

Effect of Zn Substitution on Structural and Magnetic Properties of Cu-Ferrites Nanoparticles

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ABSTRACT

In this research prepared samples of CuZn-ferrites were substitution of copper ions by zinc ions as a composition formula $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite (with $x = 0.0, 0.1, 0.2, 0.3$) and studying the properties of composition using FTIR spectroscopy established creation of spinel ferrite and presented the features of absorption bands around $561.29\text{--}405\text{ cm}^{-1}$. X-ray diffraction (XRD) exposed that the structure of these nano particles is spinel and crystallite size lies in the range (12.22–23.9) nm. observed when added zinc ions, found increase in particle size and lattice constant while decrease in Xrd-density, and also have been identified the behavior of material Ferrite in low frequencies permeability magnetic used LCR meter , found when increasing the frequency (1-200) KHz decries in magnetic permeability (μ') this usual behavior in ferrites and observed a significant increase in magnetic permeability when increasing zinc ions due to the effect of zinc on the internal structure of copper ferrite. At Low frequency institute that the permeability raises with Zn contented rise from (0 - 0.3) in Cu-ferrites.

Keyword: ferrites, LCR meter, permeability, spinel structure, XRD density.

INTRODUCTION

Ferrites with spinel structure very important magnetic materials having eventual applications and the practical research. Copper – Zinc Ferrites are a polycrystalline complex system combined of crystallites, grain boundaries and pores [1], with excellent soft magnetic properties and used in electronic and telecommunication industries. [2]for the most part of bulk CuFe_2O_4 had an inverse spinel structure, with Cu^{2+} occupying B sites , as ZnFe_2O_4 was commonly be a normal spinel and Zn^{2+} ions preferentially occupy A sites while Fe^{3+} ions would be displace from A sites for B sites. Zn-substitution will be change a cations in chemical composition and a different distribution of a cations between A and B sites. That cause the magnetic properties of spinel ferrites will change with changing cation distribution. [3] ferrite with polycrystalline has received special interest because of their excellent magnetic properties and high electrical resistivity under a large range of frequencies; from a few hundred Hz to more than a few GHz. ferrites Spinel type was usually used in several electronic and magnetic devices because of their high magnetic [4,5] permeability and low magnetic losses. Cu-Zn ferrites were considered as the most significant magnetic oxides because of tailoring flexibility in the properties of magnetic, use at higher frequency, low cost, high mechanical hardness and high corrosion resistivity. The intent of material was providing permittivity bigger than μ_0 since the inductor may become further densely with turn of wires [7]. These could reduction losses of skin effects in the wire and reduction coupled to other inductive component in

circuits, but the losses of circuit might be imperfect by magnetic materials themselves [8].the aim of that research is to study the effect of zinc ions in the in magnetic permeability (μ') at low frequency (1-200) KHz and also to study that effect in the structure properties.

Experimental

The ferrite $Cu_{x-1}Zn_xFe_2O_4$ has been prepared by the chemical auto combustion method in different content of Zn, (with $x = 0.0, 0.1, 0.2, 0.3$), as show in the table (1). The starting materials for the preparation the powder, High purity cupric nitrate hydrate, $Cu(NO_3)_2 \cdot 6H_2O$, Zinc nitrite hydrate $Zn(NO_3)_2 \cdot 2H_2O$, ferric nitrate monohydrate $Fe(NO_3)_3 \cdot 9H_2O$ are used as outset materials. The combination were add to a citric acid solution ($C_6H_8O_7 \cdot H_2O$) 2M, in molar ratio citric (acid: nitrates) of 3:1. Mixed solutions of these materials were prepared in deioniz water with vigorous stirring until the solution being a gal (2 hour.).Where the powder pressed by holy circler die toroid formed the samples by pressed the powder and sintered at $860^\circ C$ for 4 hour in air and then cools in the furnace. After that wrap the wire around toroid (samples) for preparer them to masseur the indication by use LCR meter.

Table (1): present chemicals formulas of samples.

Sample	Zn content	Chemical formula
A	0	$Cu Fe_2O_4$
B	0.1	$Cu_{0.9}Zn_{0.1}Fe_2O_4$
C	0.2	$Cu_{0.8}Zn_{0.2}Fe_2O_4$
D	0.3	$Cu_{0.7} Zn_{0.3}Fe_2O_4$

At room temperature with the LCR meter the inductance of the toroid (ring) sample assessed in the low frequency range (1 -200) kHz. The permeability μ' is evaluated by equ. (1). [4]

$$\mu' = \frac{L}{2 \times 10^{-7} \times N^2 \times H_T \times \ln \frac{D_O}{D_i}} \dots\dots\dots(1)$$

Where, L is Inductance, N is turns No. Ht is core Height, D_O is core Outer diameter D_i is core Inner diameter, 2×10^{-7} is Conversion factor.

Phase analysis was done by (Philips PW 1050) XRD, diffract meter has been used.Where used the equation (1) for a cubic system for most intensity peak (311) to collected the lattice parameter (a);

$$a^2 = (h^2 + k^2 + l^2) \cdot d^2 \dots\dots\dots (2)$$

h,k,l is miler index, d is the inter planer spacing.

