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Structural and magnetic properties of nanocrystalline Ni_{1-x}Cu_xFe₂O₄ prepared through oxalates precursors

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ABSTRACT

Spinel ferrites of the composition $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0–1.0) have been prepared through the thermal decomposition of their respective impregnated oxalates. The oxalate decomposition process was followed using differential thermal analysis-thermogravimetry techniques (DTA-TG). The synthesized nanocrystallites were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR). The formation of single-phase ferrite is confirmed by XRD. Tetragonal deformation is observed for samples with composition $x \ge 0.7$. The increase in the lattice parameter with increasing Cu content can be explained based on the relative ionic radius. The TEM image shows spherically non-agglomerated particles with an average crystallite size that agrees well with that obtained from XRD. FT-IR studies show two absorption bands (v_1 and v_2) near to 600 and 400 cm^{-1} for the tetrahedral and octahedral sites, respectively. The hysteresis measurements were done using a vibrating sample magnetometer (VSM). The cation distribution in these compositions is calculated from the magnetization data. With increasing Cu content, the saturation magnetization (M_s) was observed to decrease while the coercivity (H_c) increases. The possible reasons responsible for the composition dependence of the magnetic properties were discussed. The Curie temperature, measured through the temperature dependence of the dc-molar magnetic susceptibility, was found to decrease with increasing Cu content.

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1. Introduction

Ferrites [1] are magnetic ceramics of great importance in the production of electronic components. Their applications range from simple function devices, such as small permanent magnets, to sophisticated devices for the electro-electronic industry. Some interesting applications of these materials are in computer peripherals, telecommunication equipment, permanent magnets, electronic and microwave devices, magnetic media used in computers, recording devices and magnetic cards. The electrical and magnetic properties are the most important properties for ferrites, depending on the processing conditions, sintering temperature and time, chemical composition and the amount and type of the additives [2].

In recent years, a number of chemical and physical methods have been attempted to produce nanosize ferrites. Some of the main physical methods include mechanical milling, [3] severe plastic deformation consolidation, [4] and inert gas condensation [5]. The widely used chemical methods are electro-deposition [6], hydrothermal reactions [7], oxidative precipitation [8], the organic

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precursor method [9], sonochemical decomposition [10], the solgel synthesis technique [11] and the reverse micelle technique [12].

Nickel ferrites, typically inverse spinel ferrites, have been extensively used in electronic devices because of their large permeability at high frequency, remarkably high electrical resistivity, mechanical hardness, chemical stability and cost effectiveness [13]. Substituted nickel ferrites are widely used as magnetic materials due to their high electrical resistivity, low eddy current and dielectric losses [14].

Bulk copper ferrite, CuFe₂O₄, is stable in the cubic form only at higher temperatures, $T > 400 \,^{\circ}\text{C}$ [15]. At room temperature it is found only in the tetragonal form due to Jahn–Teller distortion arising from the Cu²⁺ (3d⁹) ions in octahedral sites. Hoquea et al. [16] investigated the crystal structure, X-ray density, porosity, compressive strength of Ni_{1-x}Cu_xFe₂O₄, along with scanning electron microscopy (SEM) to study the effect of composition and microstructure on the magnetic and electrical properties. Initial magnetic permeability and saturation magnetization were found to be maximal for a composition of x = 0.2. Doha et al. [17] prepared Ni_{1-x}Cu_xFe₂O₄ nanopowders using the coprecipitation method with ultrasound irradiation. Single phase Ni_{1-x}Cu_xFe₂O₄ nanopowders were obtained with grain sizes between 20 and 30 nm. The maximum value of saturation magnetization was



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obtained for x = 0.5. Azadmanjiri et al. [18] prepared Ni_{1-x}Cu_xFe₂O₄ nanopowders using the sol-gel auto-combustion method. It was found that the Cu content has a significant influence on the electromagnetic properties. Roumaih [19] prepared Ni_{1-x}Cu_xFe₂O₄ using the usual ceramic method. The phase purity of the samples was checked by XRD and IR spectroscopy. Msomi and Moyo [20] studied the magnetic properties of $Ni_{1-x}Cu_xFe_2O_4$, prepared through the usual ceramic method, using Mössbauer spectroscopy and VSM techniques. Single phase formation of the compound was confirmed by XRD. The coercive field (H_c) was found to increase with the reduction in grain size. Tan et al. [21] synthesized $Ni_{1-x}Cu_{x-1}$ Fe₂O₄ using the sol-gel combustion method. The synthesized nanocrystallites were characterized by XRD, TEM, IR and X-ray photoelectron spectroscopy. The TEM results indicated an increase in lattice parameters and particle size with the increase of copper content, in accordance with the XRD analysis. Patil and Chougule [22] synthesised Ni_{1-x}Cu_xFe₂O₄ using the standard ceramic method. XRD confirmed the formation of cubic single-phase ferrites. The Cu content was found to have a significant influence on the electromagnetic properties.

