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Structural, Morphological studies and Magnetic Properties of Ni Substituted Nano Crystalline Copper-Zinc Ferrites Synthesized by Citrate-Gel Auto Combustion Technique

V.V. Awati
Department of Physics, C.T. Bora College, Shirur, Dist.: Pune, MS, India
vidyadharawati@gmail.com

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Abstract

The nano crystalline Ni doped Cu-Zn ferrites having compositional formula $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ (where x=0.0, 0.2, 0.4 and 0.6) were synthesized by Citrate-Gel Auto Combustion method at a low temperature (400^oC). Analysis of the X-Ray diffraction pattern of all the samples confirmed the formation of single phase cubic final structure with an average crystallite size 38-80 nm. In the present work, the effect of nano structured particle size and Ni concentration on parameters such as bulk density, x-ray density, porosity and bond length are discussed with the help of XRD data. FE-SEM images showed homogeneous and well distributed crystallized grains of ferrite material. The composition dependence of resistivity is studied with two-probe apparatus. The saturation magnetization and remnant magnetization is found to show a increasing behavior, coresivity decreases while Y-K angle shows increasing behavior with increase of Ni content.

Keywords: Citrate-gel auto combustion method, FE-SEM, DC Resistivity, Magnetic properties.

Introduction

Spinel ferrite materials have got commercial importance because of their excellent magnetic and electric properties[1]. Polycrystalline ferrites are mainly known for their technological applications ranging from microwave to radio frequencies as they are very good dielectric materials[2]. The important characteristics of ferrites are high resistivity, low magnetic and dielectric losses[3] which make them suitable for high frequency applications. Synthesis of nano-ferrites, particularly spinel ferrites, characterized by a low size distribution is crucial due to their outstanding electrical and magnetic properties and extensive practical applications in information storage systems, ferro-fluid technology, magneto caloric refrigeration and medical diagnostics[4]. They are sometimes called multiferroics due to the dielectric behavior. They can be used in many devices such as Phase Shifter, high frequency transformer cores, switches, resonators, computers, TVs and mobile phones[5-6]. The electrical properties of ferrites are dependent on many factors such as the route of preparation, composition of constituents, grain structure or size and the amount and type of substitution[7]. The properties of nano materials are notably diverse from that their bulk counter-part.

The transport properties of the nano-materials are mainly confined by the grain boundaries than by the grain itself[8]. And because of this, the magnetic materials have wide range of applications and are replacing conventional materials. The Citrate method is utilized to synthesize the complex materials rapidly. The simplicity of process lies in its time saving and energy consumption over the traditional methods. Nano size ferrites can be prepared by various methods including glass ceramic methods[9], Hydrothermal method, Ultrasonic cavitations approach[10], Reverse micelle technique[11], Mechanical milling, Radio frequency plasma torch[12], Sol-Gel method[13], Precursor techniques[14], and co-precipitation method[15].

Methodology

Synthesis: Inspected ferrite samples were prepared by low temperature citrate-gel auto combustion method, which was already explained in our previous publication[16].

Characterization: The structural characterization of the all prepared samples were carried out by x-ray diffraction (XRD) and it confirms the well defined single phase spinel structure. XRD data were taken at room temperature using Cu-Kα radiation. The Scanning Electron Microscope (SEM) JEOL JSM -6360A was used to study the morphology and to estimate grain size. The electrical resistivity measurements were carried out by two probe method at room temperature. Hysteresis Tracer was utilized to study the magnetic properties of the samples in the field of 10 kOe at room temperature.

Results and Discussion

XRD Analysis: Figure-1 shows the XRD patterns for the sample of Ni doped Cu-Zn ferrites having chemical formula $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$. The figure shows a typical cubic spinel structure. The diffraction peaks are broad because of the nanometer size of the crystallites.

