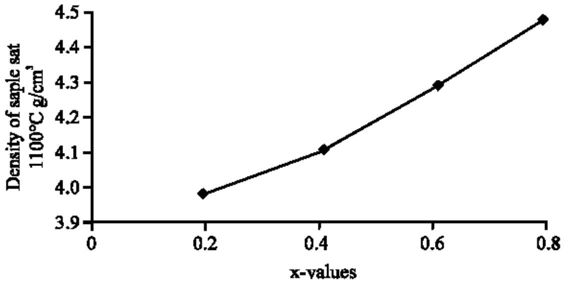

Fig. 3: The relation between density versus x-value

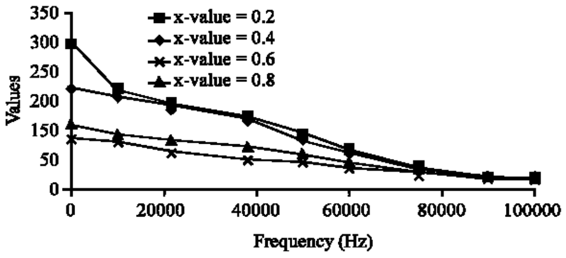

Fig. 4: The relation between ε_r' versus frequency at range (20 Hz-100 kHz)

contributing to dielectric constant (ε_r) through dipolar polarization and by dipole relaxation to dielectric loss (ε_r'') (Verma *et al*., 2000). Figure 5 shows dielectric constant values decrease sharply with increased frequency at range (20 kHz-3 MHz) that's due to the four polarization mechanism (electronic, ionic, orientational and space

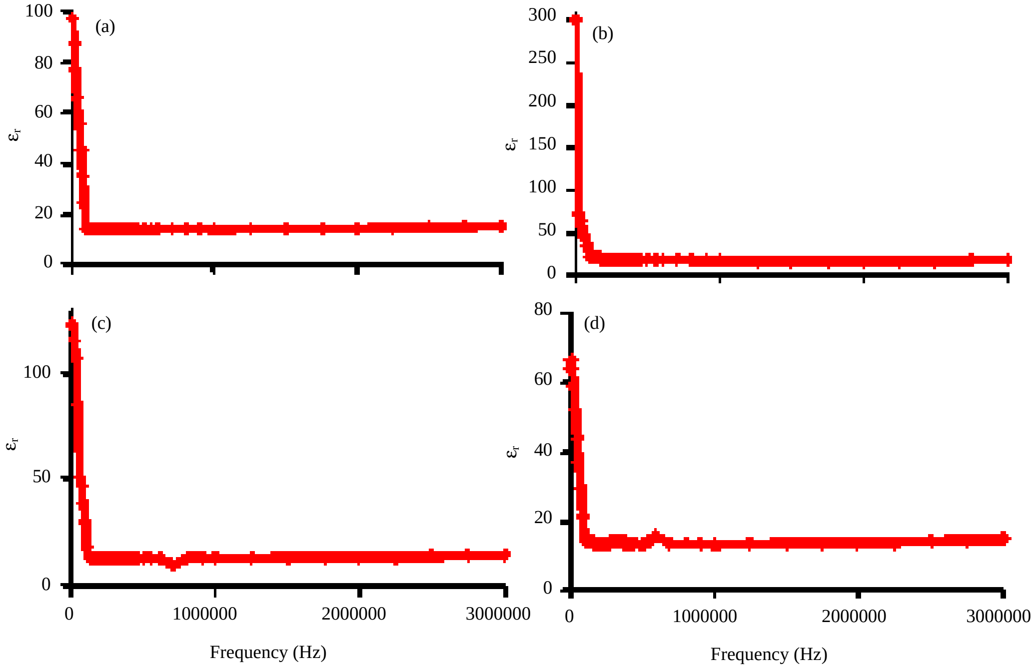

Fig. 5: The relation between ε_r' versus frquency at range (20 Hz-3 MHz): a) x-value = 0.2; b) x-value = 0.4; c) x-value = 0.6 and d) x-value = 0.8

