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Synthesis, Structural and Magnetic Properties of Copper Substituted Nickel Ferrites by Sol-Gel Method

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ABSTRACT

The $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0) ferrites have been prepared by sol-gel method in order to obtain homogeneous crystal structure and they are sintered at high temperature. The effect of copper doping on the structural and magnetic properties of nickel ferrites sintered at 1000˚C has been examined. The X-ray diffraction measurements clearly showed the formation of single phase spinel ferrite structure in all the prepared ferrite compositions. Because of the high sintering temperature the particle size is observed beyond the nano-scale range in all the compositions. The lattice parameters are found to increase with increasing doping concentration of the copper content. Magnetization results exhibit a non-collinear ferrimagnetic structure for x = 0.0 to 0.5 and Neel's collinear ferrimagnetic structure for x = 0.5 to 0.9 suggesting a change in magnetic ordering.

Keywords: Ferrite; High Sintering Temperature; X-Ray Diffractograms; Spinel Structure; SEM; Magnetic Properties

1. Introduction

Ferrites are technologically essential materials that are used in the fabrication of magnetic, electronic and microwave devices. They have gained technological importance by virtue of their high resistivity and negligible eddy current losses [1,2]. Nickel and copper substituted nickel ferrites are the important class of spinel ferrites [3]. According to crystal structure, nickel ferrite is an inverse spinel ferrite and possesses high electrical resistivity and low eddy current losses. The substitution of copper in nickel ferrite modifies the properties of nickel ferrite which are useful in many device applications. Nickel-copper ferrites play significant role among magnetic materials due to their high electrical resistivity, high saturation magnetization and high magnetic permeability [4,5]. The structural and magnetic properties of spinel ferrites depend on the magnetic interaction and cation distribution in the two sub-lattices *i.e.* tetrahedral (A) and octahedral (B) lattice sites. Ni-Cu ferrites have appealing electrical and magnetic properties, as copper ferrite is one of the most interesting spinel ferrite among all the ferrites. It undergoes a structural phase transition accompanied by a reduction in the crystal symmetry to tetragonal [6].

It has been reported by several research groups that, the magnetization in Ni-Cu ferrites decreases with increasing Cu content and vice-versa [7-14]. The Cu content was found to have a significant influence on the electromagnetic properties. Therefore it would be meaningful to investigate the structural and magnetic properties of Ni-Cu ferrites. Thus, in this paper, we present the systematic investigations of Cu substituted nickel ferrites.

2. Experimental Procedure

Ni-Cu ferrites with a generic formula $Ni_{1-x}Cu_xFe_2O_4$ ($0.0 \le x \le 1.0$) were synthesized by sol-gel method [15]. All of the chemicals were analytical grade with purity ≥99% and were used. In a typical procedure, the nickel nitrate hydrate $Ni(NO_3)_2 \cdot 6H_2O$, cupric nitrate hydrate $Cu(NO_3)_2 \cdot 6H_2O$, ferric nitrate nonahydrate $Fe(NO_3)_3 \cdot 9H_2O$ were used as starting materials. The synthesis process is described elsewhere [15]. The final powder samples obtained were sintered at 1000˚C for 24 h.

Structural characterization of the ferrite powders was carried out on Panalytical Expert Diffractometer (XRD), PW 3040/60 Philips with CuKα radiation (wavelength, λ = 1.54 Å). The scanning electron micrographs of all the samples were taken on JEOL JSM 6360 SEM machine. Magnetization measurements were performed using the vibrating sample magnetometer (VSM).

3. Results and Discussions

Figure 1 shows the XRD patterns of $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le$

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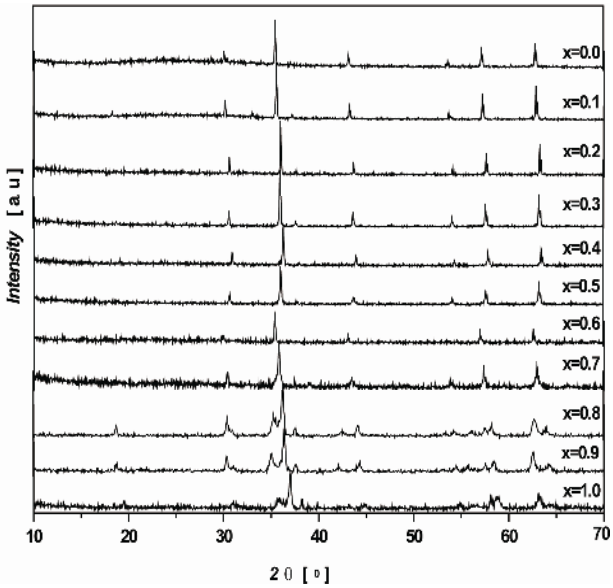

Figure 1. X-ray diffractograms of $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le x \le 1.0$) ferrites.

