

Preparation and Characterization of Nickel and Copper Ferrite Nanoparticles by Sol-Gel Auto-Combustion Method

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Abstract— Ferrites with spinel structure are the most widespread materials in radio engineering, electronics and communication industry, microwave devices and computer facilities. The change of synthesis temperature of ferrites results in cation redistribution of iron, which updates crystal properties, as macroscopic magnetic properties of ferrites. Among this extensive class of compounds nickel and copper ferrite has been investigated because of its interesting crystallographic and electrical properties. Studies on NiO_4 showed that, the Ni^{2+} ion has a stronger octahedral site preference than Fe^{3+} in the inverse spinel $\text{Fe}[\text{Ni}, \text{Fe}]\text{O}_4$. Several studies on CuFe_2O_4 showed a cubic structure. The cation distribution of CuFe_2O_4 is determined by tendency of the Cu^{2+} ions to occupy B-site, and leading to an inverse structure. Hence Ni and Cu ferrites were synthesized by the sol-gel auto-combustion method.

Keywords- Ferrites, Spinel structure, Cation distribution.

I. Introduction

Nanostructured ferrites containing transition metal oxide materials are known to exhibit interesting physical and chemical properties, significantly different from those of conventional bulk materials, due to their extremely small size and large specific surface area. And transition metal ferrite nanoparticles have found considerable interest due to their technological promising applications in the microwave industries, in fields as magnetic storage, for high speed digital tape or disk recording and application in biomedicine, ferrofluids, catalysts and magnetic refrigeration systems. And Ferrite as a semiconductor has attracted considerable attention in the field of technological application in a wide range of frequencies extending from microwave to radio frequency [1–3].

Spinel ferrite nanoparticles with the general formula MFe_2O_4 (where M is +2 cation of Ni, Cu, Mn, Zn or Co) are very important materials because of their interesting magnetic and electrical properties with good chemical and thermal stabilities [1]. Nickel and Copper ferrite are one of the most important spinel ferrites. Despite the wide-spread application of nickel and copper ferrite nanoparticles, there is a serious lack of information concerning the toxicity of these nanoparticles at the cellular and molecular level. Synthesis of nano-crystalline ferrite through different routes has become an essential part of research and development in order to obtain materials with the desired physical and chemical properties. Various chemical and physical methods including chemical co-precipitation, high energy milling, hydrothermal processing, sol-gel and mechanical mixing method have been attempted to produce nano-crystalline ferrites [1-3]. These techniques have some disadvantages such as complex processes, expensive precursors and low production rates. Recently, a sol-gel auto-combustion method has been utilized to synthesize simple and mixed metal oxides at a lower temperature in a surprisingly short time. This quick, straightforward process can be used to synthesize homogeneous, high-purity, crystalline oxide ceramic powders including ultrafine ferrite composites with a broad range of particle sizes [4]. In this present work, a novel route for production of nanostructured nickel ferrite and copper ferrite nanopowders was investigated. The effects of magnetic properties, structural, compositional studies have been investigated of nickel and copper ferrites using XRD, SEM, EDAX FTIR and VSM.

II. Experimental detail

The sol - gel method is widely used in synthesis of ferrite nanocrystals because of its high reaction rate, low preparation temperature, and production of small particles. Hence, in present experiment, two preparations: nickel ferrite and copper ferrite. Magnetic nanocrystalline nickel ferrite was synthesized by this method. Citric

acid, nickel nitrate nanohydrated, ferric nitrate hexahydrated were produced by Merck company and were used as raw materials. The stoichiometric amount of nitrates and citric acid were dissolved separately in distilled water to make 0.1 M. Fig. 3.2 & 3.3 shows the flow chart of sol-gel method for nickel ferrite and copper ferrite respectively. The mole ratio of the metal nitrates to citric acid was taken as 2:1. The ammonia solution was added into the solution to adjust the pH value to 7 and stabilize the nitrate-citrate solution. During this procedure, the solution was continuously stirred using a magnetic agitator and kept at a temperature of 50 °C. Then, the mixed solution was poured into a vessel, heated slowly to 100 °C and stirred constantly until it became viscous and color changed as the solution turned into a green porous dry gel. The dried gel was completely burnt out to form a loose powder [6, 7]. The same procedure involves in the preparation of copper ferrite by adding copper nitrate hexahydrated. The as-prepared powders were then calcined at different temperatures of 600 °C and 800 °C for 5 hrs. The prepared samples were characterized by XRD, SEM, EDAX, RS, VSM and FTIR.