Average particle size (D_x) was calculated by using Debye-Scherrer equation,

$$D_x = 0.9 \lambda / (\beta \cos \theta) \dots\dots\dots (3)$$

λ is wave length of XRD, β is broadening of the diffraction peak, θ is diffraction angle, the calculate crystallite size from broadening of the (311) XRD peak and equation (3) used to calculate X-ray density (ρ_x):

$$\rho_x = (8 M_w / N_a \cdot a^3) \dots\dots\dots (4)$$

M_w is molecule weight, N_a is Avogadro's number, and a is lattice constant.

To characterize the samples with a primary the sintered ferrites microstructures take by using scanning electron microscopy (SEM, the VEGA Easy Probe)). The micrograph was taking on flat faces of the pellets designed sample.

Fourier Transform Infra-Red studies were carried out by Spectroscopy (FT-IR) from (Shimadzo Irapinity) FTIR Sector meter in the range of 400–1000 Cm^{-1}

Results and Dissection

Phase analyzer:

Fig (1) represents the X-ray powder diffraction pattern of synthesized $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite samples annealed at 500°C (where, $x = 0.0, 0.1, 0.2, 0.3$). The packs show creation a single-phase cubic spinel structure with different reflection planes indexed as (111), (220), (311), (222), (400), (511) and (440). These patterns showing well defined reflections with extra peak phases represent CuO phase can be remove when sintering the samples at high temperature .

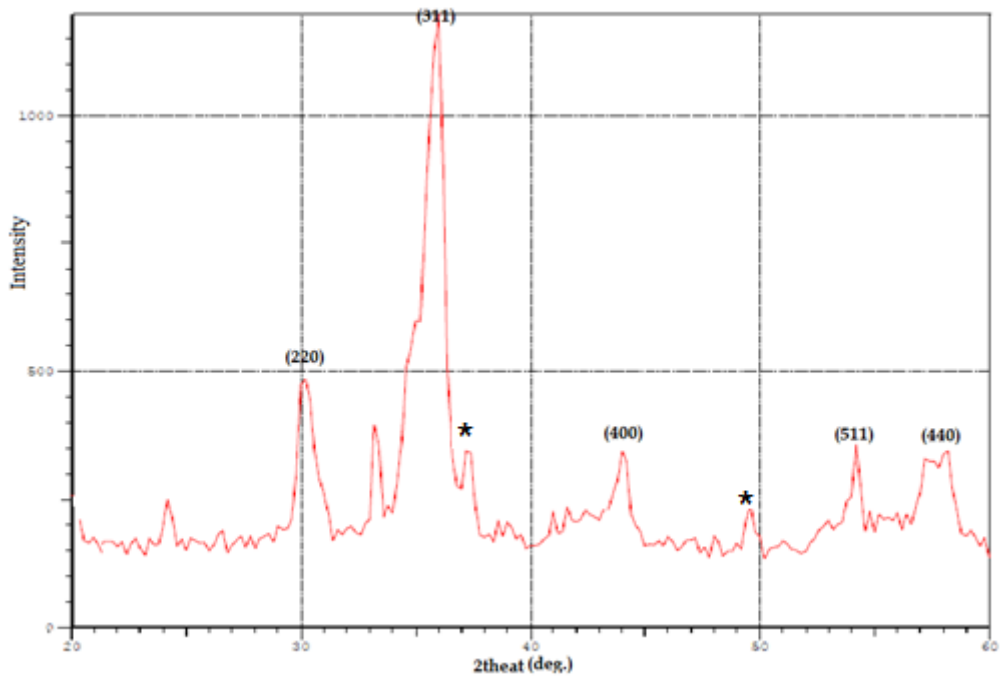
As a result, the mean particle size was found in the range of (12.22–23.9nm) calculated from the peak (311) of the XRD diffract gram employing by Scherrer's formula where the particle size found increase when Zn content increased as seen in fig(2). Hence calculate the X-ray density and lattice constant by used of a X-ray data. The lattice constant calculated by the Nelson R. extrapolated technique [5], since lattice constant was rising with further add of Zn^{2+} ion as give in Table (2), that because of ionic radius of Zn^{2+} ions ($R_{\text{Zn}^{2+}} = 0.82 \text{ \AA}$) was bigger than Cu^{2+} ions ($R_{\text{Cu}^{2+}} = 0.73 \text{ \AA}$) that cause increasing a lattice constant which can deals with ionic size variation. [10].

Decreasing trends in X-ray density observe with increase Zn substance as shown in Figure 3. This because of rise of Oxygen vacancies that show main part in accelerated densifications [11, 12], where decreasing in Oxygen ion (anion) diffusion could impede the densifications.