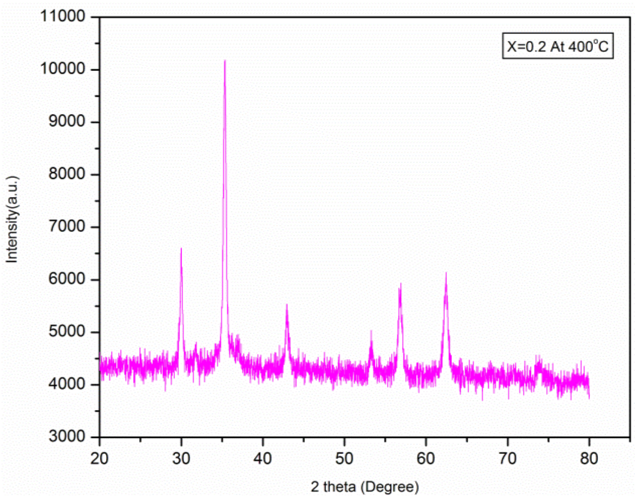

Figure-1
XRD pattern of Ni substituted Cu-Zn nanoferrites

The presence of the Ni ions causes significant changes in the structural properties of the $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ ferrite. The X- ray diffraction studies clearly showed the formation of single phase spinel structure and the grain size within nano–scale. The lattice constant and porosity shows variation, while the X- ray density increases and bulk density shows variation with increasing Ni content[17-19]. The lattice constant is found to decrease from 8.45 A^0 to 8.38 A^0 with increasing the Ni content at 400°C. Whereas, the grain size decreases from 80 nm to 38 nm on increasing Ni content as depicted in Table-1. The tetrahedral ionic radii (r_A) is observed smaller as compared to the octahedral ionic radii (r_B). The tetrahedral ionic radii (r_A) is found to decrease from 0.4794 A^0 to 0.4645 A^0 with Ni content. Octahedral ionic radii (r_B) is found to decrease from 0.7625 A^0 to 0.7453 A^0 with Ni content. Similarly the bond lengths on tetrahedral (A-O) is smaller in magnitude than the corresponding bond lengths on octahedral (B-O). The bond lengths on tetrahedral (A-O) is found to decrease from 1.8295 A^0 to 1.8146 A^0 with Ni content. The bond lengths on octahedral (B-O) is found to decrease from 2.1125 A^0 to 2.0954 A^0 [20]. The hopping lengths on tetrahedral ionic radii (L_A) is observed greater as compared to the hopping lengths on octahedral ionic radii (L_B) The hopping lengths on tetrahedral ionic radii (L_A) is found to decrease from 3.6590 A^0 to 3.6292 A^0 and the hopping lengths on octahedral ionic radii (L_B) is found to decrease from 2.9876 A^0 to 2.9632 A^0 as depicted in Table-2.

Table-1
A summary of Lattice Parameter, Grain Size and Theoretical density of $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ (X=0.2 to 0.6) nanoferrites calculated from XRD data

At 400°C Composition (X)	Lattice parameter (a) A^0	Theoretical Lattice parameter (a_{th}) A^0	Grain size (d) nm	Theoretical density (D_x) Gm/cm³
X = 0.2	8.4503	7.5457	80	31.830
X = 0.4	8.396	7.47039	56	21.878
X = 0.6	8.3814	7.4360	38	23.255

Table-2
A summary of Bulk density, X-ray density, Porosity, bond length etc. of $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ (X=0.2 to 0.6) nanoferrites calculated from XRD data

Compos -ition X	At 400° C								
	Bulk Density (P_b) Gm/cc	X-ray density (P_x) Gm/cc	Porosit y (P) (%)	Tetrahedri al onic radii (r_A) A^0	Octahedral Ionic Radii (r_B) A^0	Bond lengths on tetrahedral (A-O) A^0	Bond lengths on octahedral (B-O) A^0	Hopping lengths on tetrahedral (L_A) A^0	Hopping lengths on octahedral (L_B) A^0
X = 0.2	1.60415	5.273	0.6958	0.4794	0.7625	1.8295	2.1125	3.6590	2.9876
X = 0.4	1.4907	5.346	0.7211	0.4677	0.749	1.8177	2.099	3.6356	2.9684
X = 0.6	1.58904	5.343	0.7026	0.46457	0.7453	1.81462	2.0954	3.6292	2.9632

