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RESEARCH ARTICLE

STRUCTURAL, DIELECTRIC AND MAGNETIC PROPERTIES OF NI SUBSTITUTION IN Cu-Zn NANO FERRITES

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ABSTRACT

Nano-structured NiCuZn ferrite with composition $Ni_xCu_{0.1}Zn_{0.9-x}$ (where x = 0.0, 0.2, 0.4, 0.6) was prepared by self propagating technique. X-ray diffraction (XRD) patterns of all samples exhibited the spinel structure. Further, the XRD data have been applied to calculate the lattice parameter and grain size. The structural probes and nanometric sizes of the samples was examined by using scanning electron microscopic techniques. Dielectric constant varied from 30 to 80,000 with frequency, rise in Ni concentration and temperature. Vibrating Sample Magnetometry (VSM) was employed to study the magnetic properties of nano-ferrite. High saturation magnetization of value 62.3 emu/g was measured for the sample consisting Ni concentration X= 0.6. These nano-ferrites may have application in core materials and in electronic device technology.

INTRODUCTION

Nano sized ferrite with narrow size distribution and uniform particle size are of current research interest due to their broad application in technological fields like targeted drug delivery, medical imaging, electronic devices, magnetic storage devices etc. [1]-[4]. The chemical composition, method of preparation, nature of ions and their site preference among tetrahedral and octahedral sites in lattice influence the structural and electrical properties of spinel ferrites. Among the different spinel ferrites, zinc ferrite is one of the most versatile, due to their wide range of potential applications like as absorbent material, photo catalyst and gas sensors [5-6]. Self propagation is an attractive preparation method for ferrites due to its good stoichiometric control and production of ultra-fine particles in nano range at relatively low temperature [7]. Magnetic nanoparticles of spinel ferrites have been investigated in recent years for their usual electrical and magnetic properties and applications in information storage systems, magnetic bulk cores, microwave absorbers and medical diagnostics. The synthesis and characterization of superparamagnetic nanoparticles of spinal ferrites with the chemical formula MFe_2O_4 (M=Co, Mn, Ni, Zn, Mg, etc.) have been investigated with much interest. Nano size effect and the large surface area of nanoparticels dramatically change the magnetic properties and exhibit superparamagnetism, because each particles can be considered as single magnetic domain [8-10]. The incorporation of metal ions to the spinel structure can considerably change the magnetic and electrical properties. The structural and dielectrical properties of nickel substituted copper zinc ferrite has not been investigated in detail. In the present study, the effect of nickel substitution on structural and dielectrical properties of nano crystalline copper zinc ferrite prepared by self propagation technique is reported.

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Experimental Techniques

Synthesis of Nanoferrites

$Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ (where x = 0.0, 0.2, 0.4, 0.6) nanoferrites were prepared by self propagating way. The precursor solution was prepared using AR grade metal nitrates of $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, and $Fe_2(NO_3)_2$. These nitrates were initially dissolved separately in distilled water and stirred well for 20 minutes at 80° C, subsequently the precursor solution was prepared by adding all above solutions and continuously stirred for 30 minutes at 80° C. An aqueous solution of citric acid mixed with metal nitrate solution, then ammonia solution was slowly added to adjust the pH at 7. The mixed solution was kept on to a hot plate with continuous stirring at 100° C. When finally all water molecules were removed from the mixture, the viscous gel began frothing. After few minutes the gel automatically ignited and burns with glowing flints. The auto combustion was completed within a minute, yielding a brown colored ashes termed as precursor. The as prepared powders were sintered at 400° C for two hours to get the final product. Also the prepared ferrite mass was pressed in the form of pellets of 10 mm diameter with the help of hydraulic press by applying pressure of 60 kg/ cm^2 for 1-2 minute. These pellets were sintered at 400° C for two hours in air medium.

Characterization

Powder X- ray diffraction (XRD) pattern was carried out on a X- ray diffractometer (Model Bruker D8), with CuKα irradiation (λ = 1.5405 Å). The lattice parameter, crystallite (grain) size of the prepared samples were calculated from the XRD data. The Scanning Electron Microscope (SEM) JEOL JSM-6360A was used to study the morphology and to estimate grain size. The dielectric constant, loss factor (tan δ) was measured by two probe method using precision LCR meter bridge (HP 4284 A) in the frequency range of 100 Hz to 1

MHz at room temperature. Vibrating Sample Magnetometer (VSM) was employed to study the magnetic properties of the samples in the field of 5 kOe at room temperature.