Oxalates are generally the preferred precursor for the synthesis of ferrites because of their low solubility and low decomposition temperature, and they yield a homogeneous product as fine particles in a short time. Their prime advantage is in achieving intimate mixing on an atomic scale, resulting in the formation of a true solid solution [23].

The aim of the present work is to prepare nano-sized Ni_{1-x}Cu_x. Fe₂O₄ through the thermal decomposition of the corresponding impregnated oxalates. The introduction of Cu²⁺ ions in the structure of NiFe₂O₄ will be expected to modify its structural and magnetic properties, which will result in different types of applications. The cation distribution will be estimated using structural and magnetic properties.

2. Experimental

Pure oxalates of nickel, copper and ferrous were prepared through the coprecipitation method. In the impregnated process, distilled water was added in drops to calculated amounts of the metal oxalates with vigorous stirring to assure complete homogeneity. The wetted oxalate mixture was then dried at 100 °C for about 2 h. The complete ignition of the precursor in a muffle furnace at 1000 °C resulted in the formation of the corresponding ferrites.

The simultaneous differential thermal analysis-thermogravimetry (DTA-TG) behavior of the mixtures was investigated using a Shimadzu DT-60 thermal analyzer in the temperature range from room temperature to 1000 °C at a heating rate of 5 °C min⁻¹. The experiment was preceded in a flowing air atmosphere (50 ml min⁻¹). The structural and phase composition of samples were investigated by XRD analysis at room temperature using a D8 Advanced diffractometer, Bruker AXS (40 kV) using Cu Ka radiation (λ = 0.15406 nm). The crystallite size was estimated by broadening analysis of the XRD peaks using Scherrer's formula [21]. FT-IR analysis, using the KBr pellet method, was carried out over the range 4000–200 cm⁻¹ using a Jasco FTIR 310 spectrometer. The morphology of the calcined powders was examined using a JEOL 2010 transmission electron microscope, operated at 100 kV. The hysteresis and magnetization measurements were performed using a vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) with a maximum applied field of 5 kOe at room temperature. The dc magnetic susceptibility measurements were carried out using Faraday's method. The measurements were performed from room temperature to 850 K at different magnetic field intensities (1010, 1340 and 1660 Oe). In this method, a very small amount of the powdered sample was inserted into a cylindrical glass tube at the point of maximum gradient.

3. Results and discussion

3.1. Thermal decomposition of the precursors

Fig. 1 shows the simultaneous DTA-TG curves for the decomposition of the NiC₂O₄·2H₂O-CuC₂O₄-FeC₂O₄·2H₂O oxalate precursor (with 0.5:0.5:2 molar ratios) in air. Although the decomposition process is accompanied by the formation of a solid solution, the overall decomposition reaction was observed to proceed via four weight loss steps. The weight loss accompanying the first step in the temperature range 166–203 °C, can be attributed to the physical or chemical desorption of water. From the literature [24] it is well known that water eliminated at 150 °C and below can be considered as crystal water, whereas water eliminated at 200 °C and above indicates its coordination by the metal atom. Water molecules eliminated at intermediate temperatures can be coordinately linked as well as crystal water. The dehydration temperatures obtained in the present work suggest that the water molecules can be considered as coordinately linked. The accompanying weight loss of the dehydration step amounts to about 16.8%, in accordance



Fig. 1. DTA-TG curves for the decomposition of the NiC₂O₄·2H₂O-CuC₂O₄-FeC₂O₄·2H₂O oxalate precursor (with 0.5:0.5:2 molar ratios) in air. Heating rate = 5 °C min⁻¹.

with calculated weight loss of 17.1% attributed to the complete dehydration and the loss of five water molecules.

The second step starts immediately after the finishing of the first step. It is characterized by a weight loss of 24.7% at 270 °C, corresponding to the oxidative decomposition of the ferrous oxalate content to Fe_2O_3 (calc. weight loss = 24.3%) [25]. The third and fourth steps show the successive decomposition of copper oxalate and nickel oxalate contents to CuO and NiO, respectively [26]. The third step shows a weight loss of 7.1% (calc. weight loss = 6.8%) at 315 °C, while the fourth step exhibit a weight loss of 6.8% (calc. weight loss = 6.8%) at 355 °C. No further weight loss can be detected up to 1000 °C.