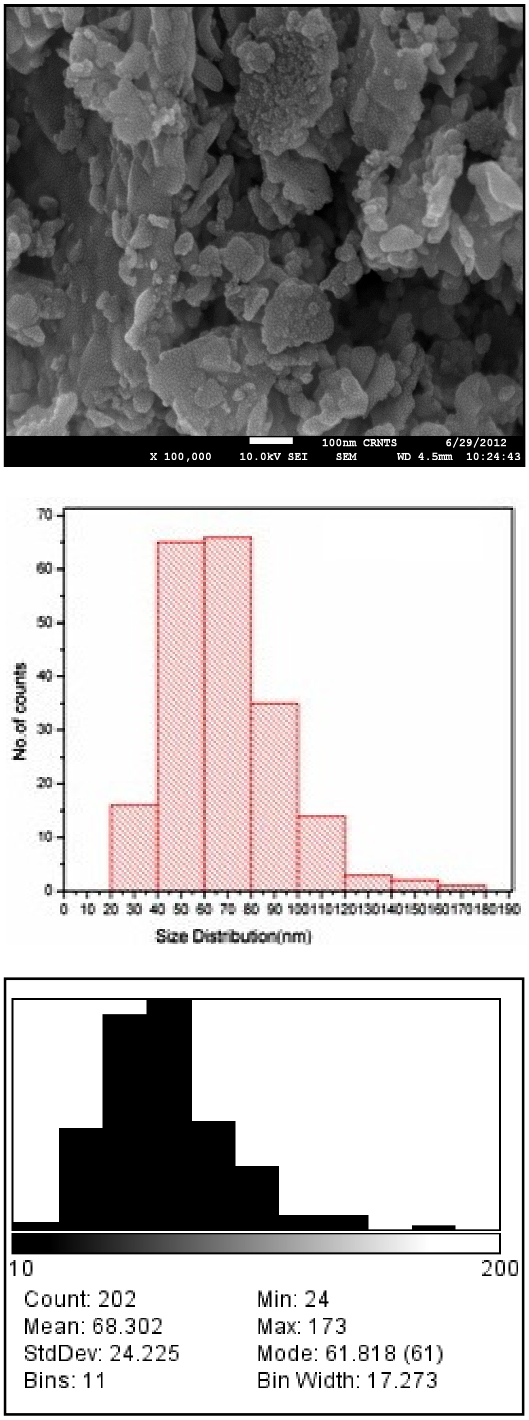

Figure-2
SEM Micrograph, Histogram and Length Distribution of the Sample

SEM Study: Figure-2 shows the SEM image of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ ferrites with 0.2 concentration of Ni for sample sintered at 400°C. It is obvious that the synthesized samples have large clusters of ferrites formed by agglomeration of small particles of nearly uniform in size with spherical shape. Similar results are reported for Cu Substituted Mn-Zn soft nano ferrites by Anwar et al.[21]. The above histogram of the sample shows the particle distribution is maximum in the range 40 nm to 80 nm. The length distribution window gives us mean particle size 68.30 nm with standard deviation 24.22.

Resistivity Measurements: DC resistivity of all samples was measured using a two-probe method as shown in Figure- 3(a, b). It is observed that DC resistivity shows a compositional variation with temperature as shown in Table-3[22]. This variation is explained by the location of the cations in the spinel ferrite. The observed variation in resistivity can be understood by considering the hopping mechanism $Fe^{2+} \leftrightarrow Fe^{3+}$ [23-24]. The increase in Ni^{2+} ions at the B site leads to replacement of Fe^{3+} ions at B site, leading to a decrease of ferrous ions formed. Alhough the Ni^{2+} ions never participate in the conduction mechanisms, they limit the degree of $Fe^{2+} \leftrightarrow Fe^{3+}$ transfer, hence obstructing electron hopping and resulting in change in resistivity. The similar nature of resistivity has been explained earlier[25]. The conduction in the samples is due to grain boundaries. The high values of DC electrical resistivity support this result.