III. Results and Discussion

A. X-RAY DIFFRACTION

XRD pattern of nickel ferrite nanoparticles of as prepared sample, calcined at 600 °C and 800 °C for 5 hrs is shown in Fig. 1.1(a) & 1.1(b). The calcined samples show the reflection peaks at (111), (222), (311), (400), (422), (511), (440) planes which indicates the presence of single phase NiFe_2O_4 & CuFe_2O_4 with spinel cubic structure, impure phase of $\text{-Fe}_2\text{O}_3$ is found in as-prepared samples and occurs naturally as hematite at (220), remaining peaks corresponds to the standard pattern of NiFe_2O_4 & CuFe_2O_4 . The result shows that the diffraction peaks become sharper and narrower with increase in intensity as the calcination temperature increases which indicates intensification in crystallinity that originates from the increment of crystalline volume ratio due to particle size enlargement of the nuclei. This increase in intensities of all the peaks may be attributed to the increase in grain growth with the increase in the annealing temperature.

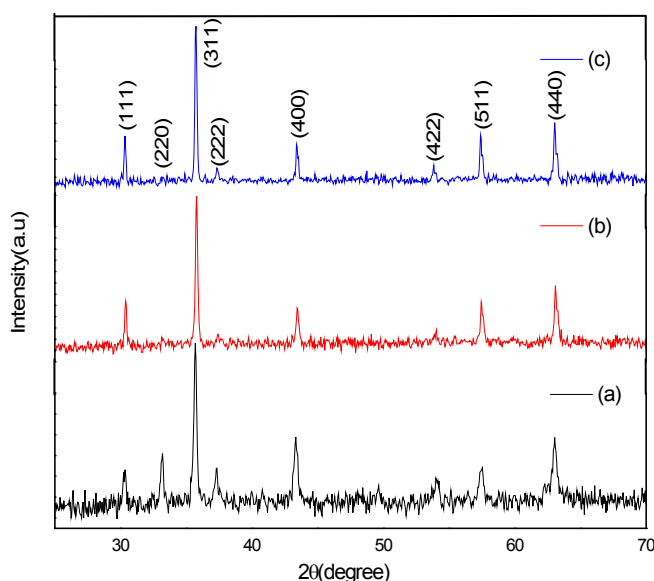


Fig. 1.1(a) XRD patterns of (a) NF as prepared sample (b) NF annealed at 600 °C
(c) NF annealed at 800 °C

Table 1.1 XRD parameters of nickel ferrite

Samples	Grain size (nm)	Lattice parameter (a) Å	Dislocation Density ($\times 10^{14}$ lines/m ²)	Strain ($\times 10^{-3}$ lines ² m ⁻⁴)
NF-AS	37.80	8.3362	6.9960	9.5747
NF-600 °C	59.35	8.3323	2.6777	5.9247
NF-800 °C	61.10	8.3211	2.8389	6.0997