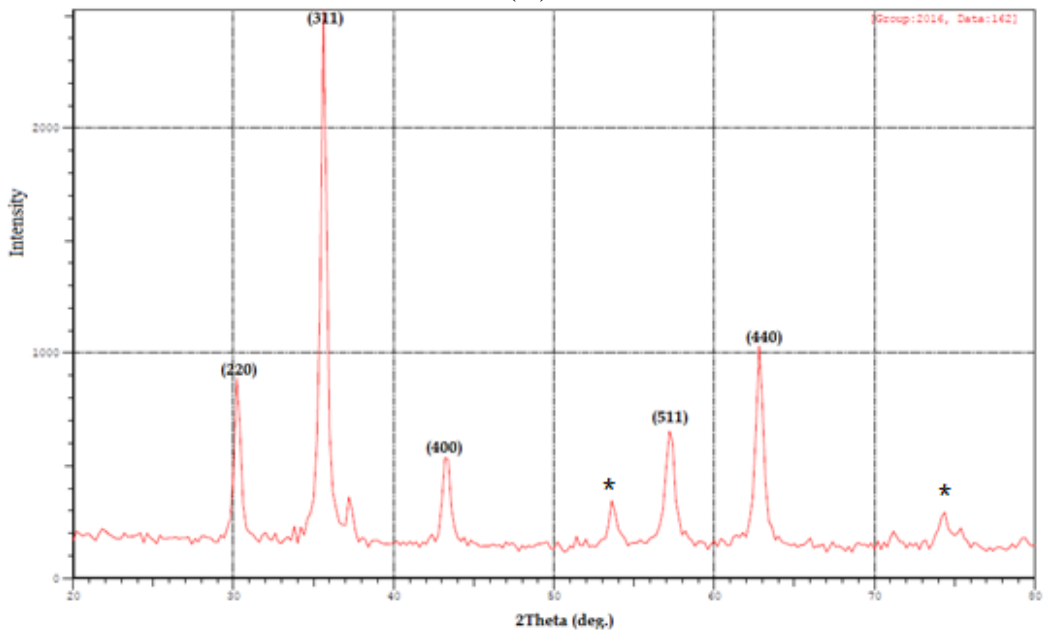
Also observed as show in figure (3) the density increase when the sintering the samples because of evaporate the Zn ions and consequently the pores decrease through diffusion kinetics.

Table (2): Lattice constant (\AA), Particle size (nm), XRD density (g/cm^3), of samples calcint at 500°C

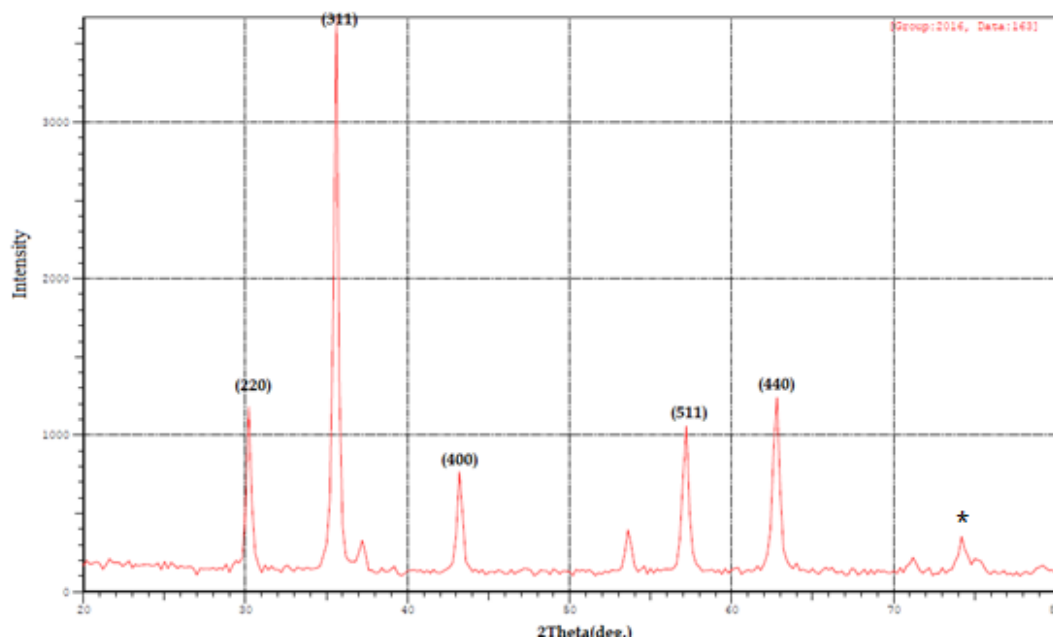
Samples	Lattice constant(\AA)	XRD density (g/cm^3)	Particle size(nm)
A	8.312	5.528	12.223
B	8.356	5.441	26.519
C	8.367	5.420	31.544
D	8.381	5.393	23.950



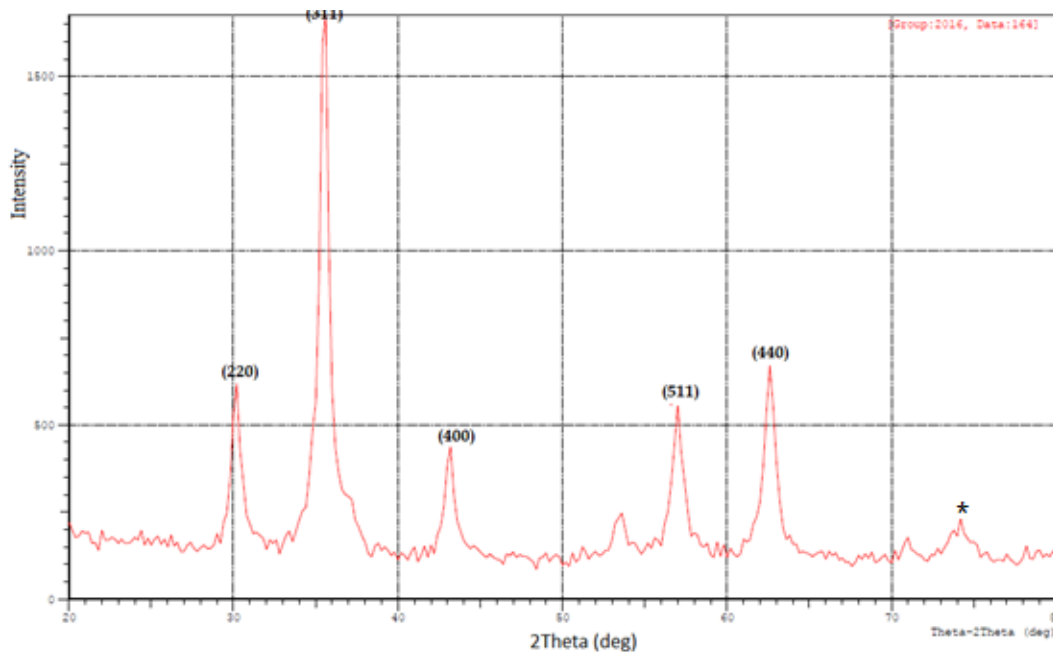
(A)



