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Synthesis and Structural Characterization of Cu Substituted Ni-Zn Nano-Ferrites Prepared By Citrate-Gel Auto Combustion Technique

N. Hari Kumar[1], G. Aravind[1], D. Ravinder[1*], T.Somaiah[2], B. Ravinder Reddy[3]
[1]Department of Physics, Osmania University, Hyderabad, 500007-India.
[2]Department of Physics, Engineering College, Osmania University, Hyderabad, India
[3]Dept of Physics, College of Technology, Osmania University, Hyderabad, India.

Abstract
The ferrite nano particles having chemical formula $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$ (where x=0.0 to 0.8 with step of 0.2) were synthesized by Citrate-Gel Auto Combustion method at low temperature. The synthesized powders were sintered at 500^{o}C for 4 hours in air and characterised by XRD, SEM with EDS. XRD analysis of prepared samples were confirmed the single phase cubic spinel Structure. The crystallite size (D) of prepared ferrites were in the range of 24-73nm. The values of lattice parameter (a) decreased and X-ray density (d_x) were increased with the increasing of Cu substitution. The surface morphology of the prepared samples was investigated by Scanning Electron Microscope(SEM). An elemental composition of the samples was studied by Energy Dispersive Spectroscopy(EDS). The observed results can be explained on the basis of composition and crystal size.
Keywords: Ferrites, Citrate-Gel Auto Combustion method, XRD, SEM, EDS.

I. INTRODUCTION

Nano materials have been produced and used by humans for hundred of years, however the understanding of certain materials as a nano structured materials is relatively recent made possible by the advant of advanced tools, that are capable of resolving information at nano scale. The properties of ferrites are sensitive to synthesis method, synthesis conditions, synthesis parameters, nature and type of substitution and cation distribution. Ferrites are very important and widely used materials in technical desining and applications at high frequencies[1]. One of the most important advantages of ferrites is their very high degree of compositional variability. Nanoparticles of ferrites are very important group of magnetic materials due to their extensive use in a wide range of applications. The properties of nano materials are remarkably different from that of their bulk counterpart. The interest in ferrite nano particles is due to their important physical and chemical properties and potential for various technological applications such as high density magnetic storage, electronic and microwave devices, sensors, magnetically guided drug delivery. The transport properties of the nano particles are predominately controlled by the grain boundaries than by the grain itself.[2]. In order to achieve a high degree of molecular mixing , chemical homoginity, control of stoichiometry, low calcination and sintering temperature/time, various chemical methods have been used for the synthesis of spinel ferrites[3-6] several researchers have reported the synthesis of Ni-Zn-Cu ferrites using different techniques like reffluxing process[7], ceramic method [8], hydrothermal method [9], combstion method[10], coprecipitation method[11], reverse micelle process[12], spark plasma sintering[13].Micro emulsion method [14] and ball milling method etc.

In the present work we reported the results of synthesis and structural properties of Ni-Cu-Zn ferrites by non conventional citrate gel auto combustion method.

II. Experimental

2.1 Synthesis: The composition of Ni-Cu-Zn ferrite particles having chemical formula $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$ (where x=0.0 to 0.8 with step of 0.2) were synthesized by Citrate-Gel Auto Combustion method at lower temperature. Nickel Nitrate, Cupper nitrate, Zinc Nitrate, Ferric Nitrate,Citric acid and ammonia(all chemicals are 99% pure AR Grade SDFCLsd fine chemical limited) are the raw materials for the synthesis process. Calculated quantities of metal nitrates and citric acid were dissolved in minimum amount of distilled water to get clear solution. Here citric acid acts as a chelating agent and helps in the homogeneous distribution of metal ions. The above mixture was stirred to get homogeneous clear solution which is heated to 80^{o}C using a hot plate magnetic stirrer. Then the pH of the solution is adjusted at 7 by addition of ammonia. A sol is formed. The resulting solution was evaporated

to dryness heating at about 180^{O}C on a hot plate with continuos stirring. The gel gave a fast flameless auto combustion reaction with the evolution of large amount of gases which results a burned powder. The burned powder was grinding using Agate Mortar and pestle to get a fine ferrite powder. Finally the grinded powder was calcinated in air at 500^{O}C for 4 hours and cooled to room temperature to obtain spinel phase.