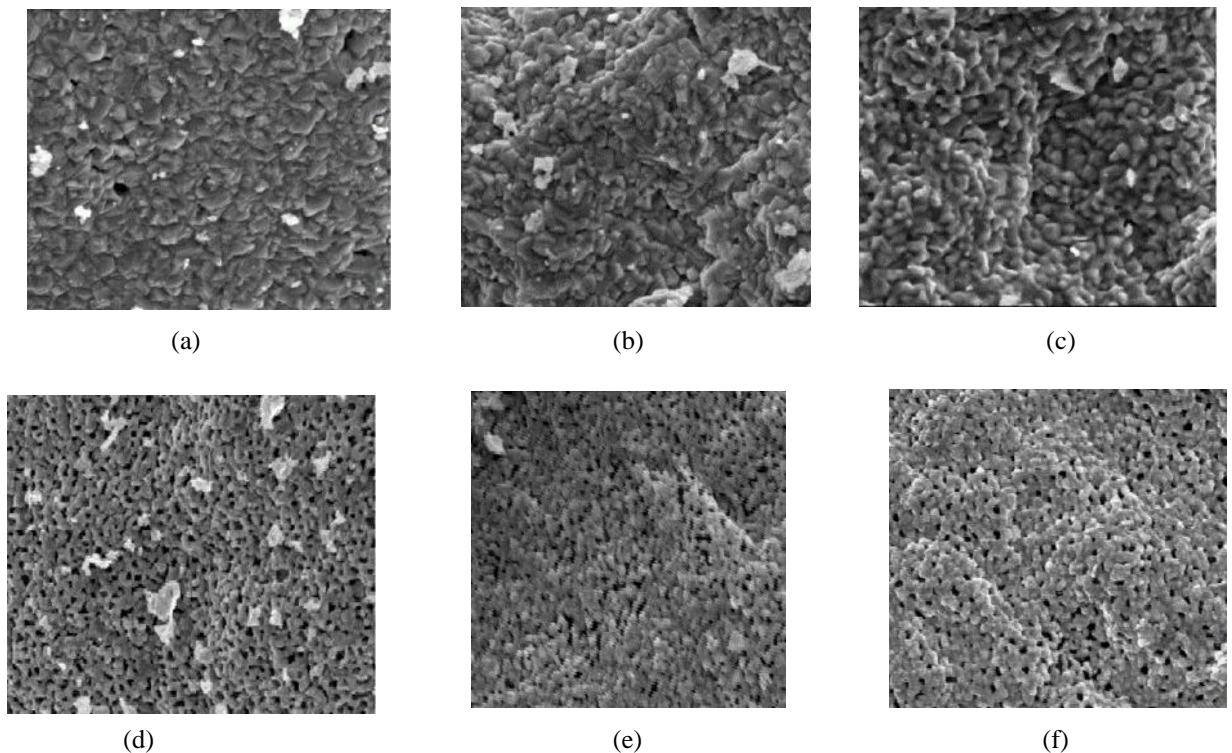
Table 1.2 XRD parameters of copper ferrite

Samples	Grain size (nm)	Lattice parameter (a) Å	Dislocation Density ($\times 10^{14}$ lines/m ²)	Strain ($\times 10^{-3}$ lines ² m ⁻⁴)
CF AS	13.20	8.3378	7.4144	9.67
CF-600 °C	27.22	8.4389	9.7424	11.29
CF-800 °C	37.42	8.3895	1.9913	5.007

B. SCANNING ELECTRON MICROSCOPY

SEM was used to analyze the microstructure of nickel ferrite and copper ferrite nanopowders after grinding. It was noticed that the crystals are distributed more uniformly having smaller grain size with some porous shown in Fig. 1.2(a). When sintering was performed at 600 °C, the micrograph shows Fig. 1.2(b) the crystals are distributed more uniformly having smaller grain size without porous. It is quite clear that there is non-homogeneity in the size of particles all over the image. When it is amplified to 10,000 times, it can be clearly viewed that such tissues are made up of large number of crystallites. When annealed at 800 °C, the grains retained their spinel shape but they grew to 5 µm size and exhibited small number of intergranular pores which is shown in Fig. 1.2(c).

