iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 6 **Issue:** V **Month of publication:** May 2018

DOI: http://doi.org/10.22214/ijraset.2018.5052

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue V, May 2018- Available at www.ijraset.com

Synthesis and Characterization of Nanocrystalline CuNiZn Ferrite Powder Through Sol-gel Auto Combustion Method

B. S. Mahanavar[1], R. D. Kale[2]
[1, 2]*Department of Physics, Tuljaram Chaturchand College, Baramati, Dist- Pune (413 102), India*

Abstract: ***The ferrite powders of nominal composition $Cu_{0.5}Zn_xNi_{0.5-x}Fe_2O_4$ were synthesised by sol-gel auto combustion method using citric acid as an oxidising agent and the values of x are varied as x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5. The process resulted in the formation of nano-sized, highly uniform powders. The ferrite powders were sintered at 1000^0C. These synthesized and heat treated powders were investigated for their structural properties such as phase purity and particle size. The average grain size obtained from XRD data in the heat treated samples is in the nano range. The ferrites are found to be soft ferrites as revealed from hysteresis data. Also, the coercively and retentivity values are small. These soft ferrites can be used for various electrical and magnetic applications.***

Keywords: Ferrites, auto combustion, magnetic properties, SEM

I. INTRODUCTION

The credit of first scientific research on magnetic materials goes to William Gilbert. In 1600, he wrote a book in which he discussed the magnetic behaviour of different materials and also diverted the attention towards magnetism retained by planet earth. After towards magnetism retained by planet earth. After the passing 200 years, Hans Christian Oersted in 1800, observed the presence of magnetic field around a current carrying a conductor and provided a foundation for electromagnetism. Later on, Ampere, Faraday, Curie, Maxwell etc. contributed their research for the development of electromagnetic theory. However, in 1930, formal research on soft ferrites was started in Japan and Netherland. Now a days, it is mainly focused on the development of innovative synthesis routes to prepare ferrites composition such as MFe_2O_4 (where M=Mn, Cu, Zn, Ni, Mg, Ba or combination of these) at nano scale. The electromagnetic properties of synthesized composition are being failures with addition/substitution of transitions metal oxide.

NiCuZn ferrites have better high frequency properties compared to that of other ferrites. It has low sintering temperature (< 950°C) and good electromagnetic properties [1-2]. Also these ferrites have low densification temperatures compared to NiZn ferrites [1, 3]. Therefore, NiCuZn ferrites are the dominant materials for various applications. NiCuZn ferrite is a spinel ferrite. The magnetic spinels have the general formula $MO.Fe_2O_3$ or MFe_2O_4 where, M is divalent metal ion. NiCuZn ferrite in spinel notation can be represented as $(NiCuZn)Fe_2O_4$. The spinel lattice is composed of a closed-packed oxygen arrangement in which 32 oxygen ions form a unit cell. There are two kinds of interstices in between the closed-packed anions as shown in Fig.1 a) tetrahedraly coordinated interstices (called 'A' site) which are by 4 nearest neighbouring oxygen ions and b) coordinated surrounded interstices (called 'B' site) which are coordinated by 6 nearest neighbouring oxygen ions. Spinel structure can be represented as AB_2O_4. One unit cell of spinel structure contains eight formula units of AB_2O_4, where, out of 64 'A' sites 8 and out of 32 'B' sites 16 are occupied by cations.

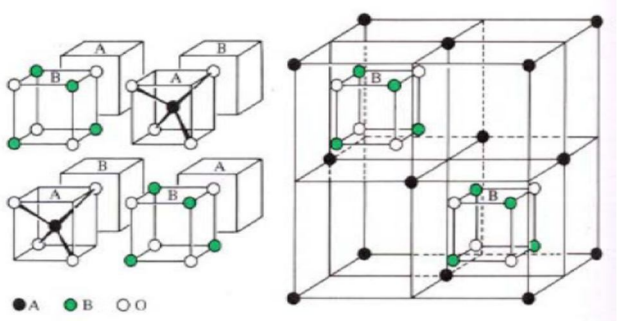

Fig. (1) Two sub cells of a unit cell of the spinel structure

The spinel is broadly divided into two groups: a) normal spinel and b) inverse spinel. In normal spinel ferrite MFe_2O_4, the divalent ions are all in 'A' sites and the Fe^{3+} ions occupy 'B' sites depending on the cation distribution in interstices. Typical example of normal spinel is $ZnFe_2O_4$. In inverse spinel the divalent ions occupy some of the 'B' sites and the Fe^{3+} ions are divided equally between 'A' and 'B' sites. Most of the magnetic spinels are inverse type like $NiFe_2O_4$, $CuFe_2O_4$ and $MnFe_2O_4$ etc. contrast is diamagnetic because the outer sub-shell of it is completely filled.