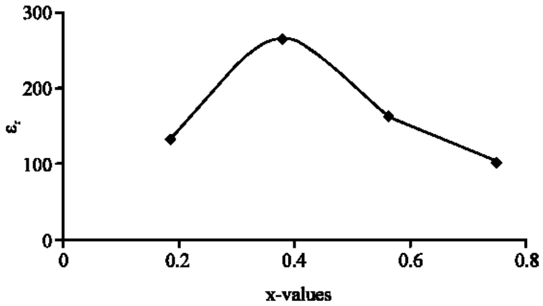

Fig. 6: The relation between ε_r' versus x-value

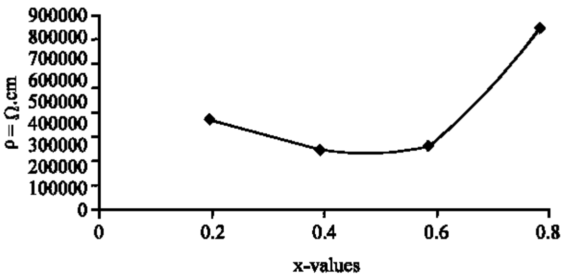

Fig. 7: The relation between electrical resistivity versus x-value

charge polarization) which acts in the low frequencies (Heck, 1974). Whereas the decrease in dielectric constant reduce in the frequency range (100 kHZ-3 MHZ) because effective of space charge charge polarization reduce in this range of frequencies and the three other types polarization continues in affects. So, the values of ε_r' decrease hundreds time. Polarization in ferrites has largely been attributed to the presence of Fe^{+2} ions which are easily polarized. The larger number of Fe^{+2} ions is higher dielectric constant would be (Verma *et al*., 2000; Snelling, 1988; Heck, 1974; Tareev, 1979).

Magnetic permeability (μL): Figure 8 shows variation the initial permeability as a function of frequency at range (20 Hz-3 MHz) using Eq. 2 to observe the behaviors that was sharply decrease with increased frequency at (20 Hz-100 kHz) then a small variations in the permeability at high frequencies. As its clear from Fig. 8, initial permeability decrease with increased frequency that's due to the relation between magnetic inductance and frequency which act as the major reason in this decrease (Resnick *et al*., 1992) 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 from Fig. 8, the initial permeability has high value absorbing materials or to be used in the high frequencies applications.

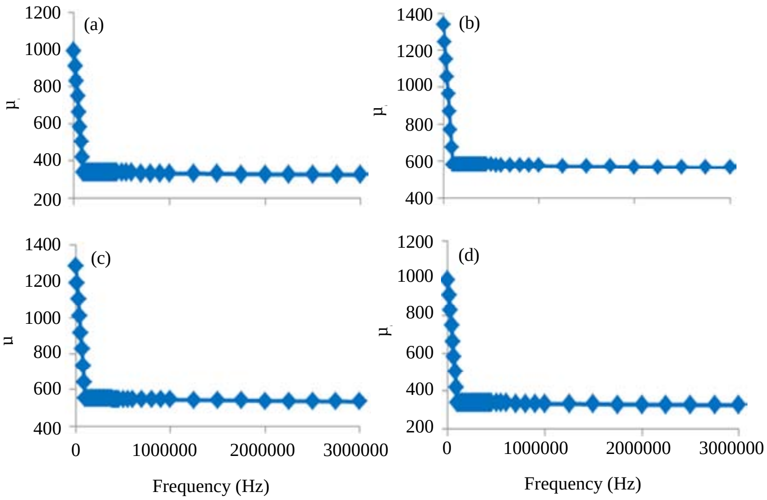

Fig. 8: The relation between μ_i versus frquency at range (20 Hz-3 MHz) for all samples: a) x-value = 0.2; b) x-value = 0.4; c) x-value = 0.6 and d) x-value = 0.6

CONCLUSION

$CoFe_2O_4$ and $ZnFe_2O_4$ phases are formed at temperatures 800°C and good crystalline quality of these samples. Density of samples decrease with increasing percentage $CoFe_2O_4$ in the system $Zn_xCo_{1-x}Fe_2O_4$. The resistivity has minimum value and dielectric constant has maximum value at x(0.4). Dielectric constant values decrease sharply with increased frequency at range (20 kHz-100 kHz), then the decrease in dielectric constant reduce in the range (100 kHz-3 MHz). The initial permeability as a function of frequency at range (20 Hz-3 MHz) was sharply decrease with increased frequency at (20 Hz-100 kHz) then a small variations in the permeability at high frequencies.

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