The Effect of pH on Partial Size of Ferrimagnetic Powders Prepared by Auto Combustion Method

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ABSTRACT

During the preparation of this research ferrites - copper powder chemical auto-combustion method ,has been studying the effect of changing of (pH=3, 5, 7, 9, 11) coefficient on the particle size of the powder, used Debye-Scherrer Formula, to calculate the particle size by use of the highest peak (311) in X-ray diffraction (XRD) were obtained particle size ranges (11.5-13.75) nm, and also has been compared to the values obtained in drawing curves that represent change the lattice constant, particle size and density as a function of the (pH), and used Infrared spectroscopy (FTIR) to determine the internal structure of models, and also has been studying the microscopic structure took photos by electron scan microscopy (SEM) where indicated formation of high porosity homogeneous this change in the acidity coefficient(pH) led to change particle size and therefore a change in the properties of structural and physical .

Keywords: Ferrtis, Auto-Combustion, Spinal. Particle size, pH.

INTRODUCTION

Spinel ferrites have the general formula of DFe_2O_4 (where $D^{2+:}$ Fe, Co, Ni, Zn, etc.) [1], and unit cell contains 32 oxygen atoms in cubic close packing with 8 tetrahedral and 16 octahedral occupied sites. By changing type of the divalent caution [2], depending on how these cations are distributed in the interstices, cubic spinel structures can be of two types: Normal spinel and Inverse spinel .Cu-ferrite has inverse spinel structure with almost all Cu^{2+} ions occupying octahedral sub lattice, whereas Fe^{3+} ions divide equally between the tetrahedral and octahedral sub lattices it is conceivable to take out significantly different physical and magnetic properties in these ferrites, [3-13] make it technologically significant group of materials due to their enhanced optical, magnetic, and electrical properties. These properties make them very important for a variety of medical or industrial applications [4]. Magnetic and electric properties of ferrites are having fundamental and technological and potential applications. Potential applications such as: high density information storage in computers; Ferro fluid technology, magneto-caloric refrigeration, magnetic resonance imaging (MRI) enhancement, magnetic guided drug delivery, microwave devices and magnetic recording media and magnetic sensors [14]. Ferrites powder prepared with deferent methods one of this methods auto computation way, which is chemical method depending on same parameters such as temperature of preparing or sintering and pH of solution [5].Auto computation method is an auspicious method for the synthesis of fine Nano sized spinel oxides. The process is environmentally benign and versatile, since it does not involve any organic solvents [6, 7]. Auto

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computation method has been widely investigated for the synthesis of metal oxides as powders, nanoparticles and single crystals [9, 10, and 11]. Observed, that pH of reaction in the auto computation method plays a deterministic role in obtaining smaller sized particles [12]. The intent of this treat survey the influence of change of ph on particle size ,where Cu Fe_2O_4 powder prepared in deferent ph =3,5,7,9,11.useing auto computation method, and this particles are to characterize with X-ray diffraction and Scanning Electron microscopy (SEM). However, in this survey, the effect of pH values of solutions was scrutinized to particle sizes and cristallinity.

Experimental Section

Synthesized by auto combustion method of Cu ferrites with a generic formula $CuFe_2O_4$, prepared with deferent (pH =3, 5, 7,9, 11) were analytical grade with purity ≥99% of All the chemicals were used. In a typical procedure, cupric nitrate hydrate Cu $(NO_3)_2 \cdot 6H_2O$, ferric nitrate monohydrate Fe $(NO_3)_3 \cdot 9H_2O$ were used as outset materials. The mixture was added to a citric acid solution ($C_6H_8O_7 \times H2O$) 2M, in molar ratio citric (acid: nitrates) of 3:1. Mixed solutions of these materials were prepared in deionized water with vigorous stirring until the solution being a gal (2houer). A specific volume of ammonia NH_4OH was added to the above mixed solution. After, the solution of NH_4OH was added until pH values, reached (3, 5, 7, 9, 11) respectively. The intrinsic factor on which the final composition of the result depends was pH of solution, which can be varied to get the desired final product. The final powder specimens obtained were calcinations at 500°C for 2 hr. This method involves exothermic and self-sustaining thermally-induced anionic redox reaction of xerogel, which is obtained from aqueous solution containing desired metal salts (oxidizer) and organic complexant (reductant) [15-21]. Proportions between complexant and salts are usually calculated according to the valences of the reacting elements in order to supply the relation of oxidizer/reluctant equal to (1) [16-22]. The nitrate salts are favored as precursors, because they serve as water-soluble low temperature NO^{-3} oxidant source for synthesis [17]. Metal nitrates possess hygroscopicity; consequently, they easily absorb moisture and become slurry. This variety of the sol–gel auto-combustion is called flash-combustion method xerogel during combustion is surely due to the heat generated from the exothermic reaction .Flame temperature during combustion could vary from 600°C to 1350°C. Decomposition of NH_4NO_3 produced O_2, thus accelerating the combustion process. Higher pH values of mixed solutions are expected for the synthesis of ferrite compounds [18-20].The chemical equation of that reaction can be presented in **Eq.(1)** as show :

