Effect of cobalt substitution on the structural and magnetic properties of nanopowders $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ by hydrothermal method

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(Received: 17 June 2016, accepted: 12 October 2016)

Abstract: In this work, the effect of Co substitution in the structural and magnetic properties has been investigated in Ni-Cu-Zn ferrites $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$, $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ (x=0, 0.2, 0.4) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ (x=0, 0.1, 0.2). Nanoparticles of ferrites were obtained by hydrothermal method with stirring. A single phase from Ni-Cu-Zn ferrites with cubic spinel structure was formed for all the powders. The lattice parameter has been found to decrease with increasing Co content for all the samples, and this variation in the spinel unit cell is attributed to the difference in the ionic radius of Ni^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+} ions. The results show an improvement in magnetic properties by substitution with cobalt, especially for the samples $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ and $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ with x=0.2. The saturation magnetization (Ms) of samples increases with the increase of crystallite size after sintering to reach the value of 81.68 Am^2kg^{-1}. However, the Curie temperature decreased with increasing Co content for the spinel ferrite $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ and does not change for $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$.

Keywords: Spinel Ni-Cu-Zn ferrites, hydrothermal method, cobalt substitution, magnetic properties.

INTRODUCTION

Ferrites Ni-Cu-Zn has become a promising magnetic material in many applications such as spintronic applications [1], recording heads, microwave and magnetic storage devices, etc.

These have been extensively used in recent years because to their low eddy current losses, high electrical resistivity, moderate saturation magnetization, low coercivity, high Curie temperature, good mechanical hardness, chemical stability, resistance to corrosion and reasonable cost [2-4]. Different techniques are used to synthesize pure $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ ferrite such as sol-gel methods, co-precipitation and ultrasound [5]. The hydrothermal technology with agitation is very versatile method because of its economics and high degree of compositional control. Fairouz et al. have used this method to synthesis pure $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ ferrite at low temperature (~200 °C) [6]. The properties of spinel ferrites are highly dependent by their compositions, synthesis methods, and cation substitutions [7]. Several researchers have focused their attention on enhancing the properties of ferrite substitution with divalent ions. Generally the divalent metal ions (M^{2+}), Ni, Zn, Cu, Mg, Mn, Co or mixtures of them was substituted in the spinel ferrites. Substitutions have different seating preferences for two sites ('A' and 'B') in the spinel structure and can change many properties with the change of cations distribution in the ferrite. In order to change the magnetic properties, substitution of other elements such as cobalt was proposed by many researchers. B.P. Rao et al. reported the Co-dependent magnetic behavior of $Ni_{0.35}Zn_{0.65-x}Co_xFe_2O_4$ (x=0 to 0.25) synthesized using a conventional ceramic technique [8]. S. R. Shannigrahi et al. has been found that Co doped ferrite shows the best saturation magnetization in $(Ni_xCo_{1-x})_{0.5}Zn_{0.5}Fe_2O_4$ composite [9]. J.S. Ghodake et al. have reported the permeability and magnetic behavior of Co-substituted Ni-Zn ferrites

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processed using an oxalate precursor method [10]. S.L. Pereira et al. investigated the modifying magnetic behavior of Co substituted Ni-Zn ferrite synthesized using a hydrothermal process [11]. L.Z. Li et al. studied the influence of Cu and Co substitution on the properties of Ni-Zn ferrite thin films synthesized using a sol gel method [12]. According to many research, the cobalt substitutions on ferrites Ni-Cu-Zn were found to be suitable for enhanced properties, such as saturation magnetization, coercivity and Curie temperature. In the present work, nanoparticles of spinel ferrites $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$, $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ ($0 \leq x \leq 0.4$) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ ($0 \leq x \leq 0.2$) were prepared using hydrothermal method.

Properties such as particle sizes, saturation magnetization and Curie temperature parameters were studied.