The DTA curve shows four peaks closely corresponding to the weight losses obtained on the TG curve. The first peak attributed to the dehydration reaction is endothermic while the other three peaks, attributed to the oxalates decomposition, are exothermic.

The precursor at complete decomposition is assumed to contain a mixture of iron, copper and nickel oxides, which will be converted to the corresponding ferrite on further calcination at higher temperatures, as will be indicated using XRD measurements.

3.2. X-ray diffraction

X-ray diffraction patterns of the different compositions in the Ni_{1-x}Cu_xFe₂O₄ system calcined at 1000 °C are presented in Fig. 2. A homogeneous solid solution was obtained for the range of Cu concentrations $0.0 \le x \le 0.5$. The miller indices in this range of compositions are unmixed and the most significant lines are successfully indexed to a cubic spinel structure [27]. By increasing the copper concentration, weak diffraction peaks attributed to the presence of CuFe₂O₄ in a tetragonal crystal structure started to appear, and these predominated in the pure copper ferrite. This tetragonal distortion is due to the Jahn–Teller effect of the Cu²⁺ ions located in the octahedral sites of spinel in a large concentration [9]. The experimentally observed d-spacing values and relative intensities are in well agreement with those reported in the powder diffraction file of JCPDS patterns of pure NiFe₂O₄ and pure Cu-Fe₂O₄ [28].

The lattice parameters have been determined by using the method of least squares to an accuracy of around ± 0.02 Å, and these are presented in Table 1. The obtained values agree well with the previously reported results [16,21]. It can be observed from the table that the variation of the lattice parameters with composition is almost linear and obeys Vegard's law [16] in the cubic spinel region. The increase in the lattice parameter with increasing Cu con-



Fig. 2. X-ray diffraction patterns of the different compositions in the $\rm Ni_{1-x}Cu_xFe_2O_4$ system calcined at 1000 °C.

Table 1

Lattice parameters (*a*), average crystallite sizes (*L*), X-ray densities (ρ_x) and FT-IR spectral data (v_1 , v_2) of the Ni_{1-x}Cu_xFe₂O₄ system.

Copper content (<i>x</i>)	a (Å)	L (nm)	$ ho_{ m x}$, (g cm $^{-3}$)	v_1 (cm ⁻¹)	v_2 (cm ⁻¹)
0.0	8.3192	147	5.4072	593	404
0.1	8.3244	143	5.4082	588	400
0.3	8.3317	140	5.4163	585	396
0.5	8.3475	52	5.4075	585	396
0.7	8.3557	46	5.4138	579	395
0.9		41		574	398
1.0	a = 5.8053 c = 8.6548	34	5.4152	571	402

tent can be attributed to the greater ionic radius of Cu^{2+} (0.72 Å) in comparison to Ni²⁺ (0.69 Å) and indicates the occupancy of copper ions in the B-sites of the spinel. The obtained lattice parameter for the pure tetragonal copper ferrite gives a value of about 1.49 Å, which is comparable with the literature data [29,30].

The values of X-ray density (D_x) for different compositions, calculated from molecular weight and the volume of the unit cell, have been presented in Table 1. From the table it is clear that the increase in the molecular weight of the sample, attributed to the larger atomic weight of the copper compared with that of nickel, which is accompanied by an increase in the lattice constant, produces nearly a constant X-ray density at different compositions.

The broad peaks obtained in the XRD patterns indicate a fine particle nature of the particles. The broadening was observed to increase as the copper content increased. The average crystallite size (*L*) of the ferrite crystal was calculated from the XRD line broadening by using Scherrer's equation [21]. The results are presented in Table 1. From the table it is observed that only the samples with a copper content in the range $0.5 \le x \le 1.0$ are nano-sized ferrites. The particle sizes decrease with Cu substitution, which can indicate that the addition of Cu has a great effect on obstructing the grain growth of the spinel. The same trend was observed in Cu-Ni ferrite prepared using the solid-state method where the introduction of Cu in the NiFe₂O₄ structure appears to lead to finer grains of a more reduced size [20].