RESULTS AND DISCUSSIONS

Structural Analysis

Fig. 1(a) and Fig. 1(b) shows XRD pattern of as prepared and samples sintered at 400° C of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ ferrites for x = 0.0 to 0.6 with the step increment of 0.2 prepared by self-propagation technique.

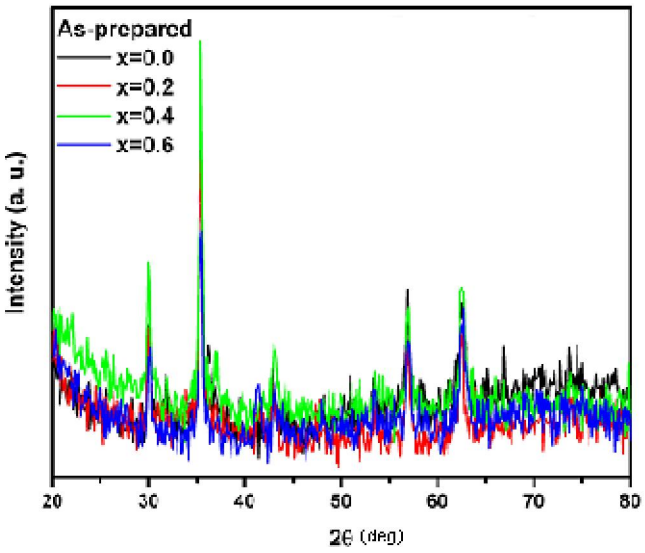

Fig.1(a) XRD pattern of as prepared samples of $Ni_xCu_{0.1}Zn_{0.9-x}$

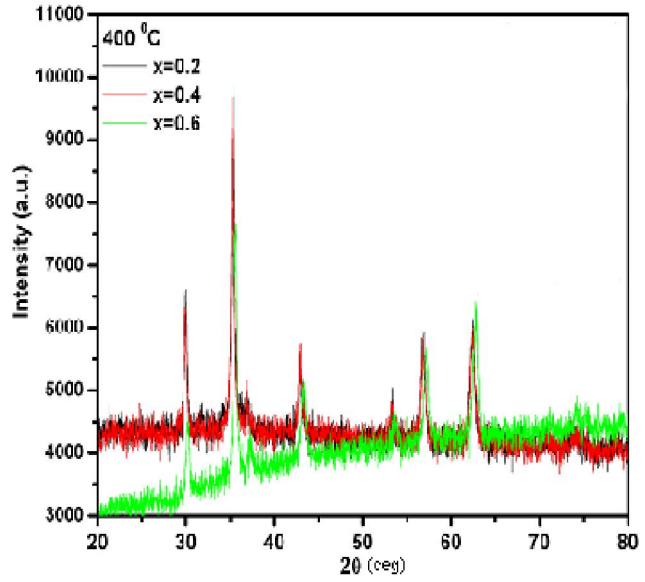

Fig.1(b) XRD pattern of samples of $Ni_xCu_{0.1}Zn_{0.9-x}$ sintered at 400°C.

XRD pattern have confirmed the spinel structure of all the samples. The peak position and relative intensity of all diffraction peak match well with the standard powder diffraction data [11], confirms the formation of ferrite phase for all compositions. Furthermore, no impurity related peaks or secondary phases were observed, which includes the formation of high purity crystalline $Ni_xCu_{0.1}Zn_{0.9-x}$ (where x = 0.0, 0.2, 0.4, 0.6) ferrites. The broad amorphous nature of XRD peaks indicates the formation of nanoferrites. The average particle size of each composition was calculated for (311) plane using Scherrer formula [12]. The values of crystalline size and lattice parameters deduced from X-ray data are summarized in Table 1. Upon substitution of Ni^{2+} ions, the lattice parameter was found to be initially decreased and later on increased with increasing concentration of substituted ions. This change in lattice parameter was expected as the ionic radius of Ni^{2+} ions (0.69 Å) is greater than the ionic radius of Fe^{3+} ions (0.67 Å) [13]. The observed lattice parameter and specific indices are characteristics of spinel structure confirm the formation of cubic spinel structure in ferrite [14-18]. The XRD results do not show any unidentified peak, confirms no chemical reaction or diffusion occurred during sintering. The X-ray density, the theoretical density is computed for all the samples. Figure 2(a) and 2(b) shows the SEM images of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ ferrites with 0.2 concentration of Ni for as prepared and samples sintered at 400°C.