EXPERIMENTAL

1. Preparation of the powders

The samples were prepared by hydrothermal method, and crystallization took place in a stainless steel autoclave. The initial chemicals were analytical grade nickel sulfate [$NiSO_4,6H_2O$], copper sulfate [$CuSO_4,5H_2O$], iron nitrate [$Fe(NO_3)_3,9H_2O$], zinc sulfate [$ZnSO_4,7H_2O$], and cobalt sulfate [$CoSO_4,7H_2O$]. Stoichiometric amounts of each chemical were carefully dissolved in 40 ml deionized water. The pH of the solution was adjusted to 13 using sodium solution (5M) and this solution has put in an autoclave at a temperature of 220 °C for 4 h. After the autoclave was naturally cooled and depressurized, the resulting powders were collected by filtration, washed with HCl and distilled water to remove any possible impurities, and finally dried at 100 °C under an oven during 24 h.

2. Characterization

X-ray powder diffraction pattern was recorded using a Bruker D8 Advance model diffractometer in the two theta range 20 - 70° operating with Cu Kα radiation. The average crystallite size was calculated by Scherrer's equation [13].

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

In which, D is the crystallite size, λ is the wavelength of X-ray radiation (Cu Kα), θ is the Bragg angle and β is the full width at half maximum (FWHM) of the most intense diffraction peak. Magnetic measurements, such as saturation magnetization (Ms) and coercivity (Hc) are made on Lake Shore 7400 vibrating sample magnetometer (VSM).

In order to figure out the Curie temperature (Tc) of different substituted spinel ferrites, a magnetic thermogravimetric analysis was performed.

This analysis consists in associating a magnet capable of creating a strong magnetic field at the sample without disturbing the balance, which allows the characterization of magnetic properties of the sample as a function of temperature and determining the transition temperature usually named Curie temperature T_C. This technique consists in measuring the weight variation as a function of temperature. At the Curie temperature T_C, a large mass change is observed.

RESULTS AND DISCUSSION

1. Structural studies

The different used ions with each different ionic radii chosen for the present study, are indicated in ***Table I*** [14].

X-ray diffraction patterns of as-prepared samples $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$, $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ (x=0, 0.2, 0.4) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ (x=0, 0.1, 0.2) obtained by hydrothermal method before and after sintering at 935 °C for 4 h are presented in ***Figs. 1*** and ***2***.

A single phase of Ni-Cu-Zn ferrites with cubic spinel structure was formed for all the powders. No extra lines corresponding to any other phases can be detected. Lattice parameters (a), crystallite size (D) and unit cell volume of Ni-Cu-Zn substituted ferrites are listed in ***Table II***.

Table I. Ionic radius, site preference and ionic magnetic moment (μ_B) of different used cations for spinel ferrites.

Ion	Ionic radius (Å)	Site preference (A or B)	Magnetic moment (μ_B)
Fe^{3+}	0.49 0.55	A B	5
Ni^{2+}	0.69	B	2
Zn^{2+}	0.6	A	0
Cu^{2+}	0.73	B	1
Co^{2+}	0.65	B	3

Table II. Lattice parameters (a), crystallite size (D) and unit cell volume of substituted ferrites before and after sintering.

Samples	Before sintering				After sintering		
	x	a (Å)	D (nm)	V (Å^3)	a (Å)	D (nm)	V (Å^3)
$Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$	-	8.396(0)	23.47	591.866(7)	8.386(4)	291.82	589.826(0)
$Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$	0.2	8.388(2)	21,88	590.202(4)	8.393(1)	194.99	591.235(1)
	0.4	8.378(8)	21.63	588.228(4)	8.406(6)	136.27	594.093(7)
$Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$	0.1	8.373(4)	21.28	587.097(5)	8.385(8)	130.88	589.711(7)
	0.2	8.371(6)	20.86	586.720(6)	8.388(6)	86.74	590.293(8)
$Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$	0.2	8.381(7)	33.15	588.841(6)	8.381(7)	105.64	588.841(6)
	0.4	8.350(6)	37.44	588.301(5)	8.380(9)	130.62	588.668(6)

For the first series of $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ (x=0, 0.2 and 0.4), it was found that crystallite size (D) slightly decreases with cobalt substitution from 23.47 to 21.63 nm. This might be due to the replacement of Ni^{2+} ions (ionic radii = 0.69 Å) by smaller Co^{2+} ions (ionic radii = 0.65 Å) in octahedral sites, resulting to size decreases of unit cells.