Since cations are separated by oxygen, cation - cation direct (ferromagnetic) interactions are negligible. When cations are bonded covalently to the O^{2-}, p-orbital of oxygen interact with d-orbital of cations with; C-↑-↓-O-↑-↓-C (where C represents cation and O represents oxygen) anti-parallel spins of cations. This mechanism of indirect interaction is called super-exchange. There may be three types of interactions like A-O-B, B-O-B and A-O-A. Among them A-O-B interaction is the strongest one. As the number of unpaired electrons in different cations is not same, the resultant magnetization (moment/unit volume) is thus the difference between the magnetic moments of the octahedral lattice and that of the tetrahedral lattice. This type of magnetism is called ferrimagnetism and NiCuZn ferrite is a ferrimagnetic material. The magnetic properties of the ferrites can be modified by distribution of cations in 'A' and 'B' sites through substitution. Typical example is the substitution of Ni by Zn. Half of the Fe^{3+} are in 'A' sites; remaining half and Ni, Cu share 'B' sites in the NiCu inverse spinel ferrite. When Zn is substituted for Ni, Zn preferentially enters into the 'A' sites by displacing a proportionate number of Fe^{3+} from 'A' to 'B' sites with a cation is distribution as stated in fig5. Because of that there is the significant increase in magnetic moments in octahedral site as well as in the unit cell. Permeability is the important parameters used in evaluating magnetic materials. The electromagnetic properties of NiCuZn ferrites are highly sensitive to the processing parameters like sintering conditions and the amount of constituent metal oxides in their composition [4-5].

Several groups have studied NiCuZn ferrite to enhance its properties. Important approaches adopted are: (a) the reduction of the particle size to improve densification, (b) using sintering aids for better densification and (c) substitutions at tetrahedral and octahedral crystallographic site in the spinel ferrite to improve electromagnetic properties. Various compositions in the system $(Ni_{1-x-y}Zn_xCu_y)$ Fe_2O_4 were investigated. Cu is used in this ferrite to decrease the sintering temperature so that it can be co-fired with Ag internal electrode. However, for its high frequency applications decreases the resistivity due to Cu is not desirable. So, optimization of Cu content with respect to densification and resistivity of the ferrite is very important. Changes in electromagnetic properties are also have also been reported with various Zn concentrations in NiCuZn ferrites [6-7]. Optimization of Zn concentration with respect to Ni and Cu is essential to achieve desirable electromagnetic properties in the ferrites where, Zn enters into the 'A' sites (Fig.1) by displacing a proportionate number of Fe^{3+} from 'A' to 'B' sites [6-7].

II. EXPERIMENTAL PROCEDURE

A. Materials

The extensive literature survey reveals that the synthesis of nano –crystalline CuNiZn ferrite powder through sol-gel auto combustion method has been attempted by number of researchers. The temperature at which the ferrite is sintered critically depends on the chemical composition. The electromagnetic properties such as permeability and resistivity are dependent on the densification and microstructure of the ferrite. The application prospects in electronic devices have led to more expensive studies on Ni-Zn ferrites to meet the desired characteristics of electronic component. The Ni-Zn ferrites are widely used in frequency devices for low conductivity and high resistivity.

The CuNiZn ferrites are very broadly applicable in electrical industry. The sol-gel method gives the metal oxide. Citric acid is used as the burning agent and the metal nitrate-to-citric acid taken as ratio 1:3. The sol-gel method is useful in material science and ceramic industry compared to other method sol-gel auto combustion method gives very good quality of ferrite powder. Ferrite powders were prepared by sol-gel auto combustion method. Analytical grade Nickel Nitrate [$Ni(NO_3)_2.6H_2O$], Zinc Nitrate [$Zn(NO_3)_2.6H_2O$], Copper Nitrate [$Cu(NO_3)_2.3H_2O$], Iron Nitrate[$Fe(NO_3)_3.9H_2O$], Citric Acid [$C_6H_8O_7.H_2O$] were used as raw materials in Sol-Gel auto combustion method. All the chemicals were from E-mark, India (GR grade with99.9% purity).

Compound	Atomic no.	Mass no.	B.P in ^OC	M.P in ^OC	Structure	Oxidation state
Cu	29	63.546	2562	1084.62	FCC	+1,+2 ,+3, +4
Ni	28	58.693	2913	1455.00	FCC	+4,+3, +2, +1
Zn	30	65.380	907	419.53	hexagonal	+2,+1,0
Fe	26	55.845	2862	1538.00	BCC	+3,+2

Table (1) : Basic information of materials.