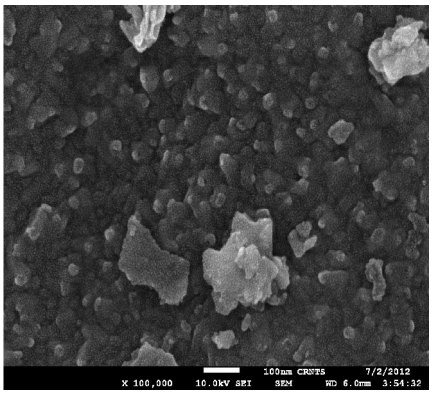

Fig.2(a)

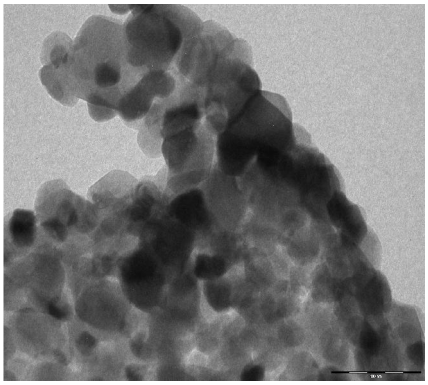

Fig.2(b)

Fig.2(a). Scanning electron micrograph of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ (x=0.2) for as prepared ferrites

Fig.2(b). Scanning electron micrograph of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ (x=0.2) for sample sintered at 400°C

Table 1. A summary of Lattice parameter, grain size, X-ray density and theoretical density of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ nanoferrites calculated from XRD data

Compo-sition(X)	As Prepared				At 400°C			
	Lattice Parameter(a) Å	Grain Size (d) nm	X-ray Density D_{hkl} gm/cm^3	Theor-etical Density D_{hkl} gm/cm^3	Lattice Parameter (a) Å	Grain Size (d) nm	X-ray Density D_{hkl} gm/cm^3	Theor-etical Density D_{hkl} gm/cm^3
X=0.0	8.439	58	5.3265	23.610				
X=0.2	8.312	46	5.5435	18.390	8.4503	80	5.2757	31.830
X=0.4	8.322	42	5.4926	27.653	8.396	56	5.3487	21.878
X=0.6	8.3869	47	5.3359	4.6343	8.3814	38	5.3464	23.255

It is evident 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.* [19]. We have obtained very similar results for other. The particle were observed as uniform grains confirming the crystalline structure of copper zinc ferrite which were detected by the XRD profile. The formation of Fe_2O_3 was chemically favored during the heating, were as, the final reaction was completed during the sintering where the pores between the particles were removed combined with growth, and strong bonds between the adjacent particles were formed.

Dielectric Properties

The dielectric constant (έ) was calculated using the formula:

$$\varepsilon' = C.t / \varepsilon_o A \quad (1)$$

where C is the capacitance of pellet, t is the thickness of pellet, A is the area of sample and ε_o is the permittivity in free space. Figure 3 shows the variation of dielectric constant έ with frequency for composition x=0.6 for as prepared and samples sintered at 400°C. The dielectric constant έ decreases with increase in frequency showing the dispersion in a certain range of frequency and it remains constant for higher frequencies. As sintering temperature increases dielectric constant also enhances. The large value of έ at lower frequency has been attributed to the effect of heterogeneity of the samples [20]. The summary of dielectric constant for various compositions and at low and high frequencies is depicted in Table 2. The dielectric dispersion in ferrites has been explained on the basis of Maxwell–Wagner model [21] and Koop's [22] phenomenological theory of dielectrics. At low frequencies, έ falls rapidly for the composition having higher value of dielectric constant indicates the large dispersion in the composition with large value of έ. The exchange of 3d electrons between Fe^{3+} and Fe^{2+} which are localized at the metal ions, results in local displacement of electrons in the direction of field which determines the strength of polarization. The low value of dielectric constant (268.76) was observed for the sample $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ nanoferrites with x = 0.2. The low value of dielectric constant could be due to the synthesis method which suppresses the formation of Fe^{2+} ions. At low frequency, the tan δ value was observed to be large and it decreases with increasing frequency and temperature. The physical significance of tan δ is the energy dissipation in the dielectric system. For higher frequency range, the loss vanishes and the dipole orientation contributes to the polarization (Fig. 4). The ac resistivity ρ_{ac} was calculated from dielectric data and loss tangent using the following relation;