$$Cu(NO_3)_2 \cdot 6H_2O + 2Fe(NO_3)_3 \cdot 9H_2O + 3C_6H_8O_7 + 9H_2O \longrightarrow CuFe_2O_4 + 4N_2 + 6CO_2 + 24H_2O + 8O_2 \quad \ldots (1)$$

Results and Discussions:

XRD Patterns:

The XRD model of $CuFe_2O_4$ (pH=3, 5, 7, 11) samples shows in. **Fig.(1)** Sharp and well defined peak are obtained for all samples, XRD patterns consistence of extra peak of CuO, and Fe_2O_3, which can evasive by sintering of samples in high temperature to get pure $CuFe_2O_4$, XRD patterns show that all peaks indexed to pure cubic phase, where (220), (311), (400), (422), (511), and (440) be a symbol for the main crystal phase in $CuFe_2O_4$ spinel ferrite. Formation of single phase spinel ferrites structure clearly denote, by X-ray diffract grams. Where used the **Eq.(2)** for a cubic system for most intensity peak (311) to collected the lattice parameter (*a*);

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

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

Average grain size (*D*) and X-ray density (ρ_x) are listed in **Table(1).** The XRD patterns were compared for deferent amount of pH value. As seen from **Fig.(2)**, Average particle size (D_X) was calculated by using Debye-Scherrer Formula, from **Eq.(3)**

$$D_x = 0.9\,\lambda / (\beta \cos\theta) \quad \ldots (3)$$

λ=wave length of X-ray, β=broadening of the diffraction peak, θ= diffraction angle, the calculated crystallite size from the broadening of the (311) XRD peak. And **Eq.(4)** used to calculate X-ray density (ρ_x):

$$\rho_x = (8\ Mw / Na.a^3) \quad \ldots (4)$$

M_W=molecule Wight, N_a= Avogadro's number, a=lattice constant., the value of D_x varies from (13.53 nm) of pH=3 to (11.72 nm) pH=11 which denotes an increase of average grain size with increasing pH value, that was attributed to higher combustion temperature because of increase in (NH_4OH) amount, which is as a fuel in the chemical reaction .Show in **Fig.(3)** increased in lattice constant, any change in the lattice constant lead to a change in density according to mathematics equation **Eq.(4),** where the relationship is inversely proportional with lattice constant and the density , that was obtained practically as show in **Fig. (4).**

Table (1): present value of lattice constant, XRD density, particle size of samples.

Samples	Lattice constant(A^0)	XRD density (g/cm^3)	Particle size(nm)
pH=3	8.318	5.515	13.537
pH=5	8.309	5.533	9.2623
pH=7	8.312	5.528	12.223
pH=9	8.317	5.517	13.059
pH=11	8.327	5.499	11.721