(B)

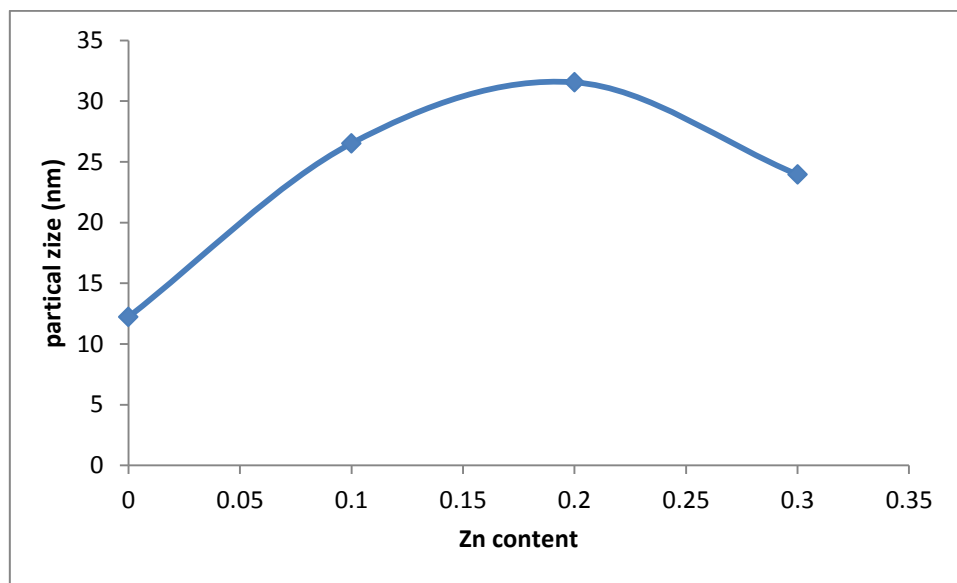


(C)



(D)

Figure(1):X-ray powder diffraction pattern of synthesized $Cu_{1-x}Zn_xFe_2O_4$ ferrite samples calsint at $500^{\circ}C$ with deferent content of Zn where find extra peak denote by (*), the samples: A)x=0,B)x=0.1,C)x=0.2,D)x=0.3.