2.2 Characterization: BrukerD8 advanced X-ray diffractometer with Cu Kα (λ= 1.5405A^{O}) was used to study the single phase nature and nano phase formation of the Ni-Cu-Zn ferrite system at room temperature by continuos scanning in the range of 10^{o}-80^{o}C. Micro structure analysis of the prepared samples was carried by Scanning Electron microscopy(SEM) and Elemental compositional analysis for all samples were done by Energy Dispersive Spectroscopy(EDS).

III. Results and Discussions:

3.1 XRD Analysis: the X-ray Diffraction pattern of all the samples were shown in fig(1) which confirms the single phase cubic spinal structure formation with out any impurity peak. The strongest reflection has come from (311) peak for every sample. The crystalline size of all samples was calculated from the Half Width at Full Maximum (HWFM) of the (311) reflection peak in the XRD pattern using Debye-Scherrers formula[15].

Scherrer Formula:

$$Crystalline\ size\ of\ the\ sample\ \boldsymbol{D} = \frac{\boldsymbol{0.91\lambda}}{\boldsymbol{\beta\ cos\theta}}$$

Where λ =wavelength of X-ray used

B= Full Width Half Maxima(FWHM) in radians.

θ = peak position.

Lattice parameter(a) of the sample was calculated by the formula

$$a = d * (h^2 + k^2 + l^2)^{1/2}$$

Where a= Lattice Constant

(hkl) are the Miller Indices

d = inter planner spacing,

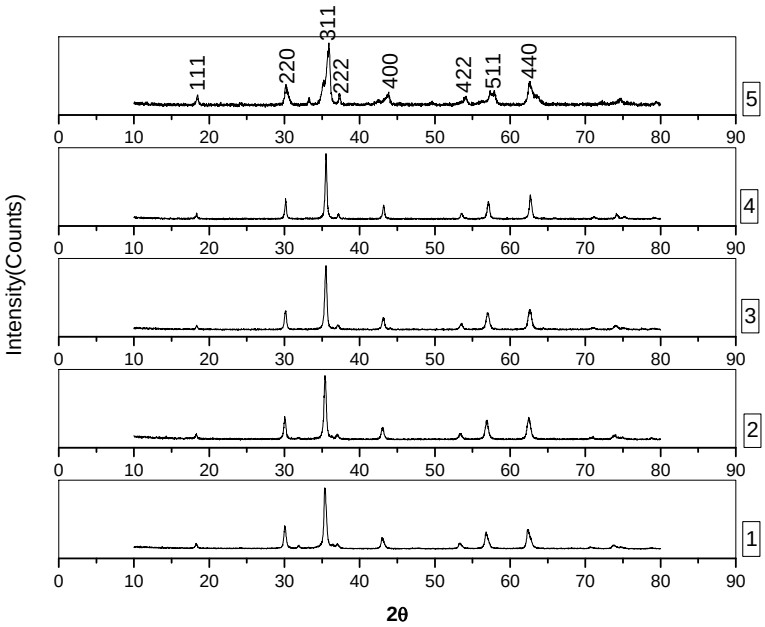
The X-ray density $\boldsymbol{dx} = \frac{\boldsymbol{nM}}{\boldsymbol{a^3 N}}$[g/cm^3] [16]

Where M = molecular weight of the sample

n =number of molecules in a unit cell of spinel lattice.

a =lattice parameter and N is the Avogadro number.

The Volume of the Unit Cell **V= a^3**



Fig(1).XRD Pattern of Cu Substituted Ni-Zn Nano-Ferrites

Values of Crystallite size, lattice parameter, X-ray density and volume of all the samples were given in the table(1).