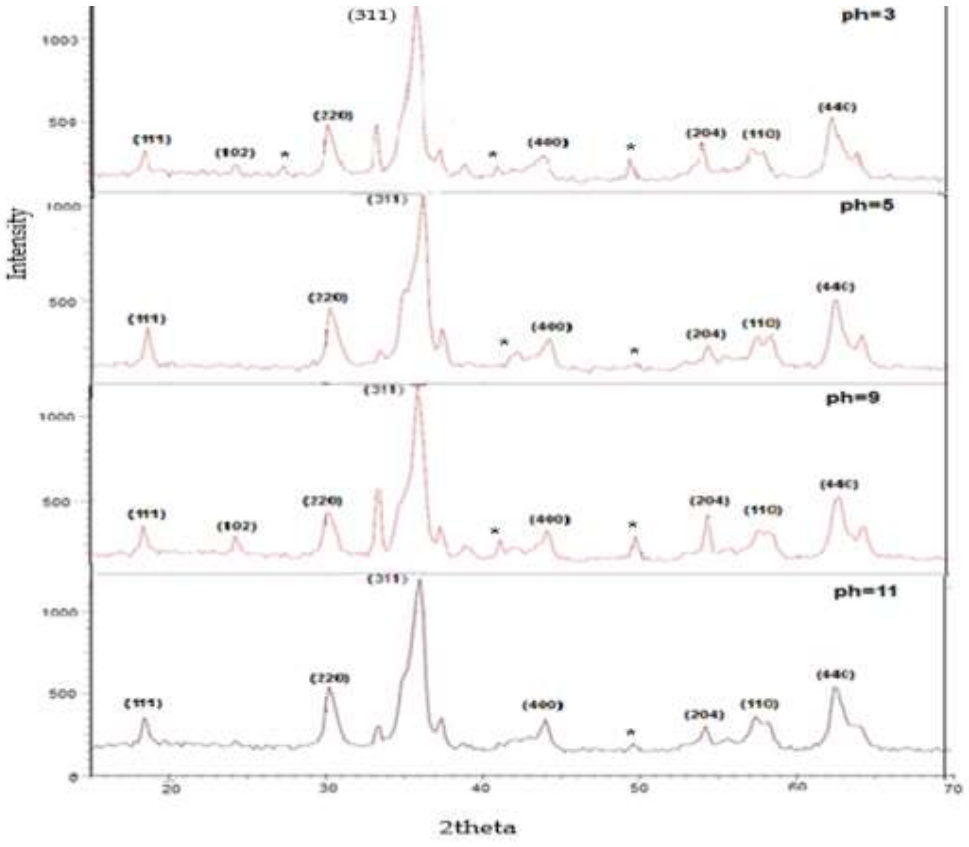


Figure (1): XRD patrons of samples with deferent pH, show that all peaks indexed to pure cubic phase, with extra peak denote by (*)of CuO, and Fe_2O_3

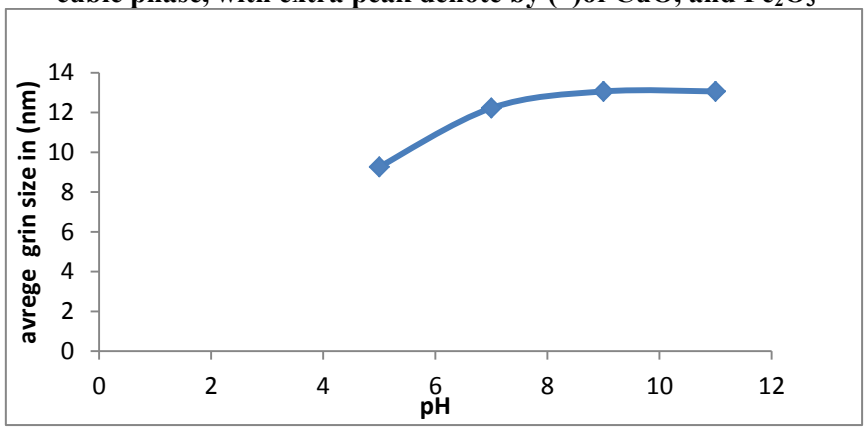


Figure (2): Plot of average grin size of samples as a factor of pH denotes an increase of average grain size with increasing pH value.