Figure(2): Present particle size of samples calsint at 500⁰C

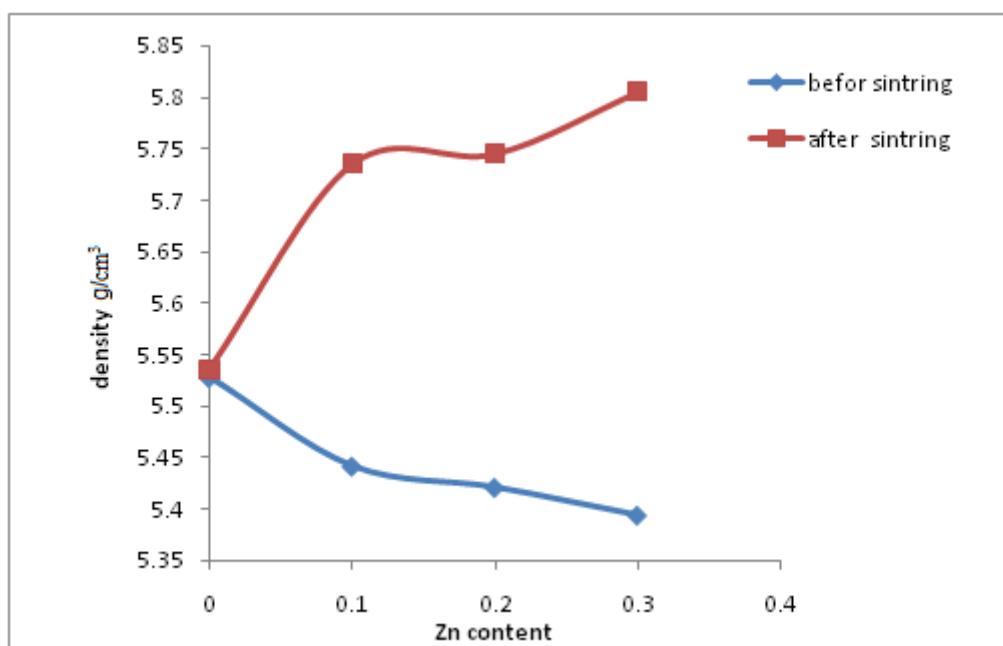
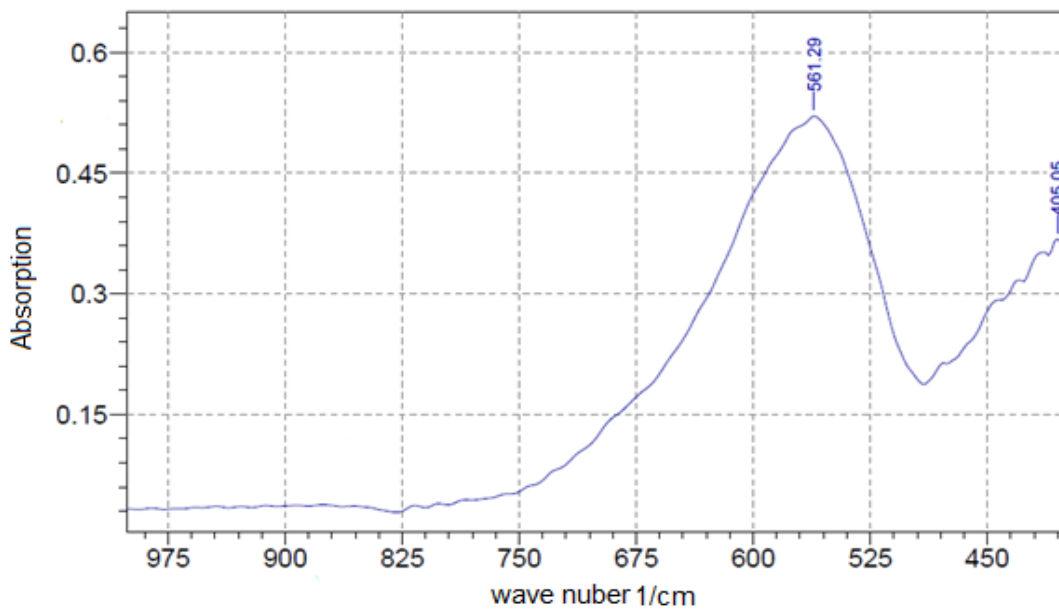


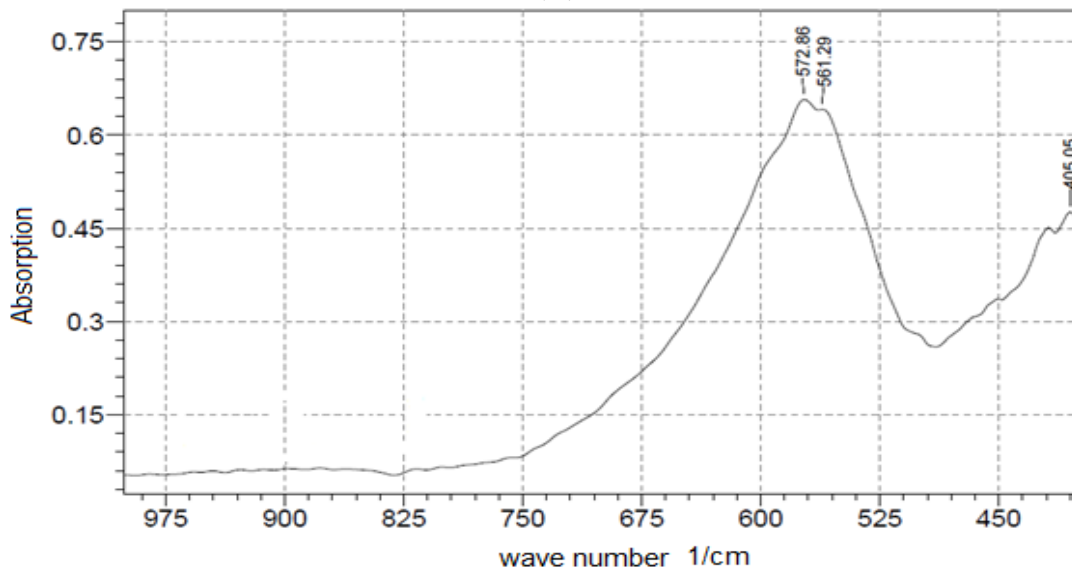
Figure.(3): present the density of samples as a function of Zn content where red line for samples sintered at 860⁰C and blue line for as prepared samples

the samples $Cu_{1-x}Zn_xFe_2O_4$ with ($x=0, 0.1, 0.2, 0.3$) study by using IR spectrophotometer, at the frequencies a round ($675 - 450$) cm^{-1} show two strong absorption bands the variation of ν_1 and ν_2 bands were shown in Figure (4).to all of the configurations the absorption bands noted within that exact frequency bounds expose the creation of single phase Spinel composition with two sub lattices, tetrahedral (A) place and octahedral (B) place [13]. ν_2 was noted at about 405.05 cm^{-1} gave octahedral group complexes and the absorption band ν_1 noted at about 561.29 cm^{-1} which gave