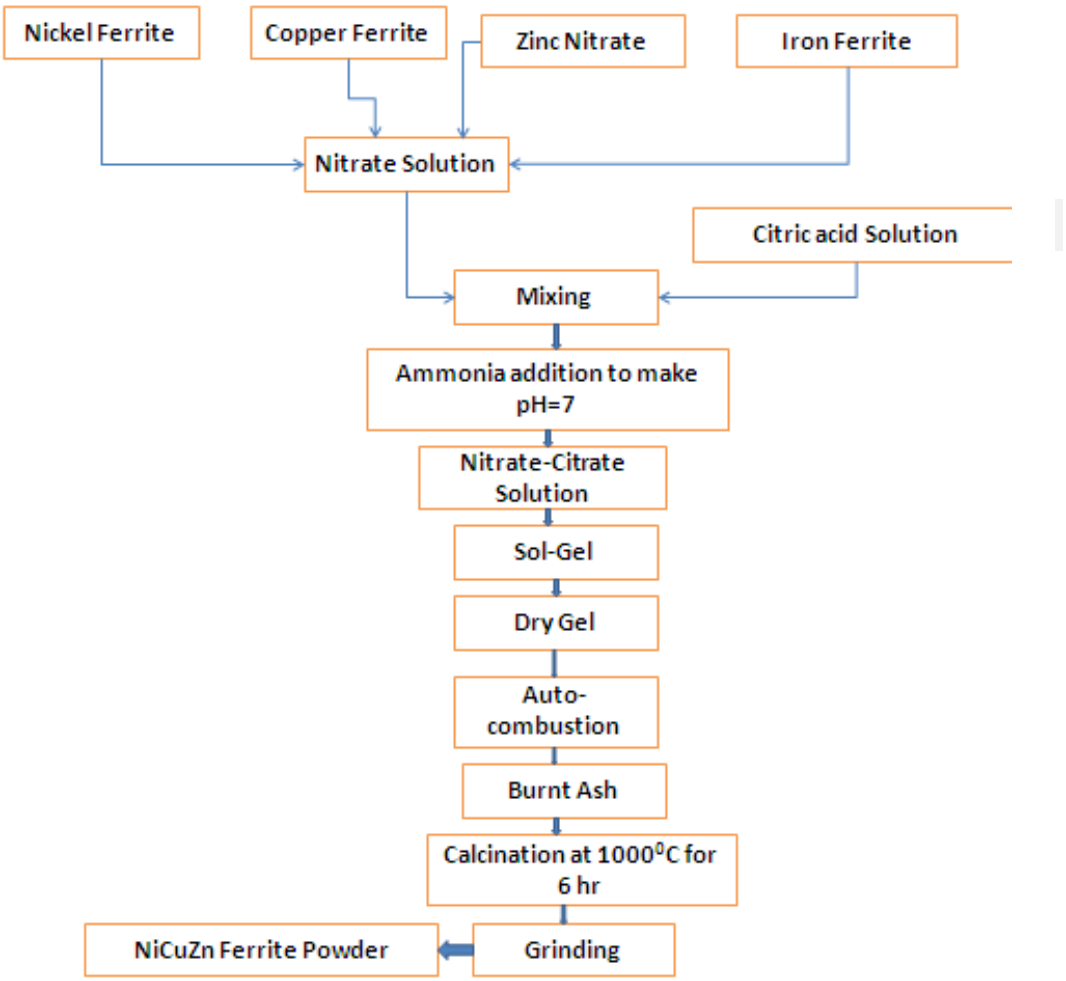

Fig. 2 : Schematic Flow Chart of Sol-Gel Auto combustion Procedure

In the present work, a wet chemical method known as sol-gel method has been used to produce $Cu_{o.5}Zn_xNi_{0.5-x}Fe_2O_4$(x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) nano ferrites and discuss the result of structural, magnetic properties and size of particles.

For formation of 10 gm ferrite powder we have taken different concentrations of the Metal Nitrates and Citric acid as given in the following table.

Concentration	Copper Nitrate	Nickel Nitrate	Zinc Nitrate	Ferric Nitrate	Citric acid
X = 0.0	5.0985	6.1618	0.0	34.0990	26.6070
X = 0.1	5.0866	4.8731	1.2526	34.0235	26.6070
X = 0.2	5.0705	3.6593	2.4973	33.9158	26.6070
X = 0.3	5.0570	2.4330	3.7360	33.8252	26.6070
X = 0.4	5.0430	1.2130	4.9680	33.7350	26.6070
X = 0.5	5.0301	0.0	6.1935	33.6452	26.6070

Table 2. Concentration wise weight of different metal nitrates and citric acid

The desired quantities of nickel, cupric, ferric and zinc nitrates salts were dissolved in double distilled water and required amount of citric acid were added as a fuel for auto combustion taken as of the ratio 1:3 and mixed this all solution in appropriate beaker as shown in below Fig.3

ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
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Fig. (3) : Saturated solution of metal nitrate and citric acid

The mixed solution was heated up to 60^0C and maintains the P_H at constant temperature 60^0C up neutral. By further increasing the temperature in between 90^0C to 100^0C. After 2 to 3 hour we got gel and some minutes later we got dry gel. Then continuously by heating the dry gel self combustion occurs at same temperature in Fig.3 during this process of combustion the citric acid was burnt out and we got a fluffy lose powder formed in Fig. 4(b). Then a prepared fluffy powder continuously grinded for 2-3 hour. This ferrite grinded powder annealed at 1000^0C for 5-6 hour in the furnace. It was again grinded and again put for annealing up to 5-6 hour in the furnace. Then this annealed powder is grinded we got homogeneous single phase ferrites.

a) dry gel b) fluffy powders

Fig .4 : Combustion procedure of Sol-Gel Method

The X-ray diffraction (XRD) and SEM (Scanning electron microscope) shows the synthesized material is ferrite. The structural and average grain size is studied by XRD, it is in crystal nature and average particle size is about few nanometers.

III.RESULTS AND DISCUSSION

A. X-Ray Diffraction Analysis

The structural characterization of the ferrite powders as prepared was carried out using XRD system. Fig.5 shows the X-ray diffractograms of $Cu_{o.5}Zn_xNi_{0.5-x}Fe_2O_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples. The XRD pattern clearly indicates that the prepared samples contain cubic spinel structure. The sizes of crystallites in the samples were evaluated by measuring the FWHM of the most intense peak (311). The phase formation behaviour was studied by XRD. The powders were in crystalline state and identification revealed spinel ferrite phases. There was no metal oxide phase in the as burnt powder. The crystallite size was calculated from full width at half maximum of the [311] peak using Scherer formula. The crystallite size of as-burnt powders can be in the range40 to 80 nm. The as burnt powders were calcined at 1000°C for 5 to 6 hrs to get more crystalline homogeneous spinel phase. The crystallite size of calcined powders was in the range 40 to 80 nm. The crystallite size increased with successive heat treatment of the ferrite.

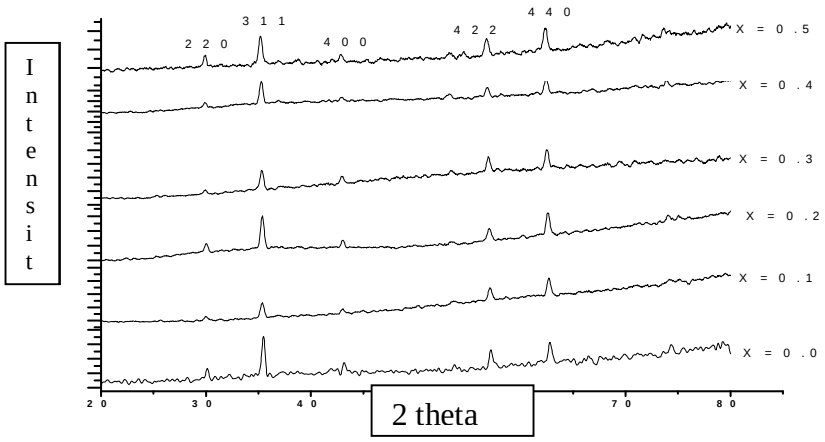


Fig. 5 : XRD pattern of $Cu_{0.5}Ni_{0.5-X}Zn_XFe_2O_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples

Samples for 'x'	Crystallite size 'D'(nm)
0.0	69.47
0.1	40.53
0.2	73.59
0.3	70.95
0.4	43.50
0.5	48.23

Table 3 : Average crystalline size of different samples calculated using Debye-Shirrer equation

B. Magnetic Properties

The Hysteresis curve Show that magnetic properties of the material. The hysteresis studies the different parameter such as Saturation magnetization (M_s), Coercive force (H_c), and Residual magnetization (M_r). The low coercivity the magnetic material is soft ferrite. The below Fig.6 Shows that the composition of Zn increases the enhance the soft magnetic behaviour, exhibiting decrease of coercivity. The powder $Cu_{o.5}Zn_xNi_{0.5-x}Fe_2O_4$(x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) is soft ferrite powder because the hysteresis loop is narrow i.e area under the hysteresis loop is very small.