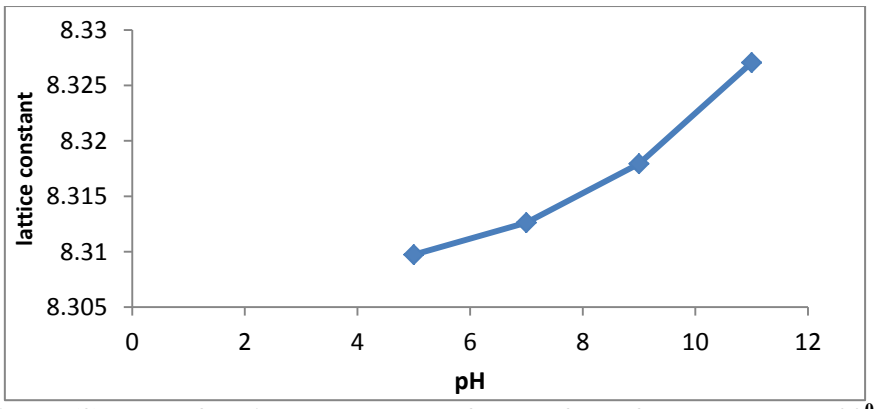


Figure (3): Plot of lattice constant as a factor of pH, for powders at 500^0C

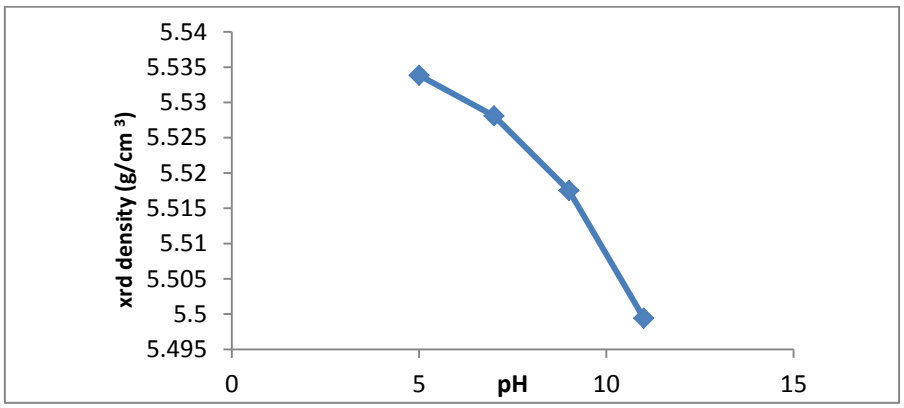
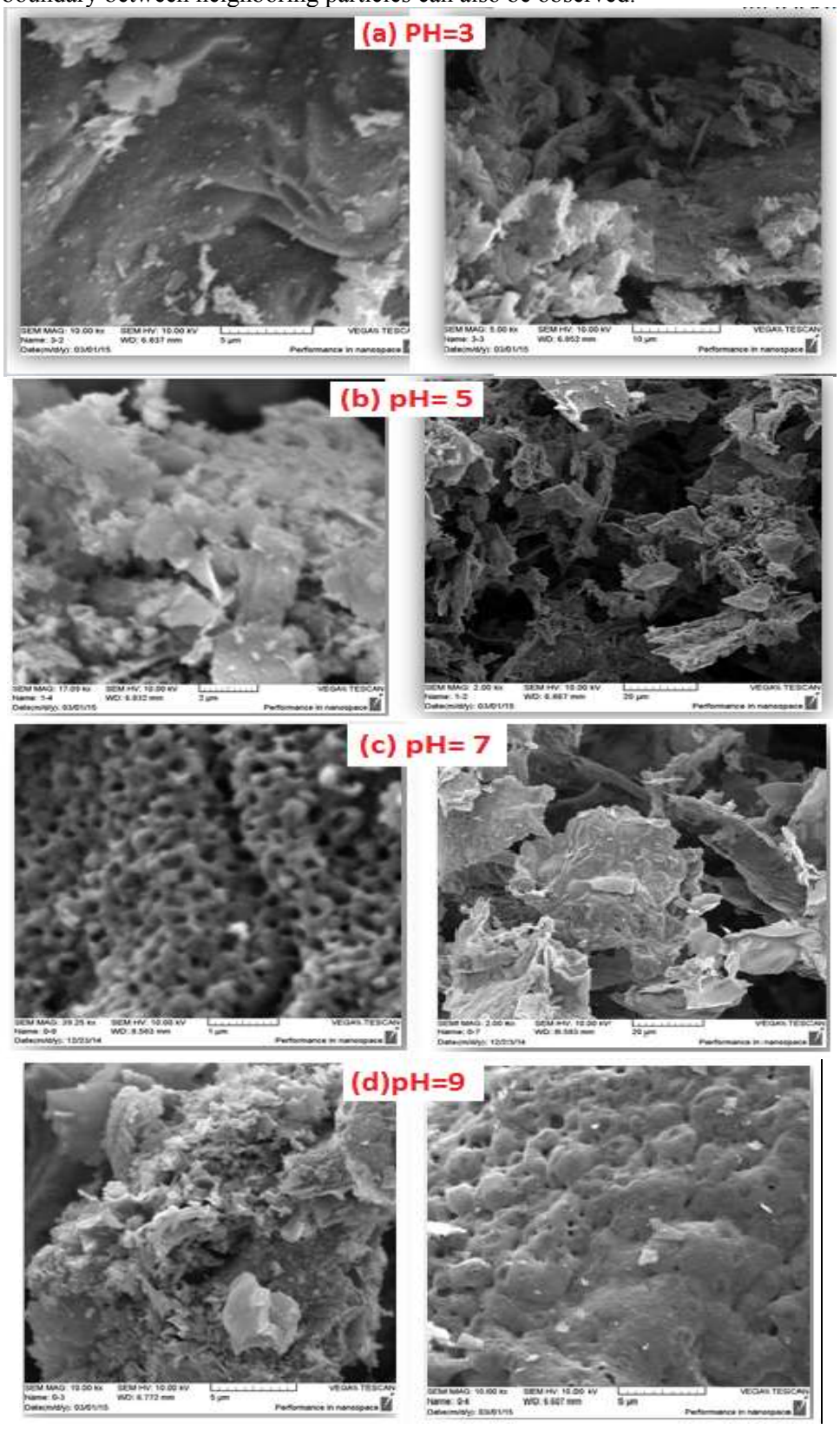