In the second series $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$, the decrease in lattice constant and crystallite size (D) has been assigned to the ionic radii of replacing ions (Co^{2+}) is less than that of the replaced Cu^{2+} ions for any value of x.

The crystallite size calculated for $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ increases with increasing Co content.

The increased intensity of the major peaks of Ni-Cu-Zn ferrites demonstrated the improvement in the degree of crystallinity of the sintered samples.

2. Magnetic studies

The saturation magnetization (Ms) and coercive field (Hc) values of different compositions are gathered in ***Table III***. The magnetic properties of the synthesized were analyzed using a

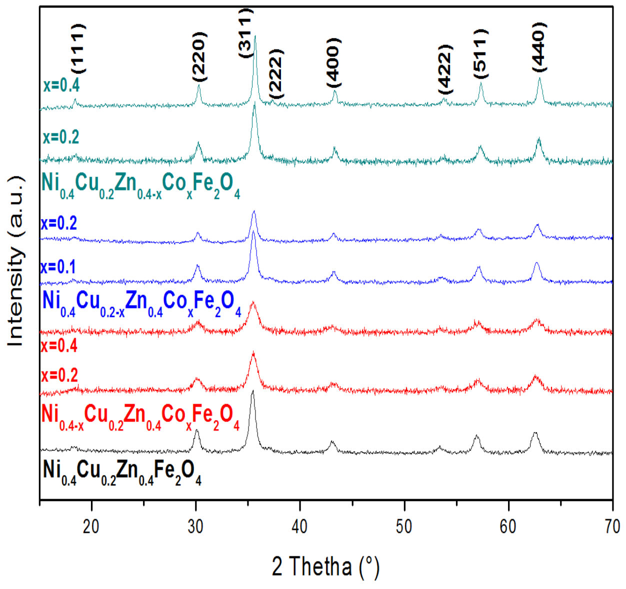

Fig. 1. XRD patterns of as-prepared substituted Ni-Cu-Zn ferrites.

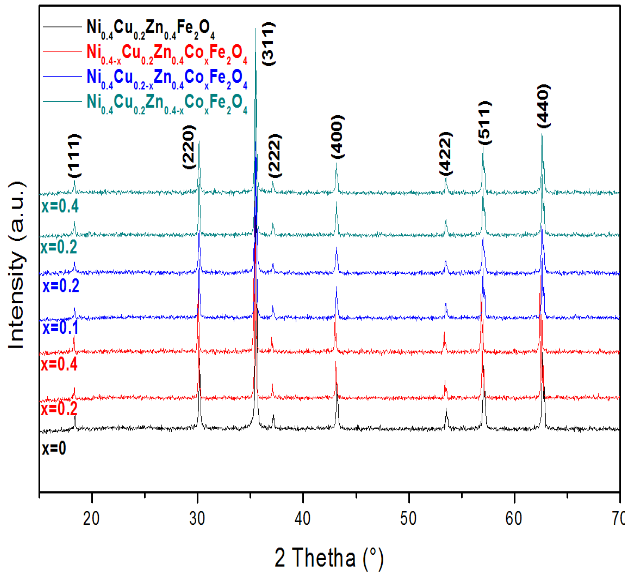

Fig. 2. XRD patterns of substituted Ni-Cu-Zn ferrites sintered at 935 °C for 4 h.