$$\rho_{ac} = \varepsilon' \varepsilon_o \omega \tan\delta \quad (2)$$

where, ω is the angular frequency, tan δ is the loss factor and έ is the real part of dielectric constant. The AC resistivity of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$, samples were found to be increases with the substitution of Ni up to x = 0.2 and subsequently it decreases for the samples for x >0.2. The highest value of AC resistivity (4.64 X 10^4 V-cm) was observed for Ni substituted nanoferrites for samples sintered at 400°C(Fig. 5). The observed values are compararble than those reported in the literature for Cu–Zn ferrites [23]. The conduction in ferrites is reported due to the hopping of electrons upon application of electric field. The increase of Fe^{2+} concentration in the sample increases the hopping probability resulting in decease of resistivity at higher frequencies [24]. Similar results are reported for Cu–Zn ferrites by Sattar *et al.* [25] and El-Syed [26] suggested the conduction mechanism could be predominantly due to hopping of electrons or ions.

Table 2. Summary of dielectric constant for $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ (X=0.0≤0.6) at low and high frequency

Composition X	At Low Frequency(100 Hz)		At high Frequency(5 MHz)	
	As prepared	At 400°C	As prepared	At 400°C
0.0	2.43 x 10^4	2.43 x 10^4	1.16 x 10^3	2.79 x 10^1
0.2	4.38 x 10^4	1.06 x 10^4	1.74 x 10^2	2.68 x 10^2
0.4	7.21 x 10^5	3.91 x 10^3	2.26 x 10^4	4.75 x 10^2
0.6	1.65 x 10^4	2.09 x 10^4	1.67 x 10^2	1.15 x 10^3

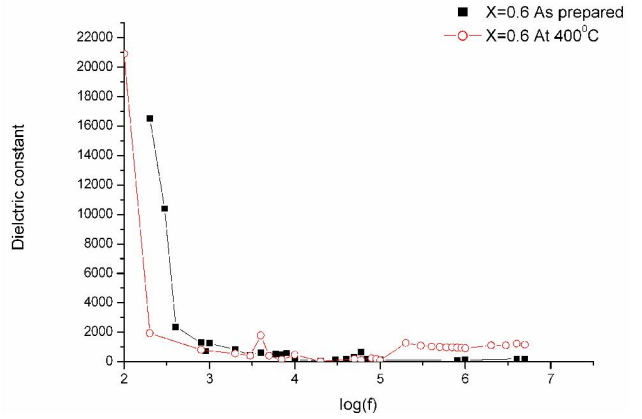

Fig. 3. Variation of dielectric constant with frequency for $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ nanoferrites for x=0.6

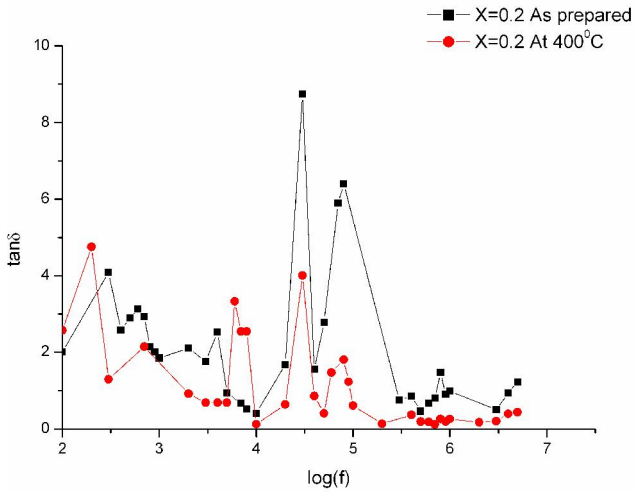

Fig.4. Variation of loss tangent with frequency for $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ nanoferrites with x=0.2