Figure (4): Plot of XRD density as a factor of pH, for powders at 500^0C.

Microstructure

The SEM images showed uniformity and homogeneity of the synthesized $CuFe_2O_4$ particles, the present powder as flicks and clear that powder has high porosity is correspond with XRD density where the density is decrease when porosity is increased. The scanning electron micrograph for $CuFe_2O_4$ shows they are dense and distributed regularly with-in the whole area

as show in **Fig.(4).** In addition to this, these smaller crystallites are so closely arranged together, a clear boundary between neighboring particles can also be observed.



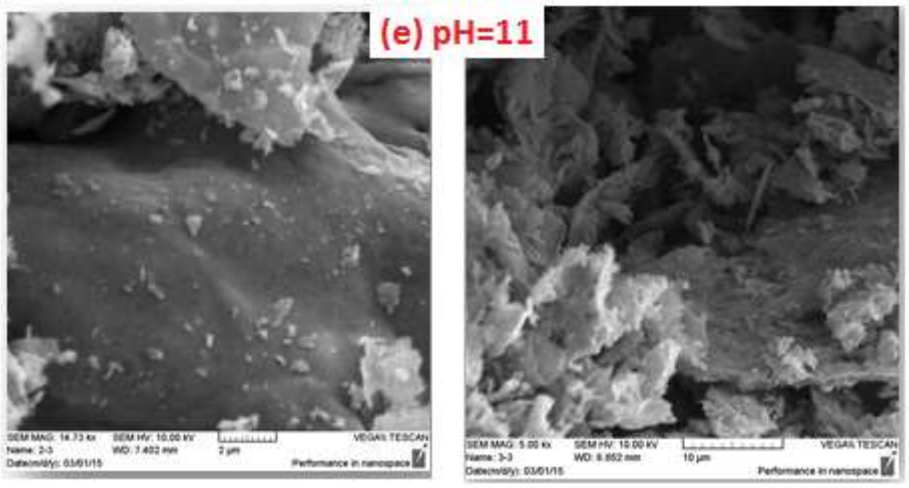


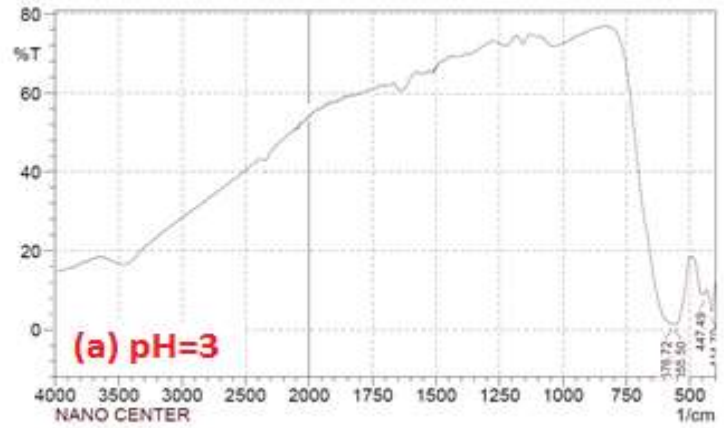
Figure (4,a,b,c,d,e): SEM images of $CuFe_2O_4$ samples after calcination 500^0Cpresent porosity and **boundary between neighboring particles can also be observed**