Table III. Saturation magnetization (Ms) and coercive field (Hc) of substituted Ni-Cu-Zn ferrites before and after sintering.

Samples	x	Before sintering		After sintering	
		Ms ($Am^2.kg^{-1}$)	**Hc (T)**	**Ms ($Am^2.kg^{-1}$)**	**Hc (T)**
$Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$	-	58.56	4.005	73.02	4.952
$Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$	0.2	63.22	4.754	81.61	8.642
	0.4	55.64	4.646	76.01	10.15
$Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$	0.1	59.53	4.787	80.73	6.946
	0.2	63.03	3.112	81.68	6.898
$Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$	0.2	54.10	5.575	74.05	13.34

Magnetometer (VSM) at room temperature (20 °C). The hysteresis loops (***Figs 3. 4** and **5***) of as-prepared and sintered ferrites $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$, $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ (x=0, 0.2, 0.4) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ (x=0, 0.1, 0.2), show a typical soft material with small coercive field (Hc).

For the system $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$, the obtained value of saturation magnetization (Ms) is 58.56, 63.22 and 55.64 $Am^2.kg^{-1}$ at x=0.0, 0.2 and 0.4 respectively. It was found that the saturation magnetization increases from x=0 to x=0.2 then decreases to the composition x=0.4

A similar result was obtained by Huili et al. [15]. In our case the variation of the saturation magnetization can be explained by:

In the mixed spinel structure, the magnetization depends heavily on the superexchange interaction between magnetic ions in octahedral (B) and tetrahedral (A) site [16].

a) For x=0.2, the replacement of Ni^{2+} ions with magnetic moment ($2\mu_B$) at octahedral sites by Co^{2+}

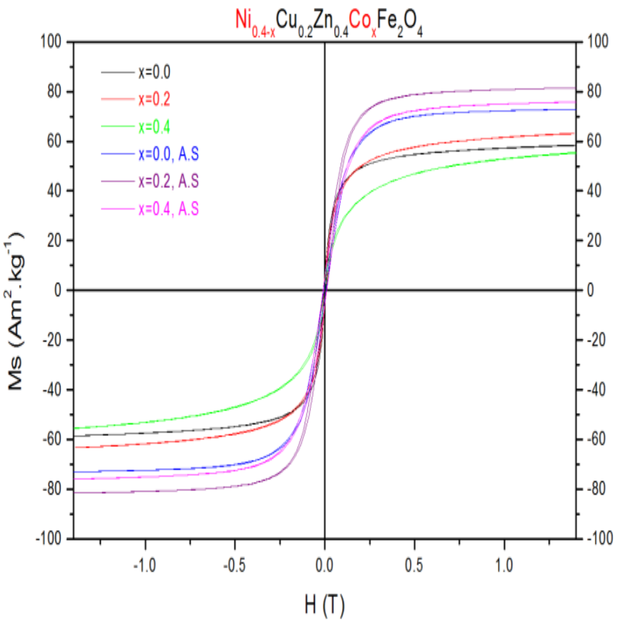

Fig. 3. Room temperature hysteresis loops of $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ ferrites before and after sintering.

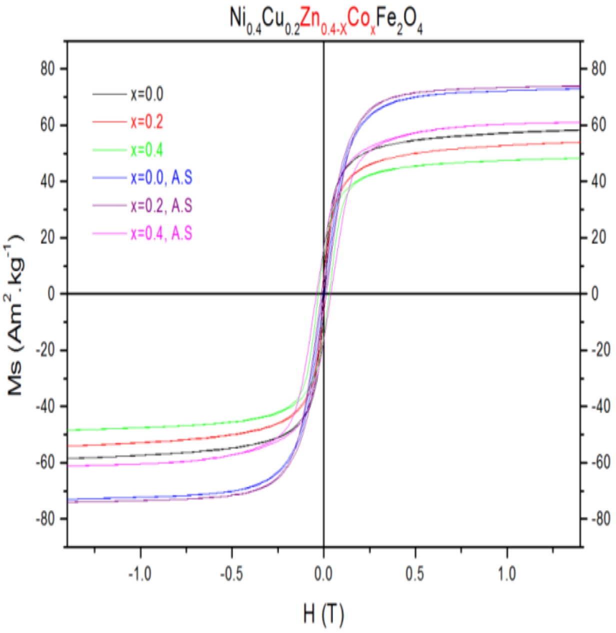

Fig. 4. Room temperature hysteresis loops of $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ ferrites before and after sintering.