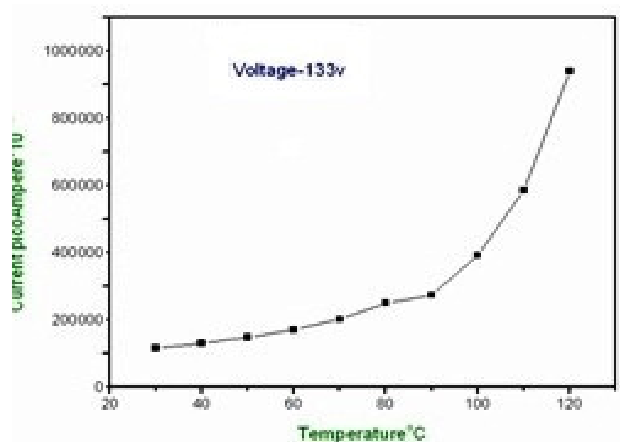

Figure-3(a)
Current-Temperature characteristics at constant voltage

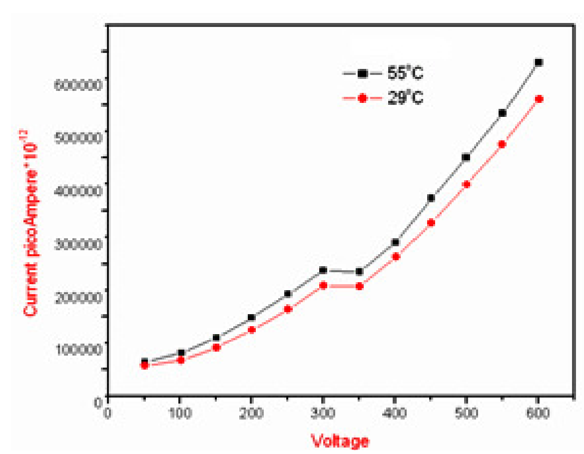

Figure-3(b)
Current-Voltage characteristics at varying temperature

Table-3
Resistivity and Conductivity measurements

Sr. No.	Sample composition	Constant temperature or Voltage	Resistance (Ω)*10^{10}	Resistivity Ω-cm*10^{10}	Conductivity Per Ω-cm*10^{-10}
1	X=0.2	133V	0.2301	0.6689	1.4949
		21°C	0.273	0.7937	1.2599
		29°C	0.2780	0.8082	1.2373
		55°C	0.193	0.5611	1.7822

Table-4
Magnetic properties of $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ (X=0.2) nano ferrites

Temperature (°C)	Zn content(x)	Ms (emu/gm)	Mr (emu/gm)	Hc (Oe)	Mr/Ms	Bohr Magneton	Y-K Angle
400	0.2	012.732	003.451	2010.031	0.27108	0.54593	40.7420
	0.4	025.489	008.632	1679.882	0.33866	1.08678	54.2799
	0.6	053.991	023.533	11290.81	0.43581	2.28908	57.5789

Magnetic Properties: The saturation magnetization and remnant magnetization is found to show a increasing behavior, coresivity decreases while Y-K angle shows increasing behavior with increase of Ni content[26]. The magnetic properties of the sample are mainly dominated by Zn^{2+} non magnetic ions replacing Ni^{2+} ions as well as migration of Fe^{3+} ions from octahedral to tetrahedral sites. Low field hysteresis loop shows a decreasing trend in coresivity with Ni contents due to increased magnetic softness[26-27]. All the coersivity value were sufficiently low to confirm that the ferrite was soft ferrite. Y-K angle shows increasing behavior with increase of Ni content. Bohr Magneton shows increasing behavior with Ni content. Bohr magneton shows maximum value of 2.2890 at x=0.6 as depicted in Table-4.