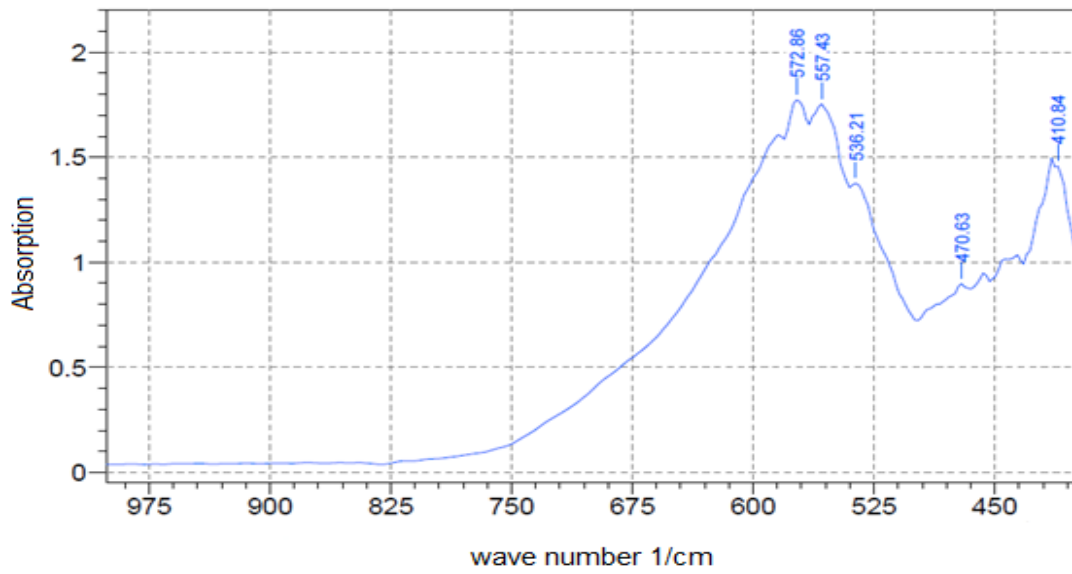
the tetrahedral site. It is obtained that the locations of bands were dependent in conformation. The wave number of band ν_1 shifts to lower rates due to increasing in Zn concentration (x). That change in the band locations because of differences in the bond length of cation-oxygen .These results can be explained as flows. The addition of Zn^{2+} (from $x=0.1$ to $x=0.3$ for ,Cu ferrites) ion in the tetrahedral sites with larger radius and greater atomic weight, lead to the Fe^{3+} ions drift to Octahedral site, and consequently decreasing vibration frequency of Tetrahedral. Likewise, drive of the Fe^{3+} ions to the octahedral site increasing the octahedral vibration frequency. While in sample (B) had no change in ν_1 and ν_2 value might be the amount of Zn^{+2} not great to make the change.



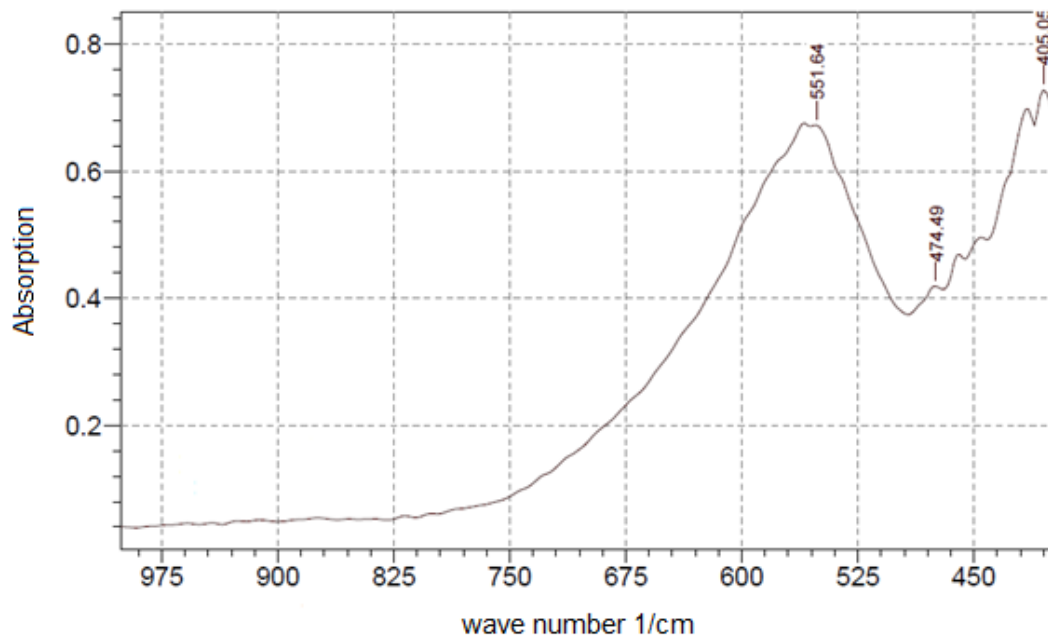
(A)



(B)



(C)



(D)

Figure(4):FTIR plots of synthesized $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite samples calsint at 500°C with deferent content of Zn : A) $x=0$,B) $x=0.1$,C) $x=0.2$,D) $x=0.3$.

Table (3): present value of wave number (V_1 (1/cm) due to $(Fe^{+3}-O^{-2})$ complex at A sites and wave number (V_2 (1/cm) band due to vibration of octahedral metal complexes.