ions with large magnetic moment ($3\mu_B$) leading to a increase of magnetization [17].

b) For x=0.4, the incorporation of Co^{2+} ions not only completely replaces Ni^{2+} ions in B site but also causes migration of some Cu^{2+} ions to A site from B site. This migration is accompanied by transfer of the Fe^{3+} ions to B site from A site with higher magnetic moment ($5\mu_B$) [18].

However, increasing the amount of Fe^{3+} ions in B site are able to enhance the BB exchange interaction resulting in antiparallel spin coupling configuration in the octahedral sublattice. So, a global decrease in the saturation magnetization was noted [19].

For the system $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$, the saturation magnetization of the Co-Zn substituted ferrite decreased with the increase in Co concentration. When Co^{2+} was substituted in place of Zn^{2+}, it forces migration of Fe^{3+} ions from the octahedral sites to the tetrahedral sites. As no magnetic moment of Zn^{2+} ($0\mu_B$) in the A site are replaced with higher magnetic moment of Fe^{3+} ($5\mu_B$), the magnetic moment of the A site increases. Consequently, increasing amount of Fe^{3+} in A site are able to weakening inter-sub-lattice A-B super-exchange interaction between the magnetic ions of the sub-lattices, this causes a decrease in the magnetization.

For $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$, the obtained values of saturation magnetization (Ms) are 58.56, 59.53 and 63.11 $Am^2.kg^{-1}$ at x=0, 0.1 and 0.2 respectively. In this case, the substitution of Cu^{2+} ions with less magnetic moment ($1\mu_B$) by Co^{2+} ions with large magnetic moment ($3\mu_B$) at octahedral site leads to enhance the saturation magnetization.

It appears, in ***Table III*** an improvement in magnetic parameters such as saturation magnetization and coercive field after sintering at 935 °C for 4 h.

In the present work, we note that the average crystallite size (D) increases after sintering for all the ferrites (***Table II***). This increase matches well with the increase of saturation magnetization [20].

As the grain size increases, formation of domain walls become possible and magnetization increases due to domain wall movement under the action of the applied magnetic field [21].

3. Curie point measurement

Fig. 6 shows the Weight variation as a function of temperature of Ni-Cu-Zn substituted ferrites. The Curie temperature, Tc, indicating a change of magnetic ordering from ferrimagnetism to paramagnetism [22].

The change in Curie temperature was ascribed to the modification of the exchange strength of

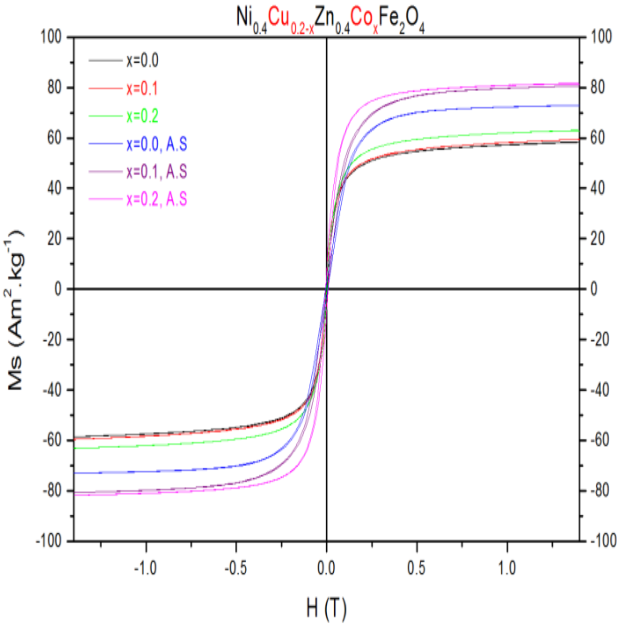

Fig.5. Room temperature hysteresis loops of $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ ferrites before and after sintering.