$x \le 1.0$) samples. The X-ray diffractograms clearly indicate the formation of single phase spinel structure. The XRD patterns were compared and indexed using ICDD card no (86-2287) and (34-0425) for Ni and Cu ferrites. As seen from **Figure 1**, the XRD peaks are very narrow indicating the higher grain size falls beyond the nanoscale region (more than 100 nm). Generally the sol-gel technique yields nano size grains in the ferrite systems [15]. But, as the sintering temperature and sintering time (1000˚C for 24 h) were very high, this resulted for larger grain size in the prepared ferrite samples.

The values of lattice parameters were obtained for all the samples using XRD data and are listed in **Table 1**. The variation of lattice parameter with Cu content is shown in **Figure 2**. From **Figure 2**, it is observed that the lattice parameter increases with increasing copper content *x*. This behavior of lattice parameter with Cu content *x* is explained on the basis of difference in ionic radii of Ni^{2+} (0.69 Å) and Cu^{2+} (0.724 Å). Similar types of results were observed in the investigation of S. Manjura Hoque *et al.* [6] and M. A. Gabal *et al*. [7]. In the case of our samples, the lattice parameters were found to be slightly higher than those reported by others. The enhanced lattice parameters might be occurred due to sol-gel method. The X-ray density of all the $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le x \le 1.0$) ferrites has been calculated from the molecular weight and the volume of the unit cell using the relation,

$$d_x = \frac{8M}{Na^3}\left[\mathrm{g/cm^3}\right] \quad (1)$$

where, *M* is molecular weight, *N* is Avogadro's number and *a* is lattice parameter.

Table 1. Lattice parameter (*a*), X-ray density (d_x), saturation magnetization (M_S) and magnetic moment (η_B) with Cu content *x*.

x	*a* (Å)	d_x (gm/cm^3)	M_S (emu/g)	η_B (μ_B)
0	8.281	4.92	35.8	1.508
0.2	8.327	4.97	37.7	1.594
0.4	8.352	4.97	44.1	1.870
0.5	8.362	5.03	46.9	1.992
0.7	8.380	4.78	41.9	1.786
0.8	8.412	4.62	32.5	1.387
0.9	8.444	4.79	26.9	1.150

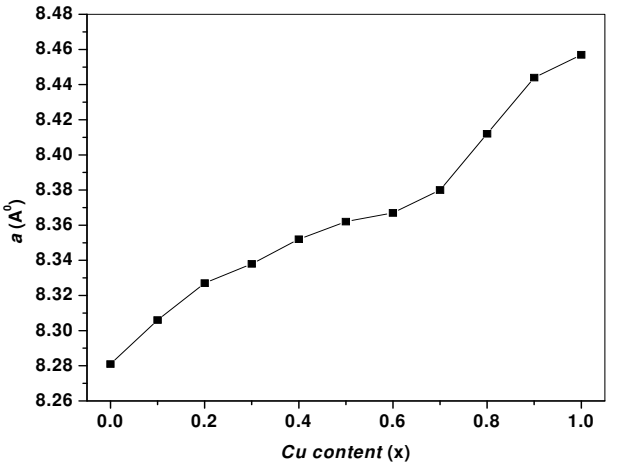

Figure 2. Variation of lattice parameter *a* with Cu content *x*.

The variation of X-ray density with copper content is also shown in **Table 1**. The X-ray density is found to decrease with increasing Cu content *x*. The X-ray density is found to depend on the lattice parameter and molecular weight of the samples.

Figure 3 shows the typical SEM microstructures of $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le x \le 1.0$) samples. From the microstructures one can clearly see the structural changes with the copper content *x*. The morphology and grain size of the samples seem to be non-uniform with somewhat agglomeration in the synthesized samples which is unavoidable. In few samples with $x = 0.2$ and 0.5, one can see that the grains are well separated. From the preliminary observations of the SEM images, we could say that the grain size is slightly affected by the Cu doping concentration.