3.3. TEM study

Fig. 3 shows a typical transmission electron microscope (TEM) micrograph of the nano-sized Ni–Cu ferrite with a copper content of 0.5. The image indicates the nano-structured nature and spherical morphology of the powder with uniform size. The particle size is about 50 nm, which agrees well with that estimated using XRD.



Fig. 3. TEM image of the sample with a Cu content of 0.5.

This reveals, as obvious from the image, that the synthesized powder is well dispersed and no aggregates are formed.

3.4. FT-IR spectroscopy

Fig. 4 shows the FT-IR spectra of the Ni–Cu ferrite system recorded between 800 and 300 cm⁻¹. The spectra elucidate the positions of cations in the crystal structure with oxygen ions and their vibrational modes, which represents the various ordering positions and structural properties for the different compositions. In ferrite, the metal cations are situated in two different sub-lattices, namely tetrahedral (A-sites) and octahedral (B-sites) according to the geometric configuration of the oxygen ion nearest neighbors. The band v_1 around 600 cm⁻¹ is attributed to stretching vibrations of tetrahedral complexes and v_2 around 400 cm⁻¹ to that of octahedral complexes [31]. The obtained FT-IR spectral data for the investigated ferrite samples are represented in Table 1.

From the table it is noticed that by increasing the copper content, the frequency v_1 is shifted to lower frequencies, while the position of v_2 slightly changed. It is also obvious that the peak intensity changes with increasing Cu content. Similar results are observed in Cu substituted nickel ferrite [21] and nickel substituted Cu–Zn ferrites [32].

The difference in the band position is expected because of the difference in $Fe^{3+}-O^{2-}$ distance for the octahedral and tetrahedral compounds. It was found that the Fe–O distance of A-sites (0.189 nm) is smaller than that of the B-sites (0.199 nm) [21]. This has been interpreted by the more covalent bonding of Fe^{3+} ions at the A-sites. It is well known that Ni^{2+} and Cu^{2+} ions show a strong preference for B-sites due to favorable fit of charge distribution, while Fe^{3+} is distributed in both the octahedral and tetrahedral sites [21,32]. So the $Fe^{3+}-O^{2-}$ stretching vibration is affected by the replacement of Ni^{2+} with Cu^{2+} ions at octahedral sites in the ferrite lattice, which have a larger ionic radius and higher atomic weight than Fe^{3+} . Due to charge imbalance, the oxygen ion is likely to shift towards the Fe^{3+} ions, making the force constant between



Fig. 4. FT-IR spectra of the Ni-Cu ferrite system.

 Fe^{3+} and O^{2-} greater. Hence, an increase in the bond stretching frequencies was expected in the inverse ferrite [21].

It is known that the intensity ratio is a function of the change in dipole moment with the inter-nuclear distance [33]. This value represents the contribution of the ionic Fe–O bond in the lattice. So the observed decrease in the peak intensity with increasing Cu content is presumably due to the perturbation occurring in the Fe–O bands by the substitution of Ni^{2+} by Cu^{2+} .

3.5. Magnetic properties study

3.5.1. VSM measurements

Fig. 5 shows the typical magnetic hysteresis loops obtained from room temperature VSM measurement for copper substituting nickel ferrites. It is typical for a soft magnetic material. The magnetic properties of the ferrites can be explained in terms of the cation distribution. The saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) values are listed in Table 1. The experimental magnetic moment (η_B) was calculated from the saturation magnetization data [34] and is presented in Table 2.

Fig. 6 shows the variation of saturation magnetization (M_s) and coercivity (H_c) with Cu content (x) in the Ni_{1-x}Cu_xFe₂O₄ system. From the figure it is noticed that the saturation magnetization decreases with increasing copper concentration. This decrease is rapid in the region from x = 0.1 to 0.3, after which a very slight change is observed up to a copper content of 0.9. A sharp decrease to 27.7 emu/g was obtained for the tetragonal copper ferrite. The remanent magnetization gradually decreases with increasing x. On the other hand, the coercivity value gradually increases up to a copper content of 0.5, then increases rapidly. As apparent from Table 2, the present saturation magnetization data are found to be in quite good agreement with those reported for Ni–Cu ferrites prepared using other different methods [16,34,35].