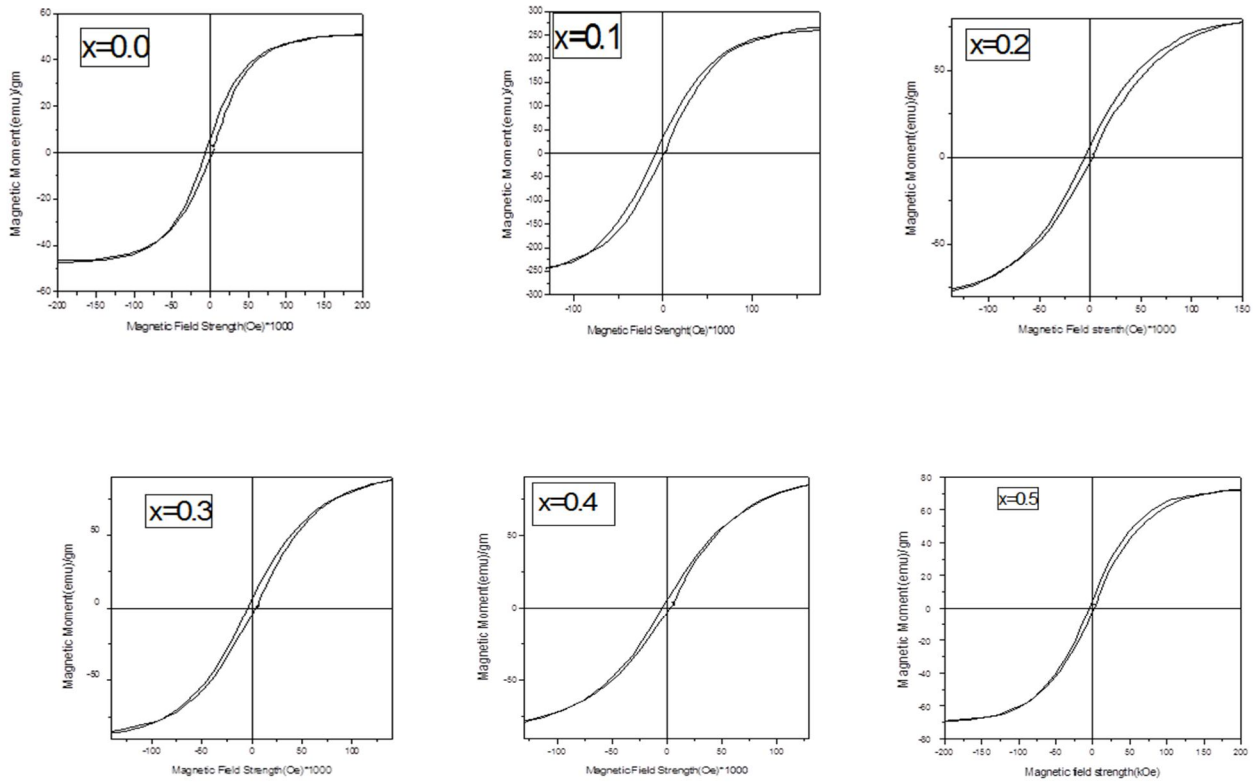


Fig. (6) : Hysterisis loop of $Cu_{0.5}Ni_{0.5-X}Zn_XFe_2O_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5)

Samples for 'x'	Coercivity H_c (Oe)	Saturation Magnetization M_s (emu/gr)	Residual Magnetization 'M_r' (emu/g)	Susc.'χ'
0.0	4995.299s0	51.1230	10.2609	0.01023
0.1	5148.6667	67.8911	11.3281	0.01318
0.2	3549.2285	83.2939	11.0808	0.02346
0.3	3213.6101	94.1438	14.2541	0.02929
0.4	3486.0755	93.3190	13.0451	0.02676
0.5	4671.257	73.1360	14.1920	0.01565

Table (4) : Change in different properties for $Cu_{o.5}Zn_xNi_{0.5-x}Fe_2O_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5)

From the variation of the coercivity (H_c) vs change in concentration of the zinc as shown in Fig. (7), it is seen that for the composition without zinc (i.e x = 0.0) the coercivity is the highest and it goes on decreasing with increasing concentration of zinc. It is minimum for the composition having x = 0.3 and after that again the coercivity increases. The variation of the saturation magnetization vs concentration of 'x' shown in Fig.7. It is seen that the saturation magnetization is lower when the concentration of Zn is low. The saturation magnetization goes on increasing with the increasing concentration of Zn in the composition up to x = 0.3 then it shows the decreasing trend.