Magnetization measurements of $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le x \le 1.0$) samples were carried out using a vibrating sample magnetometer (VSM) with the maximum applied field of 8 kOe at room temperature. The hysteresis loops were found to be well saturated with the available applied field. The obtained hysteresis loops are shown in **Figure 4**. The hysteresis loops display the characteristics of soft-magnetic materials. The saturation magnetization (M_S) was

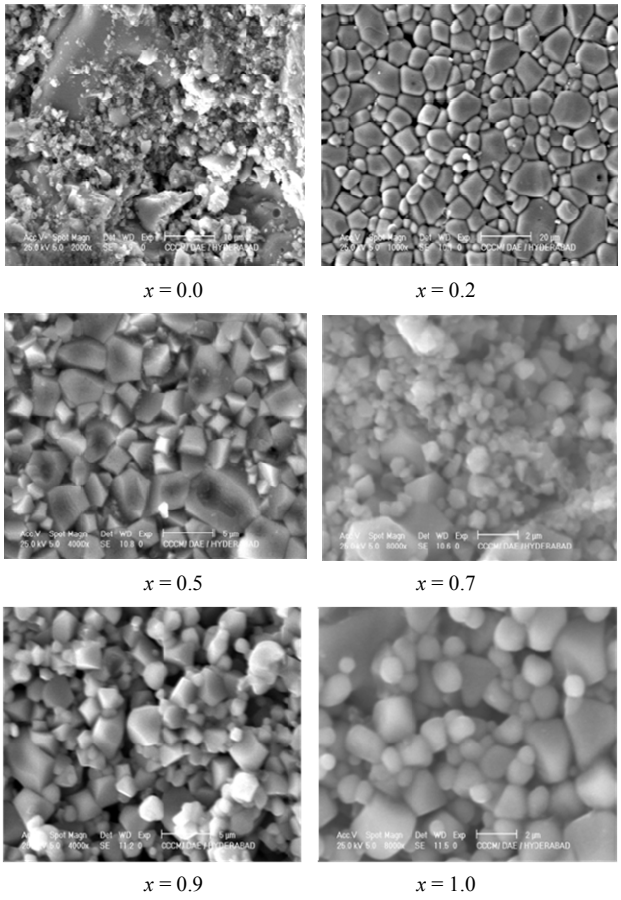

Figure 3. SEM images of $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le x \le 1.0$) ferrites.

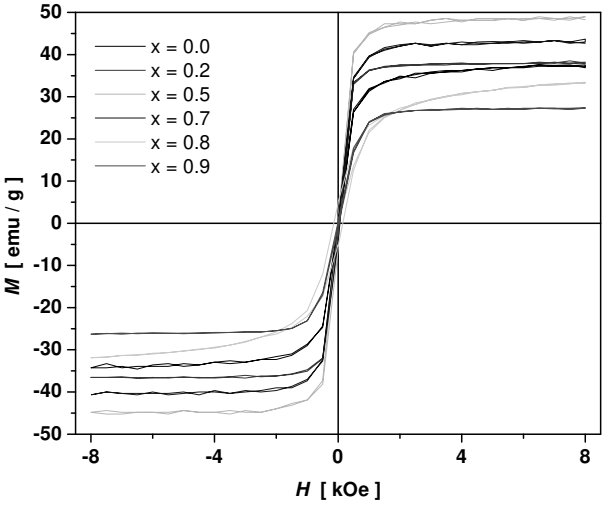

Figure 4. Hysteresis loops of $Ni_{1-x}Cu_xFe_2O_4$ ($0 \le x \le 1.0$) ferrites.

found to increase up to $x = 0.5$ and then gradually decrease with further increase of Cu content x as shown in **Figure 5**. The experimental magnetic moment (η_B) is determined from the saturation magnetization data using the following relation [7]:

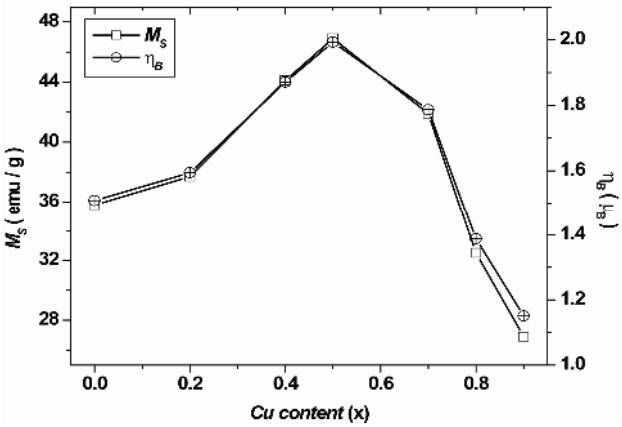

Figure 5. Variation of saturation magnetization and magnetic moment with Cu content *x*.