Sample	V_1 (1/cm)	V_2 (1/cm)
A	561.29	405.05
B	561.29	405.05
C	557.43	410.84
D	551.64	405.05

Magnetic properties

Figure (5) show the real part (μ') in the range (1- 200) kHz sintered at 860°C, observed that the real permeability, decreases when the frequency increasing, where that is the normal properties in ferrites.

Since, from Figure (6) when the Zn content was amplified from 0 to 0.3 we notes increasing low frequency permeability. That change of permeability in substituted of Zn by Cu in Cu-ferrite, from the magnetic features of $CuFe_2O_4$ system originate from Cu^{2+} ions only in the octahedral B-sites since Fe^{3+} ions are distributed equally in both the A and B-site [14], and that lead to molecular magnetic moment could be greater than before addition a little of Zn^{+2} in mixed ferrite. The substituted of Zn^{+2} which is non-magnetic (diamagnetic) in spite of that but Zn^{+2} has great effect in magnetic permeability because of effect in ion distribution in magnetic features of $CuFe_2O_4$ where the Zn^{+2} ions occupy the tetrahedral a-site replace the identical quantity of Fe^{3+} to octahedral b-sites. This could give increases B-sites a further magnetized. As effect of the B-B interaction tends to be anti-ferromagnetic [15]. It was observed the strong A-B interface was the reasons of the spins in the B-sites were parallels align. The Permeability dependence on molecular magnetism where be forcing on domain wall because of the magnetic field and the resulting magnetization changes are both relative to permeability.

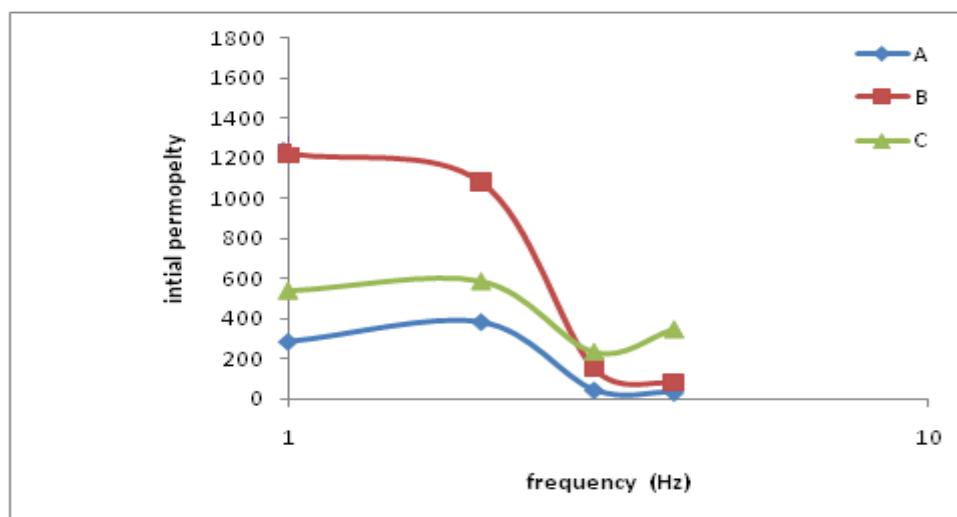


Figure (5): Permeability real part (μ') vs. Frequency (f) of $Cu_{1-x}Zn_xFe_2O_4$ sample sintering for 4 hs at 860°C.

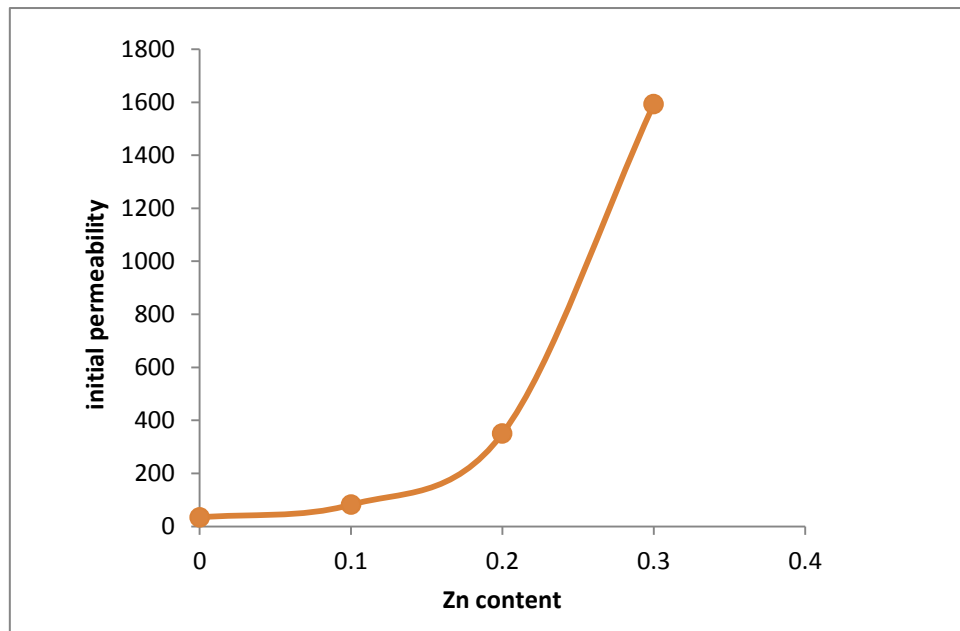
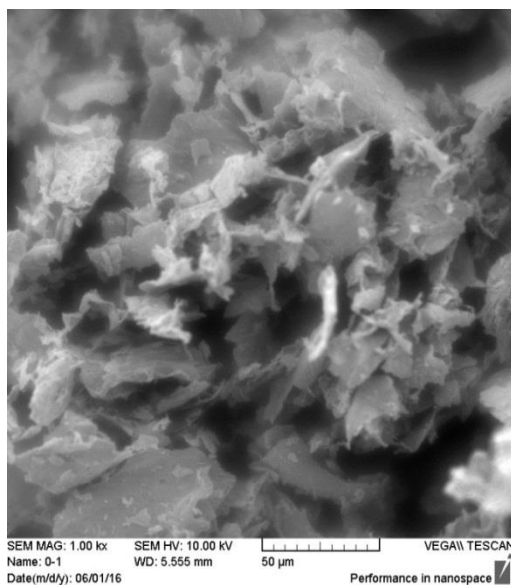