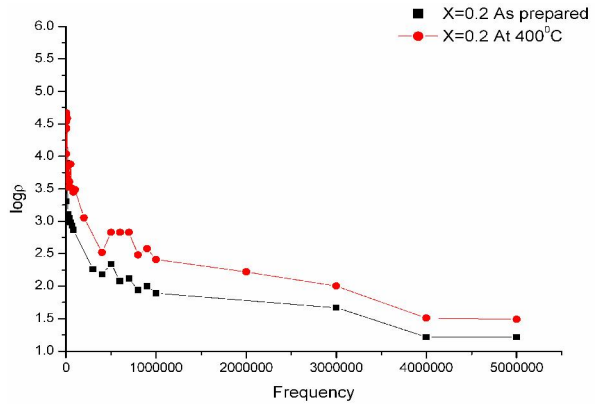

Fig.5. Variation of ac resistivity with frequency for $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ nanoferrites with x=0.2

Magnetic properties

Magnetic hysteresis lops recorded for Cu–Ni–Zn nanoferrites is shown in Fig. 6. It was observed that the magnetization increases sharply in the low field region. However, it could not reach to the saturation state after application of 5 kOe magnetic field. Similar observations at room temperature magnetization have been reported by Koseoglu *et al.* [27], and Wang *et al.* [28]. Superparamagnetic 'S' shaped hysteresis curves are obtained for all ferrite structures. The saturation magnetization M_s was found by extrapolating M_s versus 1/H plot to 1/H = 0. It was observed that the value of M_s increases with Ni doping and became maximum (62.3 emu/g) for the sample consists the concentration of Ni x = 0.6. The saturation magnetization decreases for the samples with x <0.6. This decrease of saturation magnetization can be explained on the basis of cation distribution. The concentration of Ni affects on the net magnetization [29]. However, these values are low for all compositions as a counterpart of bulk ferrites. The reduction of M_s in nanoparticles was attributed to the existence of random canting of particles caused by antiferromagnetic exchange interactions due to asymmetry of these spins [30]. The low values of coercivity indicate the transformation from ferromagnetic to superparamagnetic behavior. In the superparamagnetic state of the material, the room temperature thermal energy overcomes the magnetostatic energy, resulting in zero hysteresis. In other words, the particle itself is a single domain ferromagnet having ability to store magnetization information [31].

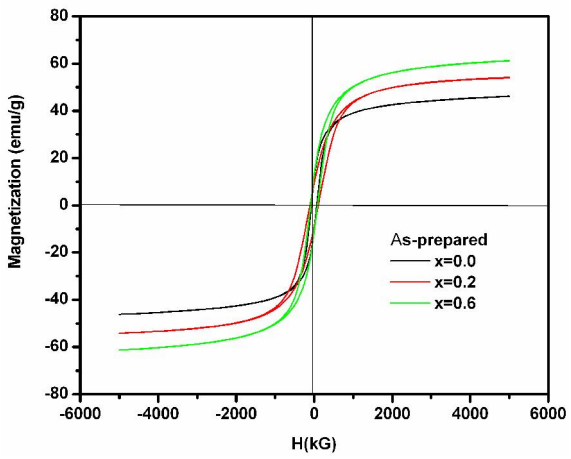

Fig. 6. Magnetic hysteresis loops of $Ni_xCu_{0.1}Zn_{0.9-x}Fe_2O_4$ nanoferrites

Conclusions

For the sample material, we use the low temperature sintering NiCuZn ferrite powder synthesized by self propagating technique for the metal nitrate and analyzed the distribution of granularities, the microstructure, and the XRD patterns of the powders acquired from calcining the NiCuZn ferrite powder at 400°C, We reached to the following conclusions:

I. The broad XRD peak indicates the formation of nanoferrites. The observed Lattice parameter and specific indices are characteristics of spinel structure with no any indentifying or secondary peak.
II. The SEM results of the sintered samples shows that the grain boundary grew as temperature increases.
III. The results of XRD pattern show that the lowest calcining temperature is around 400°C.
IV. The low value of dielectric constant is attributed to the method of synthesis (Self propagating technique) which suppresses the formation of FE^{2+} ion. The value of tan δ for these samples reduces at higher frequencies.
V. The higher values of ac resistivity (4.64 X 10^4 V-cm) for these ferrites indicate that these ferrites may be used in the application at higher frequencies.
VI. For all samples, a supermagnetic 'S' like shape hysteresis curve were observed. The value Ms increases with Ni doping upto x=0.6. It was maximum (62.3 emu/g) for the sample x=0.6.

The prepared ferrite materials have high ac resistivity, very low dielectric loss, high saturation magnetization. These results are promising for the use of these materials in high frequency application.

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