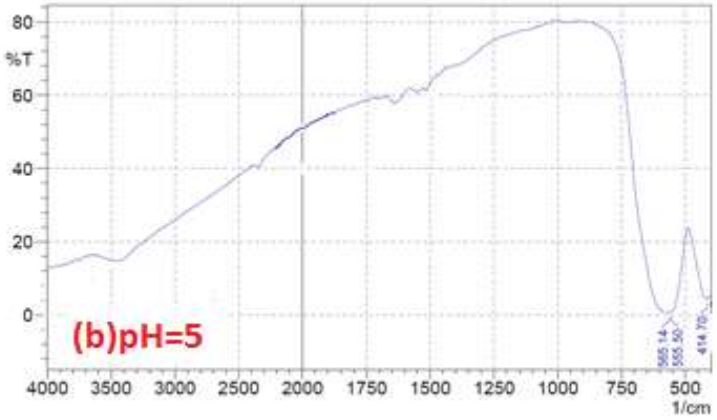
FTIR Measurement

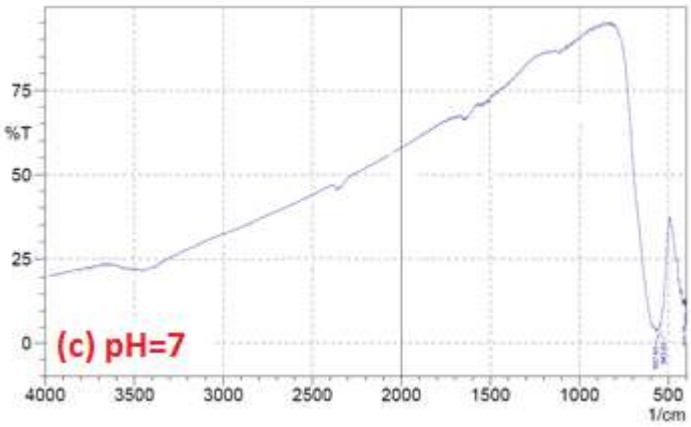
At room temperature using FTIR, spectra were registered for the copper ferrites samples were recorded in the rang of (2000-500) cm $^{-1}$ and are show in **Fig.(9)** for the (pH=3, 5, 7, 9, 11) respectively. Ferrite's structure was similar to mineral spinel crystalline structure that occurs usually in cubic form or sometimes in tetragonal form depending upon the ions participating in the solicitous solid material. The FTIR spectra of as-prepared samples in general below 1000 cm^{-1}, as show in **Fig.(9)** set the formation of spinel structure. Two main absorption band V_1 and V_2 as common feature of FTIR spectra show all spinel assembly ,in identity to Waldron [8] .The ferrites can be considered as continuously bonded crystals, via ionic ,covalent or Vander walls forces ,to the nearest neighbor . Two different sub- lattice in ferrite metal ion are located in ,namely tetrahedral (A sites)and octahedral (B sites) according to geometrical configuration of oxygen nearest neighbor ,the band V_1 around 576 cm^{-1} was attributed to stretching vibration of tetrahedral complexes and the band V_2 around 400cm^{-1} to the octahedral complexes .The values of absorption band frequency of samples with deferent pH, are given in **Table(2)** .It can be seen that the high frequency band V_1has value (576.72 cm^{-1}) for pH=3 samples. Such as copper ferrites that V_1 is due to (Fe^{+3}-O^{-2}) complex present at A sites and V_2 band due to vibration of octahedral metal complexes. The cu^{+2} ions occupy mainly the octahedral sites and same fraction goes in to tetrahedral sites according to these shoulders, where found the cu-ferret is invers spinel ferrites, also found any change in partial size leads to shafting in spectrum as in **Table (2).**