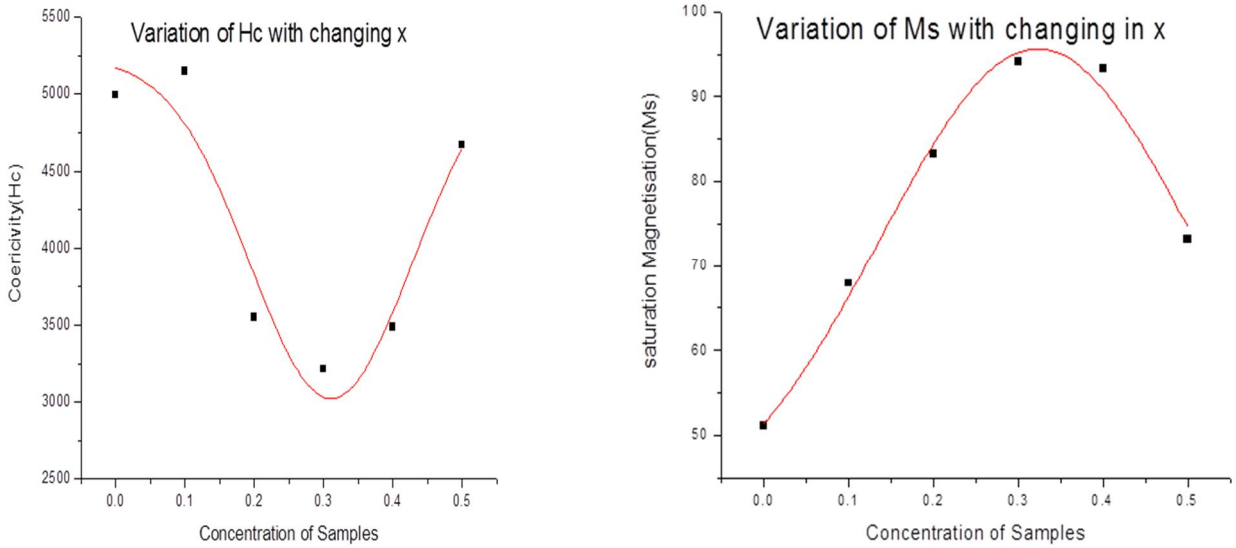


Fig . (7) : Variations of Hc and Ms With changing x

C. Sem Analysis

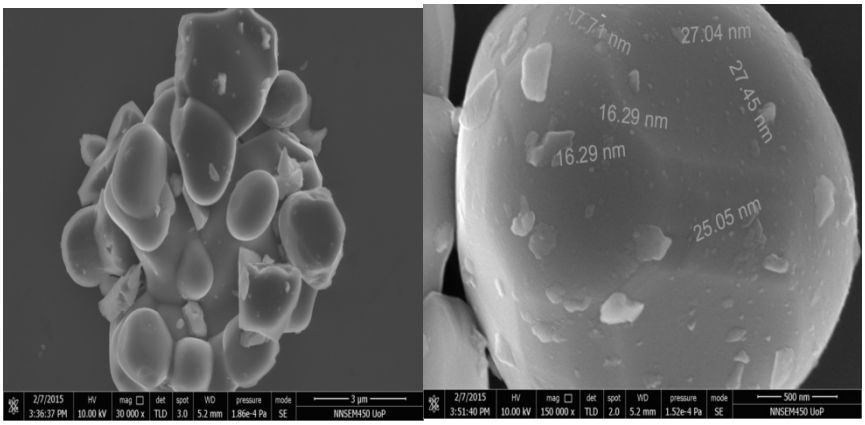


Fig.(8) SEM image for powder $Cu_{0.5}Ni_{0.5}Fe_2O_4$ (X=0.0)

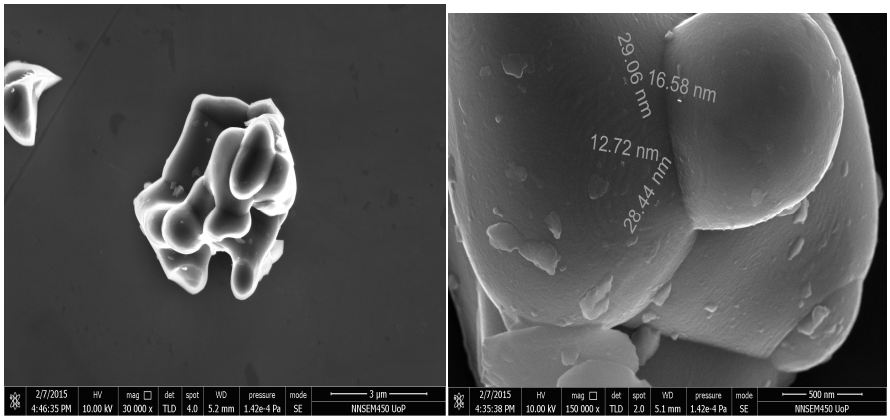


Fig.(9) SEM image for powder $Cu_{0.5}Ni_{0.2}\,Zn_{0.3}Fe_2O_4$ (X=0.3)