The magnetization behavior of nickel ferrite can be understood in terms of the cation distribution and Neel's model. Nickel ferrite (NiFe₂O₄), with an inverse spinel structure, shows ferrimagnetism that originates from the magnetic moment of anti-parallel spins between Fe³⁺ ions at tetrahedral sites and Ni²⁺ ions at octahedral sites. The obtained saturation magnetization, 47.7 emu/g measured at 3 kOe, is close to the theoretical saturation magnetization of 50 emu/g [36]. This value is also comparable to the value obtained for nickel ferrite powders synthesized by other methods [37–39]. The magnetization value of 27.7 emu/g obtained for Cu-Fe₂O₄ in the present work agrees well with that obtained for the sample prepared through the combustion reaction of ureate pre-



Fig. 5. Magnetic hysteresis loops for the Ni_{1-x}Cu_xFe₂O₄ system.

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Cation distribution	and magnetic	data for the Ni_{1-}	$_x$ Cu _x Fe ₂ O ₄ system.

(<i>x</i>)	Cation distribution	M _s (emu/g)	M _s [35]	M _s [36]	$M_{\rm r}~({\rm emu/g})$	$H_{C}(Oe)$	$\eta_{\rm B} ({\rm BM})$	$T_{C}(K)$
0.0	$(Fe^{3+})[Ni^{2+}Fe^{3+}]O_4$	47.69	47.15	46.90	13.20	10.42	2.00	851
0.1	$(Fe_{0.995}^{3+}Cu_{0.005}^{2+})[Ni_{0.9}^{2+}Cu_{0.095}^{2+}Fe_{1.005}^{3+}]O_4$	46.37			11.21	16.70	1.95	832
0.3	$(Fe_{0.996}^{3+}Cu_{0.004}^{2+})[Ni_{0.7}^{2+}Cu_{0.296}^{2+}Fe_{1.004}^{3+}]O_4$	40.21	44.79	44.00	11.32	17.20	1.70	823
0.5	$(Fe_{0.080}^{3+}Cu_{0.020}^{2+})[Ni_{0.5}^{2+}Cu_{0.480}^{2+}Fe_{1.020}^{3+}]O_4$	41.39	44.99	43.50	11.54	18.04	1.75	812
0.7	$(Fe_{0.955}^{3+}Cu_{0.045}^{2+})[Ni_{0.25}^{2+}Cu_{0.655}^{2+}Fe_{1.045}^{3+}]O_4$	41.05	45.50	46.50	8.29	30.40	1.74	796
0.9	$(Fe_{0.929}^{3+}Cu_{0.071}^{2+})[Ni_{0.1}^{2+}Cu_{0.829}^{2+}Fe_{1.071}^{3+}]O_4$	41.20	44.03	47.20	6.29	56.87	1.75	751
1.0	$(Fe_{0.979}^{3+}Cu_{0.021}^{2+})[Cu_{0.979}^{2+}Fe_{1.021}^{3+}]O_4$	27.70			6.24	151.00	1.19	



Fig. 6. Variation of the saturation magnetization (M_s) and the coercivity (H_c) with Cu content (x) in the Ni_{1-x}Cu_xFe₂O₄ system.

cursors (24.8 emu/g) [40]. Ponhan and Maensiri [41] prepared tetragonal copper ferrite through the electrospinning method. They reported a saturation value of 23.98 emu/g and a coercive force of 625 Oe. This coercivity value is higher than the value of 151 Oe obtained in the present work.

Kiran et al. [34] have estimated the cation distribution in the mixed ferrite system $Ni_{1-x}Cu_xFeO_4$ using the magnetization data. They suggested that the cation distribution can be written as:

$$(Fe_{1-(1-x)y}^{3+}Cu_{(1-x)y}^{2+})[Ni_x^{2+}Cu_{(1-x)(1-y)}^{2+}Fe_{1+(1-x)y}^{3+}]O_4^2$$

Assuming that all the Ni^{2+} ions only occupy octahedral sites, the fraction (*y*) can be calculated using the equation:

$$y = \frac{\eta_{\rm B} - x\mu_{\rm Ni^{2+}} - (1-x)\mu_{\rm Cu^{2+}}}{2(1-x)\mu_{\rm Fe^{3+}} - \mu_{\rm Cu^{2+}}}$$

where $\eta_{\rm B}$ stands for the saturation magnetic moment and x stands for the copper content. The magnetic moment of the ions $\mu_{\rm Cu^{2+}}$, $\mu_{\rm Ni^{2+}}$ and $\mu_{\rm Fe^{3+}}$ are taken as 1.0, 2.18 and 5.0 BM, respectively. According to the above equations, the cation distribution in the present work was estimated and reported in Table 2. From the table it is clear that the $\mu_{\rm s}$ and $\eta_{\rm B}$ values do not show a well defined dependence on the copper concentration in the range $0.3 \leq x \leq 0.9$. A similar less significant dependence of $\mu_{\rm s}$ on the composition in the Ni_{1-x}Cu_xFe₂O₄ spinel is found in the literature [16,34,35]. Kenfack and Langbein [35] suggested that the presence of the Cu²⁺ ions in the A-sites displaces the same amount of Fe³⁺ ions towards the B-sites. This influence can compensate the decrease of the magnetization by the substitution of Ni²⁺ by Cu²⁺. Consequently, the resultant magnetization number can remain constant.