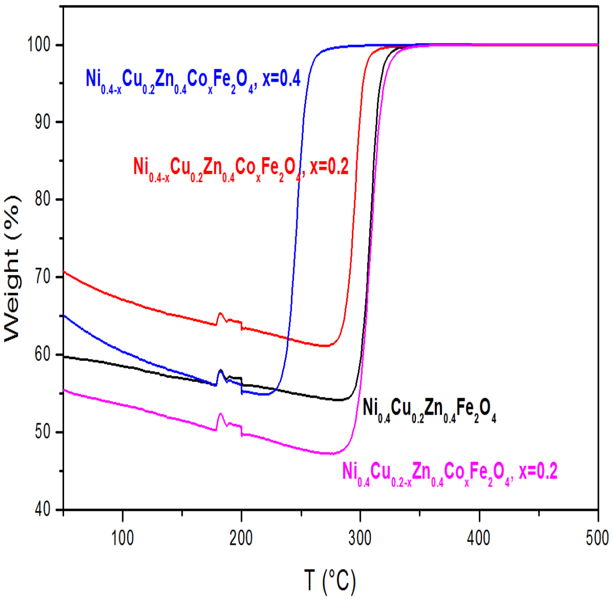

Fig. 6. Weight variation as a function of temperature of Ni-Cu-Zn substituted ferrites.

octahedral and tetrahedral interactions as a consequence of a change of the trivalent ion distribution between these two sites [23].

In the case of $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ ferrite, we note that the Curie temperature decreases with the cobalt content. This decrease in Curie temperature could be attributed to the migration of Fe^{3+} ions from tetrahedral to octahedral sites causing the weakening of AB interaction. Consequently, the Curie temperature will decrease. The value of Tc are 306, 290 and 240 °C for x=0.0, 0.2 and 0.4 respectively. These values are greater than that (148, 163 and 65 °C) reported by Huili et al. [15]. Generally, the decrease of Tc temperature was attributed to the decreasing particle size [24].

In the $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ system for x=0.2, the Curie temperature was found to be 295 °C which is close to the value of 306 °C of $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$.

It is clear that it is possible to ameliorate the properties of Ni-Cu-Zn ferrites due to the substitution with cobalt, especially for the ferrites $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ (x=0.2) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ (x=0.2).

These samples show maximum values of saturation magnetization Ms (63.22 and 63.03 $Am^2.kg^{-1}$), and Curie temperature, Tc (290 and 295 °C) respectively.

CONCLUSIONS

The present study demonstrated the effect of Co content on structural and magnetic properties of $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$, $Ni_{0.4}Cu_{0.2}Zn_{0.4-x}Co_xFe_2O_4$ (x=0, 0.2, 0.4) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ (x=0, 0.1, 0.2) synthesized using a hydrothermal method with stirring.

The XRD patterns reveal the single-phase formation of the ferrites. The saturation magnetizations (Ms) of the sintered samples are higher than the as-prepared samples.

The Curie temperature decreased with cobalt content in the system $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$. This can be due to the change of super exchange interactions.

The best characteristics (higher magnetization, good Curie temperature and low coercitive field) were found for the compositions $Ni_{0.4-x}Cu_{0.2}Zn_{0.4}Co_xFe_2O_4$ (x=0.2) and $Ni_{0.4}Cu_{0.2-x}Zn_{0.4}Co_xFe_2O_4$ (x=0.2).

These compounds might be interesting materials having effective magnetic properties.

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