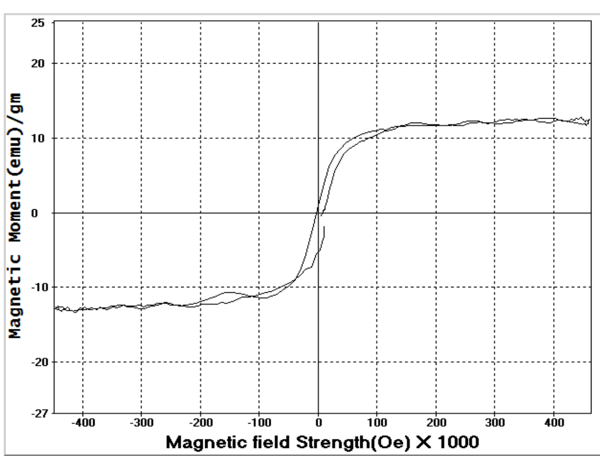

Figure-4
Magnetic hysteresis loops of $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ (X=0.2) nanoferrites

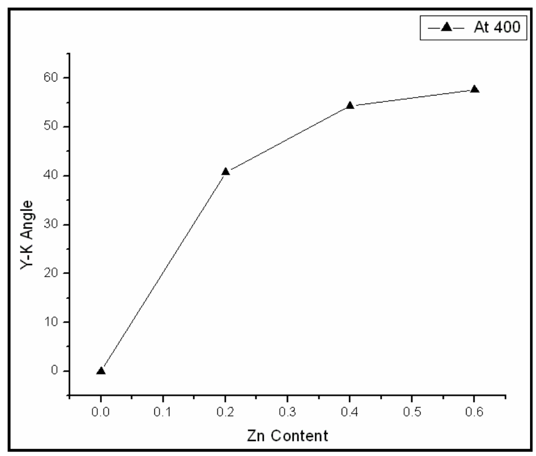

Figure-5(a)
Variation of Y-K Angle with Zn content

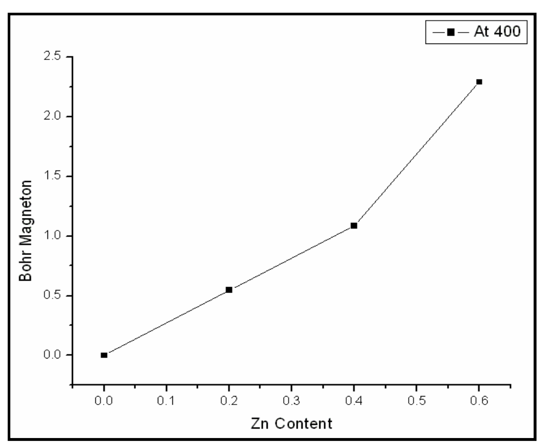

Figure-5(b)
Variation of magnetic moment with Zn content

Conclusion

i. X-ray diffraction pattern shows that studied samples confirms the formation of single phase cubic spinel structure. ii. Ferrites composition of $Ni_xCu_{0.1}Zn_{(0.9-x)}Fe_2O_4$ with an average crystallite size between 38 to 80 nm were synthesized through citrate Gel-Auto combustion method. iii. The SEM results of the sintered samples show that the grain boundary is temperature dependent. iv. DC electrical resistivity measurements prove that resistance of the samples is of the order of 10^{10} ohm indicating that material is like insulator and DC electrical resistivity varies with composition. v. For all samples, a 'S' like shape hysteresis curve was observed. The saturation magnetization (M_s) value is 12.732 emu/gm for x=0.2 at 400°C.

The prepared ferrite materials have high DC resistivity, low saturation magnetization. These results are capable for the use of these materials in high frequency functional device applications.

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