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

Sample	V_1(cm^{-1})	V_2(cm^{-1})
pH=3	576.72	447.49
pH=5	555.14	414.70
pH=7	557.43	405.05
pH=9	549.71	324.34
pH=11	567.00	420.48


80
%T
60
40
20
0
(a) pH=3
4000 3500 3000 2500 2000 1750 1500 1250 1000 750 500
1/cm
NANO CENTER


80
%T
60
40
20
0
(b)pH=5
4000 3500 3000 2500 2000 1750 1500 1250 1000 750 500
1/cm


75
%T
50
25
0
(c) pH=7
4000 3500 3000 2500 2000 1500 1000 500
1/cm

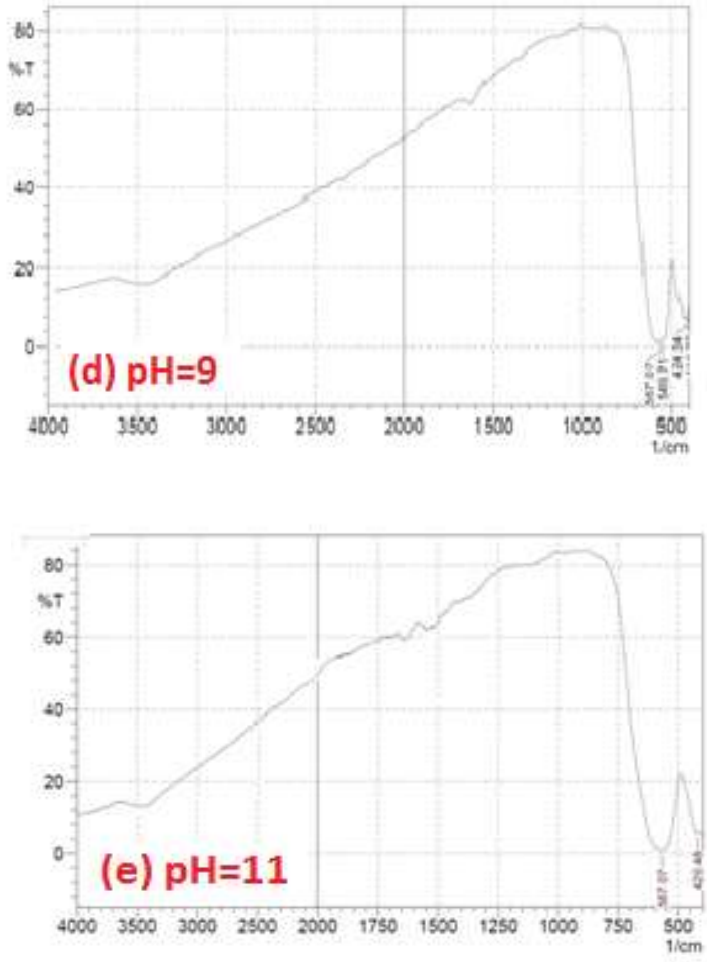


Figure (9a,b,c,d,e): FTIR patron of samples with different pH show that formation of spinel structure with two main absorption band V_1 and V_2 as common feature of FTIR in the rang of (2000-500) cm $^{-1}$

CONCLUSION

Cupper ferrite $CuFe_2O_4$ powders with nanocrystalline sizes were produced by a combination of sol-gel auto combustion of ammonia, as the fuel (the molar ratio of metal nitrates to fuel was 1: 3). The pH values were changed from 3 to 11. With an increase in the pH value, the combustion rate is increased significantly. All the samples are single phase ferrites (CuFe2O4) with cubic spinel structures. The synthesized powders had a particle size distribution in the range of (11.5-13.75) nm. The XRD results show that crystallite percent of $CuFe_2O_4$ phase grows with an increase in the pH from 5 to 7 and then it decreases. FTIR spectra results indicate that band peaking at about 570 cm^{-1}, where found the cu-ferret is invers spinel ferrites, also found any change in partial size leads to shafting in spectrum.