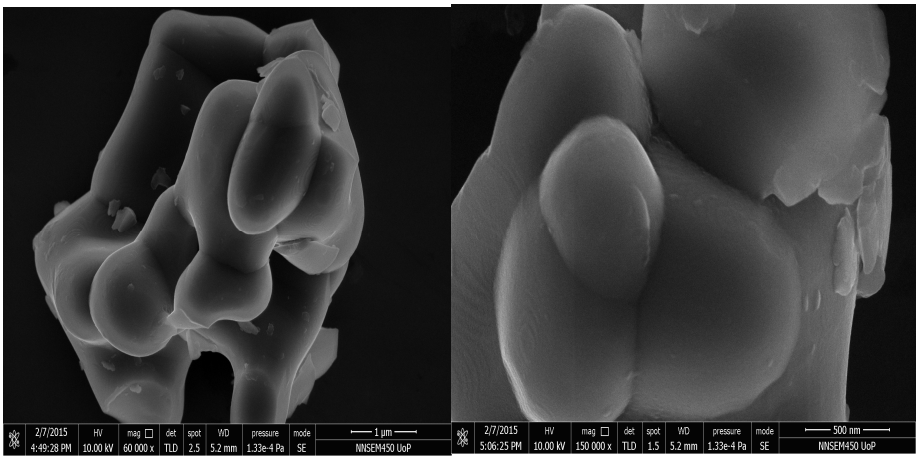
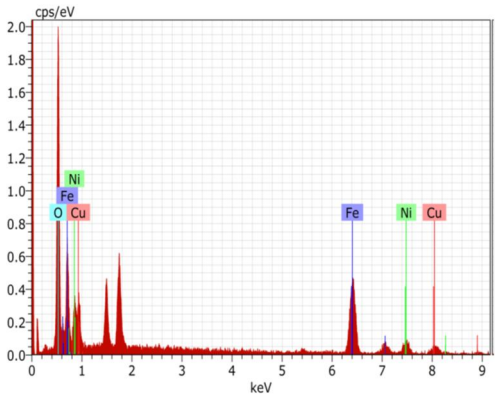


Fig.(10) SEM images for powder $Cu_{0.5}Zn_{0.5}Fe_2O_4$ (X=0.5)

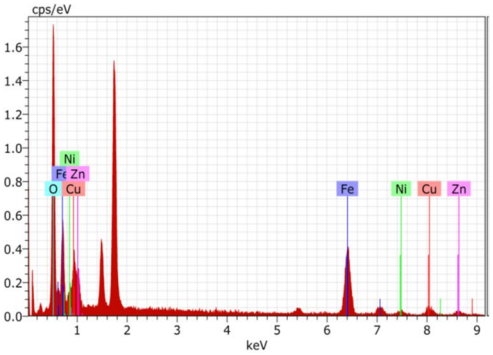
Scanning electron microscope is an instrument that is used to observe the morphology of the solid sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope. In Fig. shows the SEM photographs for different concentration of $Cu_{0.5}Ni_{0.5-X}Zn_XFe_2O_4$ (x=0.0, 0.3, and 0.5) samples with different magnification. When Zn concentration increases the size of crystal was found to be more , may be because of the sintering of the powder at 1000^0C. The SEM analysis shows that the crystalline size of ferrite powder was in few micrometers range. Few nano sized powder particles having particle size of about 12 to 30 nano meters are found to be sticked on the surface of micrometer sized crystal.

D. EDX Analysis



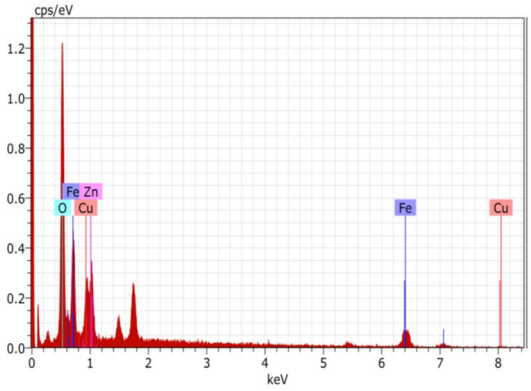
Element (x=0.0)	At. No.	Norm (Wt%)
Fe	26	45.05
O	08	33.86
Ni	28	13.08
Cu	29	09.89
Total		100

Fig.11 EDX graph for powder $Cu_{0.5}Ni_{0.5}Fe_2O_4$ (X=0.0)



Elements(x=0.3)	At. No	Norm (Wt. %)
Fe	26	42.17
O	08	31.19
Ni	28	12.80
Cu	29	08.89
Zn	30	04.96
Total		100

Fig12.EDS graph for powder $Cu_{0.5}Ni_{0.2}Zn_{0.3}Fe_2O_4$ (X=0.3)



Elements (x=0.5)	At No.	Norm. (Wt %)
Fe	26	43.68
O	08	28.83
Cu	29	15.07
Zn	30	12.43
Total		100

Fig.13 EDX Graph for powder $Cu_{0.5}Zn_{0.5}Fe_2O_4$ (X=0.5)

Energy dispersive X-ray (EDX) analysis of the as prepared specimen was carried out at different voltages on the surface of solid as shown in the figs. 11, 12 and 13.It is well known that EDX technique supplies the effective atomic concentration of different constituents on top surface layers of the solid investigated. The EDX analysis showing compositional parameters given in the side tables for each EDX. The nominal composition as determined from the EDX is in good agreement with that of the desired starting composition.