The saturation values are explained by assuming that the A–B interaction favors anti-parallel coupling of A-site and B-site groups and is strong enough to overcome any tendency for A–A or B–B couplings to disrupt the parallel alignment of all spins within the A-site or B-site groups separately. The magnetic order in the ferromagnetic spinels is due to a super-exchange interaction mechanism occurring between the metal ions in the tetrahedral A-sites and octahedral B-sites [42]. The replacement of Ni²⁺ ions (2.18 BM) by Cu²⁺ ions (1.0 BM), which have preferential octahedral site occupancy, results in the reduction of the super-exchange interaction between the A and B sites. In other words, as the copper



Fig. 7. Relation between the molar magnetic susceptibility and the absolute temperature as a function of different magnetic field intensities for the Ni_{1-x}Cu_xFe₂O₄ system.

concentration increases, the magnetization of the B-site decreases and the net magnetization decrease.

From Table 2 it is obvious that the H_c values decrease with increasing copper content. This behavior can be interpreted if we take into consideration the decrease in the crystallite size by increasing the copper content. In this case, the variation of H_c with particle size can be explained on the basis of domain structure, critical diameter and the anisotropy of the crystal [43]. A crystallite will spontaneously break up into a number of domains in order to reduce the large magnetization energy it would have if it were a single domain. Thus, the coercivity of the magnetic particles decreases with particle size.

3.5.2. Dc-molar magnetic susceptibility measurements

Fig. 7 represents the temperature dependence of the dc-molar magnetic susceptibility (χ_M) for the studied samples as a function of magnetic field intensity. The sample with a copper content of 1.0 cannot be measured under the present experimental conditions. This may be attributed to the lower magnetic properties of this sample.

From the figure, it is clear that χ_M decreases with increasing temperature. The samples can be considered as a pure ferrimagnetic material in which the thermal energy was not quite sufficient to disturb the aligned moments of the spins. After the transition temperature (T_c) , the thermal energy is high enough to disturb all the aligned spins and a paramagnetic region appears.

For all the samples, the decrease in $\chi_{\rm M}$ with increasing field intensity (Fig. 6) can be considered as a normal magnetic behavior, which can be attributed to the saturation of the ferrimagnetic domains at such a high field [9].

The Curie temperatures $(T_{\rm C})$ of the different compositions were measured and summarized in Table 2. The obvious decrease in the $T_{\rm C}$ value with increasing Cu content can be attributed to the increase in the paramagnetic region on the expense of the ferrimagnetic region, which indicates that the ferrimagnetic grains are widely separated by the less magnetic copper ions. A similar behavior was reported by Kiran et al. [34].

The Curie temperature of the ferrites is determined by the overall strength of the A-B interactions, but sometimes the intrasublattice A-A and B-B interactions may become important [44]. The occupancy of the copper ion on a B-site instead of nickel ions weakens the A-B exchange interaction, resulting in a decrease in the magnetic interaction (J_{AB}) . The internal energy required to offset the spin alignment will decrease and the Curie temperature is then expected to fall.

4. Conclusion

The oxalate impregnation method was found to be convenient for the synthesis of Ni-Cu ferrites. The oxalate decomposition process was monitored using DTA-TG techniques. The XRD study confirmed the formation of single-phase cubic spinel Ni-Cu ferrites at low copper contents. The tetragonal ferrite structure predominates in the pure copper ferrite. The lattice parameter is found to increase with increasing copper content. On the other hand, the addition of copper was found to obstruct the grain growth which results in a decrease in the crystallite size with increasing copper content. FT-IR spectra show the characteristic vibrational bands of ferrites. The copper substitution was found to have a great effect on the magnetic properties. The saturation magnetization and the Curie temperature were found to decrease with increasing copper content, while the coercivity forces increase. The results were correlated with the structural measurements and discussed. A proper cation distribution for the investigated system was suggested, depending on the magnetic measurements data.

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