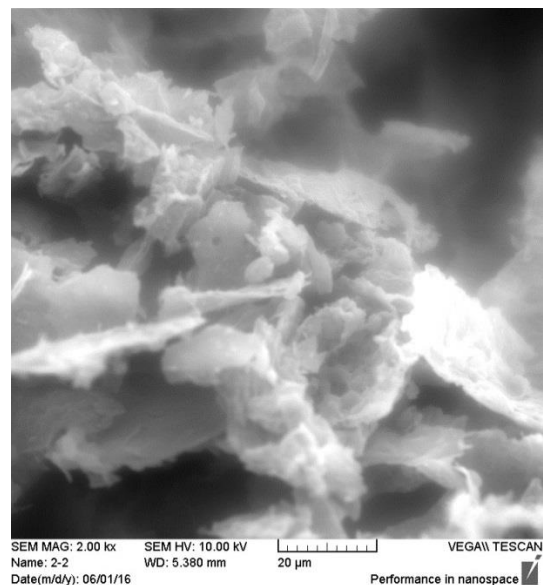
Figure (6): Permeability real part of (μ') vs. Zn content of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ sample sintering for 4 hs at 860°C .

Microstructure

All ferrites powder calcint at 500°C have been investigation.as seen in Fig(7) the SEM picture of ferrites powder have actually seam outfit structure where the powders look like ash and the pores is clear in all samples, irregular shape and size of particles was found , and see also the particle will be more picket when the Zn content be high .



X=0



X=0.1

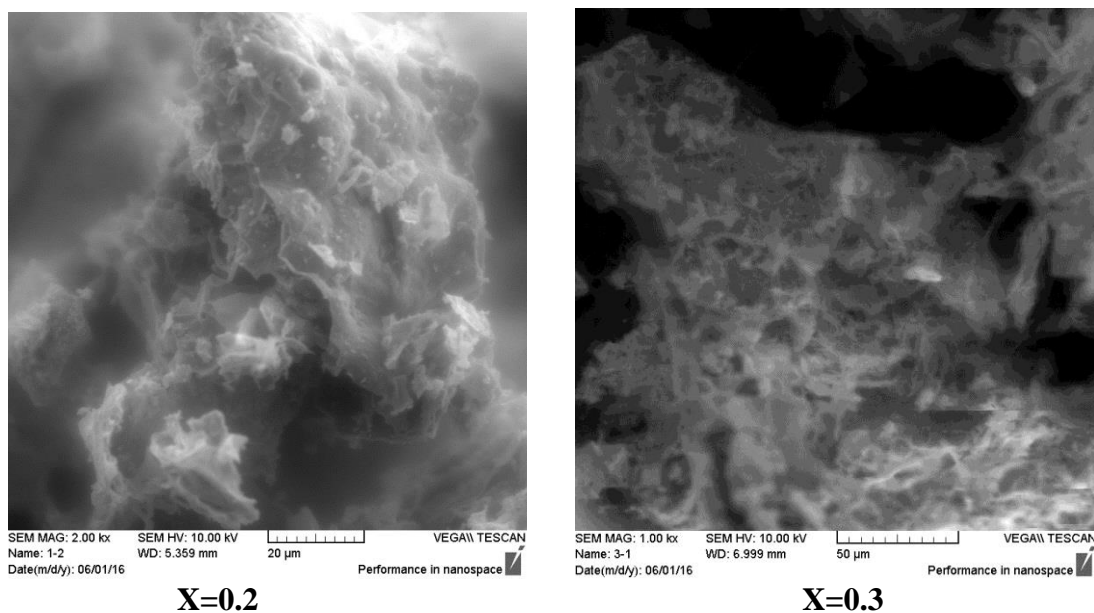


Figure (7): SEM image of ferrites powder with different Zn content of Cu1. $x\text{Zn}_x\text{Fe}_2\text{O}_4$ samples calcined at 500°C for 2 hours.

CONCLUSION

During the research investigated experimentally how properties of spinel Cu- ferrites are affected by doping of Zn. Where prepared these samples through the sol-gel method, and performed various structural and magnetic. The existence of Zn ions causes significant changes in the structure and magnetic properties in Cu ferrite, where particle size and lattice constant found a clear increase but in XRD density was decrease, were observed the effect of ions zinc added to these properties, and also it has been identified on the behavior of Ferrite material in low frequencies during permeability magnetic account, found when increasing the frequency the permeability decrease (1-200) KHz this usual behavior of ferrites materials.

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