REFERENCES

[1] Sakia Shabnam Kader, Deba Prasad Paul, and Shaikh Manjura Hoque, International Journal of Materials, Mechanics and Manufacturing, Vol. 2, No. 1, February 2014.
[2] Naim SEZGIN1, Musa Sahin, Arzu Yalcini, Yuksel Koseoglu , Ekoloji 22(89): 89-96. No: 89, 2013. (Turkey).
[3] Hiroyuki NASU,Masayuki HASEGAWA,Tadanori HASHIMOTO,Atsushi ISHIHARA, Koji Fujita and Katsuhisa Tanaka Journal of the Ceramic Society of Japan,123[5]448-451,2015.
[4] RobertoKöferstein a,n, TillWalther a, DietrichHesse b,StefanG.Ebbinghaus a , Journal ofSolidStateChemistry213(2014)57–64.
[5] Francesco Branda (2011). The Sol-Gel Route to Nanocomposites, Advances in Nanocomposites - Synthesis,Characterization and Industrial Applications, Dr. Boreddy Reddy (Ed.), ISBN: 978-953-307-165-7.
[6] Khuram Ali 1,2, Asma Iqbal1,Muhammad Raza Ahmad1, Yasir Jamil1, Sohail Aziz Khan2, Nasir Amin1, Muhammad Adnan Iqbal3, Mohd Zubir Mat Jafri2.Sci.Int. (La hore), 23(1), 21-25, 2011 ISSN 1013-5316; CODEN: SINTE 8.
[7] R.Kalai selvan,C.O.Augustin,L.John berchmans,Rsaraswathi, material research Bulletin 38(2003)41-54.
[8] R.D.Waldron, (1955)1727.
[9] Z. Karcıoğlu KarakaĢ1, R. Boncukçuoğlu1, Ġ.H. KarakaĢ2, M.T. Yılmaz1, Proceedings of the International Conference NANO Material's: Application AND Properties, Vol. 1 No 1, 01PCN47 (4pp) (2012).
[10]Sopan M. Rathod. Ashok B. Shinde, International Journal of Advancements in Research & Technology, Volume 1, Issue6, November-2012 1 ISSN 2278-7763.
[11] Rathira,Jiendra*, Bhatia Pushpinder, Neogi Rajlakshmi, International Journal of Chemical and Physical Sciences. ISSN: 2319-6602 Vol. 3 Special Issue –NCRTSM, April-2014.
[12] Gopathi Ravi Kumar1, Katrapally Vijaya Kumar2, Yarram Chetty Venudhar1, Materials Sciences and Applications, 2012, 3, 87-91.
[13] M. Sultan, R. Singh, Magnetization and crystal structure of RF-sputtered nanocrystalline $CuFe_2O_4$ thin films, Mater. Lett. 63 (2009) 1764–1766.
[14] Abdul Gaffoor, Dachepalli Ravinder, World Journal of Condensed Matter Physics, 2013, 3, 50-53.
[15] Airimioaei M, Ciomaga C E, Apostolescu N, et al. Synthesis and functional properties of the $Ni_{1-x}Mn_xFe_2O_4$ ferrites. Journal of Alloys and Compounds, 2011, 509(31): 8065–8072.
[16] Hwang C-C, Tsai J-S, Huang T-H, et al. Combustion synthesis of
Ni–Zn ferrite powder — influence of oxygen balance value. Journal of Solid State Chemistry, 2005, 178(1): 382–389.
[17] Costa A C F M, Morelli M R, Kiminami R H G A. Combustion synthesis: Effect of urea on the reaction and characteristics of Ni– Zn ferrite powders. Journal of Materials Synthesis and Processing, 2001, 9(6): 347–352.
[18] Mangalaraja R V, Ananthakumar S, Manohar P, et al. Initial permeability studies of Ni–Zn ferrites prepared by flash combustion technique. Materials Science and Engineering A, 2003, 355 (1–2): 320–324.
[19] Andris Sutka And Gundars Mezinskis, Springer-Verlag Berlin Heidelberg 2012, 2012, 6(2): 128–141.
[20] Yue Z, Guo W, Zhou J, et al. Synthesis of nanocrystalline ferrites by sol–gel combustion process: the influence of pH value of. Journal of Magnetism and Magnetic Materials, 2004, 270(1–2): 216–223.
[21] Dr.Salam H. Ali Al-Hadad.Shahad Humam Sulaiman, Eng. &Tech.Journal, Vol. 33, Part (B), No.3, 2015.
[22] Dr. Awfa Abdul-Rassol Abdullah ,Rasha Rahman Rawhdan, Eng. & Tech. Journal .Vol.32,Part (B), No.1 , 2014.