Table(1): Crystalline size,Lattice Parameter, X-ray density &Volume

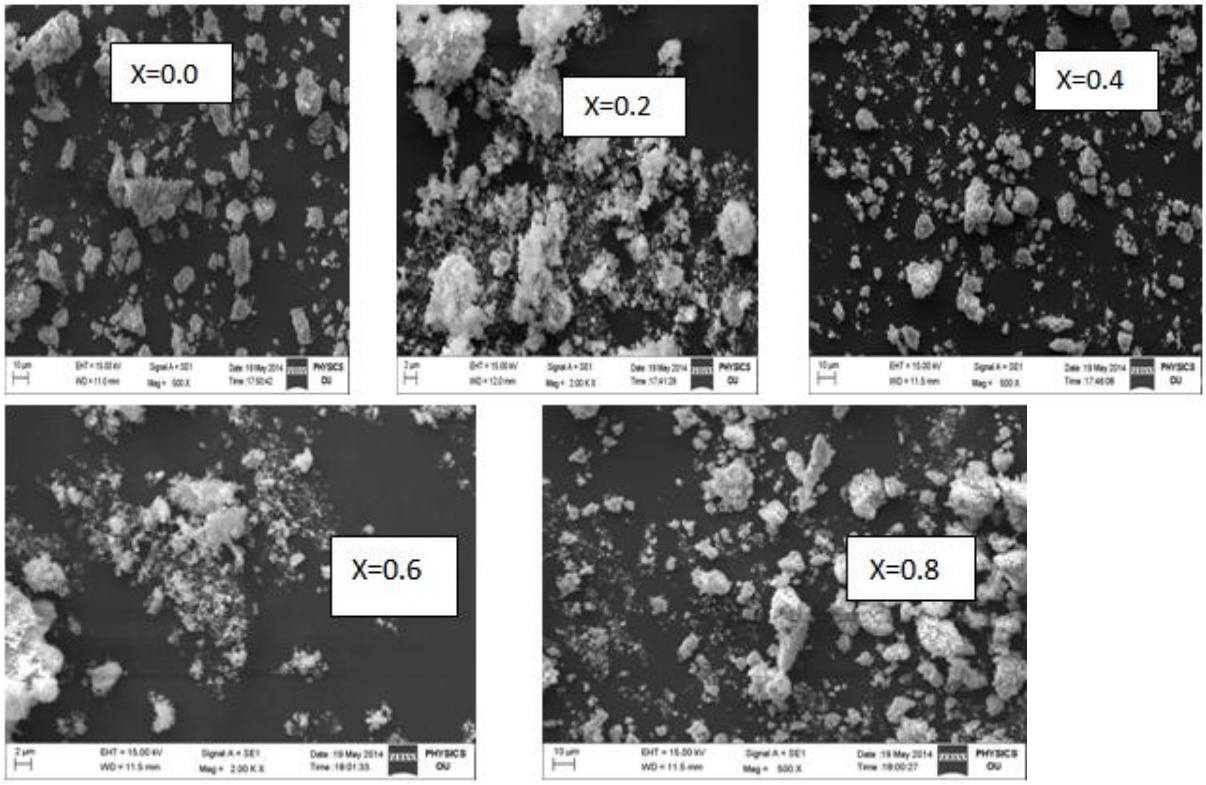
S.No	Sample	Mol.wt (gm/mol)	Crystallite size(nm)	Lattice constant (A^o)	X-ray density (gm/cc)	Volume $(A^o)^3$
1	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	239.735	54.27	8.407	5.349	594.186
2	$Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$	239.368	54.58	8.406	5.360	593.974
3	$Ni_{0.2}Cu_{0.4}Zn_{0.4}Fe_2O_4$	239.002	54.76	8.386	5.381	589.745
4	$Ni_{0.2}Cu_{0.6}Zn_{0.2}Fe_2O_4$	238.635	72.35	8.379	5.386	588.269
5	$Ni_{0.2}Cu_{0.8}Fe_2O_4$	238.268	24.13	8.313	5.507	574.477

From the table we can observe that the crystallite size of the prepared samples were in the range of 24.13nm to 72.35nm. Lattice parameters of the prepared samples were decreased by increasing the Cu concentration which obeys the Vigurd's law [17]. The observed decrease in the crystallite size can be explained by on the basis of relative ionic radii of Cu and Zn ions.