IV. CONCLUSIONS

The single phase $Cu_{0.5}Zn_xNi_{0.5-x}Fe_2O_4$ ferrite powder synthesized successfully using auto-combustion method. The powder showed soft magnetic characteristics. Variation of Magnetization saturation and Hc with increasing values of dopant concentration. Also the hysteresis curve shows soft magnetic property of ferrite. SEM images shows nano crystalline ferrite material

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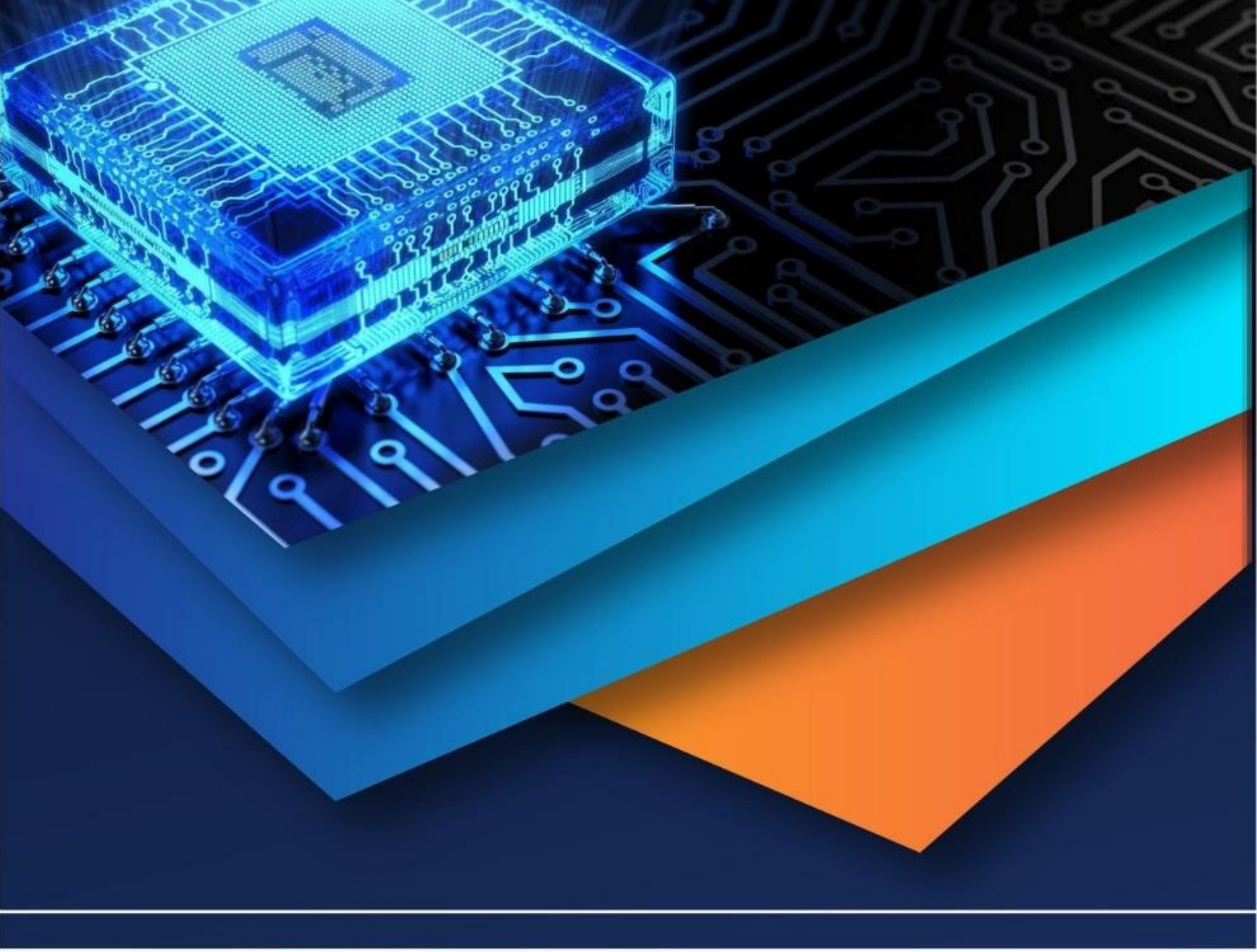

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