$$\eta_B = \frac{M_W \times M_S}{5585} \quad (2)$$

where, M_W is the molecular weight of the sample and M_S is the saturation magnetization in emu/g.

The calculated values of the experimental magnetic moment (η_B) and the saturation magnetization are shown in **Table 1**. The trend in the variation with Cu content x in both the cases is found to be similar. The variation of magnetization with Cu content x is very well in agreement with the one reported by Doh *et al.* [8] on Ni Cu ferrite prepared by coprecipitation method. Gabal *et al.* [9] have observed a decrease in magnetization with an increase in Cu content x. It is observed that the preparation technique plays an important role in modifying the magnetic properties of spinel ferrites.

From **Figure 5**, it is clear that the samples with $x = 0.0$ to 1.0 show ferrimagnetic behavior which increases initially from $x = 0.0$ to 0.5 and decrease from $x = 0.5$ to 0.9 suggesting a change in magnetic ordering [16]. The variation of η_B with Cu^{2+} content x can be explained on the basis of the fact that Cu^{2+} ions replace the magnetic Fe^{3+} ions at tetrahedral (A) site. Thus, magnetic moment of B-site decreases with Cu content x. Hence, it can be understood that Cu ions replace A-site Fe ions and as a result, A-site moment decreases. However, difference between A-site moment and B-site moment increases. Thus the increase in magnetic moment η_B with Cu content x up to $x = 0.5$ is due to non-collinear ferrimagnetic structure. The decrease in η_B for $x > 0.5$ indicates the possibility of a Neel's collinear ferrimagnetic structure. Gabal *et al.* [9] suggested that the presence of Cu^{2+} in A site could influence the decrease in the magnetization by the substitution of Ni^{2+} by Cu^{2+}.

The observed variations in the magnetization could be explained on the basis of cation distribution and exchange interaction between iron and copper ions at tetrahedral A and octahedral B sites. When Cu^{2+} ions are introduced

at the expense of nickel ions, some of the Fe^{3+} ions migrate from A to the B sites in view of the site preferences for different ions. This increases the Fe^{3+} ion concentration at B-sites. As a result, the magnetic moment of B sub-lattice increases. However, as Cu^{2+} concentration increases, the iron ions left at A-site, being small in number, the A-B interaction experienced by B-site iron ions decreases. Also, the increased number of Fe^{3+} ions at the B-site increases the B-B interaction, resulting in spin canting [17]. Consequently, the magnetization of B sub-lattice is decreased. The increase in the Cu content in the sample, therefore, decreases the magnetic moment of the A sub-lattice. The reason for decrease in magnetization may also be due to the fact that low Cu^{2+} concentration reduces the number of spins occupying the A sublattices, causing the net magnetization to increase. As the Cu^{2+} content increases, the exchange interactions are weakened and the B spins are no longer held rigidly parallel to the few remaining A spins. The decrease in the B sub-lattice moment, interpreted as a spin departure from co-linearity, causes the effect known as canting. Magnetization values of presently prepared samples are comparatively smaller than those of oxalate prepared samples [9]. Smaller magnetization, in the presently prepared samples, compared to the other synthesis methods is expected due to the surface disorder and probable modified cationic distribution [18].

4. Conclusion

The Ni-Cu Ferrites were successfully prepared by sol-gel method and they are sintered at 1000˚C for 24 hours. The sintering temperature and sintering time plays vital role in determining the particle size. The X-ray diffraction studies clearly showed the formation of single phase spinel structure and the particle size beyond the nanoscale. The lattice parameter is found to increase with increasing copper content. The copper substitution was found to have a significant effect on both the structural and magnetic properties. The saturation magnetization results exhibit a non-collinear ferrimagnetic structure for x = 0.0 to 0.5 and Neel's collinear ferrimagnetic structure for x = 0.5 to 0.9 suggesting a change in magnetic ordering.

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