As Cu^{+2}(0.73A^o)Ionic radius is smaller than that of the Zn^{+2}(0.74 A^o). X-ray density of the prepared samples were observed to be increased with increasing the Cu concentration since X-ray density of the sample depends upon the molecular weight and lattice parameter. From the table we can observe that lattice parameter of the samples were decreases so X-ray density should be increased. Volume of the unit cell was also depends on lattice parameter. Lattice parameter of the prepared samples were decreased so the volume of the unit cell also decreased

3.2 SEM ANALYSIS:

Micro structural analysis of the prepared samples was carried out by Scanning Electron Microscopy(SEM). The SEM micrographs of the prepared samples were shown in below fig(2). The SEM micrographs shows that the grains have almost homogeneous distribution and clusters between the particles. The grain size of the samples lies in the nano meter region have a spherical shape and narrow size distribution. SEM image revealed that with increasing in the Cu concentration, then the grain size has increased (except for x=0.8) which is an evidence for the XRD analysis



Fig(2).SEM Micrographs of Ni-Cu-Zn Nano ferrites

3.3 ELEMENTAL ANALYSIS BY EDS:

Energy Dispersive Spectrometer was used for the elemental analysis of all the prepared ferrites with different compositions. The EDS spectra of all prepared samples were shown in fig(3).The compounds show the presence of Cu,Zn, Ni,Fe,O with out precipitating cations.

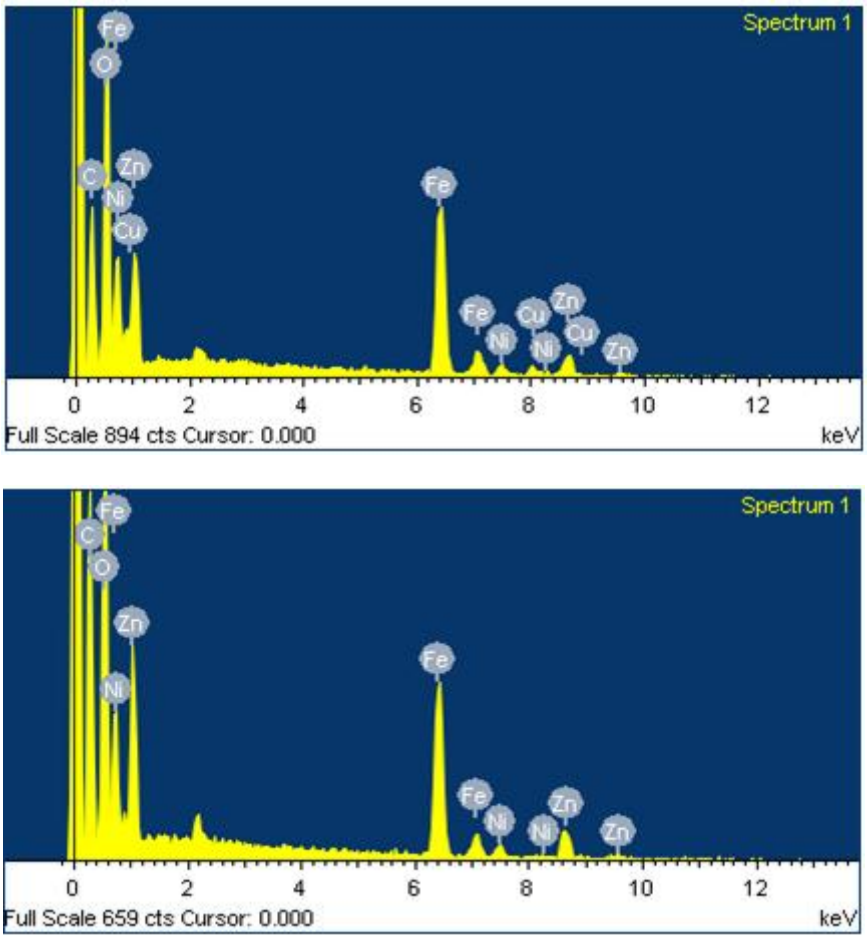


Fig (3).EDS Spectra of **Ni-Cu-Zn Nano ferrites**

IV. Conclusions

i) X-ray diffraction pattern of the prepared samples confirms the formation of single phase cubic spinal structure

ii) By the substitution of Cu in the Ni-Zn ferrite system, the lattice parameter is decreases and the crystallite size of the sample was in the range 24-72 nm.

iii)X-ray density of the samples increases with Cu Substitution.

iv) SEM micrographs of the various compositions indicate the morphology of the particles was similar. They are largely agglomerated.

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