The Fig. 1.2(d) shows the micrograph of CF as prepared sample, when it is magnified at 10,000 times, it exhibit the formation of spongy and fragile network beehive structure. The voids and pores present in the samples attributed due to the releases of some gases during evaporation process. It is observed that the sol-gel derived particles are slightly agglomerated nearly as spherical shape. Fig. 1.2(e) shows the micrograph of copper ferrite annealed at 600 °C, with some crystallites which are in 2 µm. Fig 1.2(f) shows the micrograph of copper ferrite annealed at 800 °C, when it is amplified at 20,000 times, the grains retained their shape which were in 5 µm size. It concludes that the particle size of spinels depends on the nature of transition metal. Moreover, all these copper ferrite samples are formed with mesoporous structure [7].



(d) (e) (f)
Fig. 1.2 SEM micrographs of (a) NF as prepared sample, (b) NF annealed at 600 °C, (c) NF annealed at 800 °C, (d) CF as prepared sample, (e) CF annealed at 600 °C and (f) CF annealed at 800 °C.

C. VIBRATING SAMPLE MAGNETOMETER

The increase in saturation magnetization was most likely attributed to the increasing of crystallinity and particle size of the samples and can be explained on the basis of changes in exchange interactions between tetrahedral and octahedral sub lattice. In case of nickel ferrite, any configuration of Ni^{2+} and Fe^{3+} ions in both octahedral and tetrahedral sites, tends to increase the net magnetization per formula unit. On the other hand, variation of coercivity with particle size can be explained on the basis of domain structure, critical diameter, strains, magneto crystalline anisotropy and shape anisotropy of crystal. Therefore the magnetic behaviour of nano-size nickel ferrites can be a collective effect of these interactions.

For bigger particles the larger coercivity was reported. This is expected from behaviour of superparamagnetic particles magnetization blocked by magnetic anisotropy [8]. There the coercivity decreases with annealing and our value is comparable to coercivity of sample annealed at highest temperature. This shows of samples higher order is produced during the synthesis, which this order is accessible after the strong annealing of surface disordered particles produced by sol-gel method.

The coercivity increases with annealing temperature and decreases when the annealing temperature is higher than 600 °C. The decrease in coercivity beyond 600 °C is attributed to particles exceeding the critical single domain size and becoming multi domain due to sintering. Therefore, particles annealed at higher temperature (600 °C and 800 °C) are expected to have a lower coercivity. While the coercivity reduction under 600 °C might be due to the smallest particles becomes superparamagnetic. In copper ferrite nanopowders the coercivity increases with increasing annealing temperature above 600°C, 800 °C and the values are 1472.3 Oe, 1863 Oe respectively. It reveals that the samples showed superparamagnetic behaviour [9].

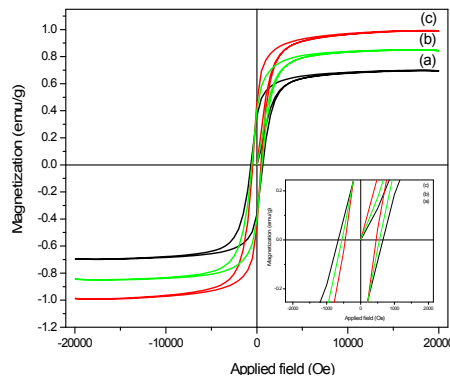


Fig. 1.3 The M-H hysteresis curve of NF nanopowder (a)NF as-prepared sample (b) NF annealed at 600 °C (c) NF annealed at 800 °C

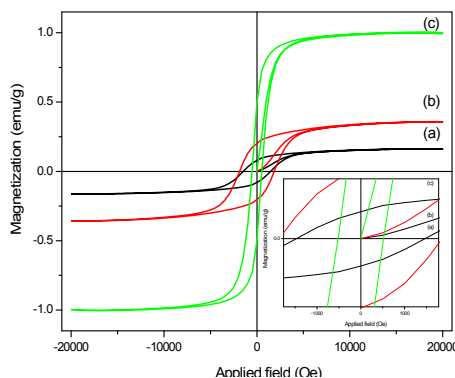


Fig. 1.4 The M-H hysteresis curve of CF nanopowder (a) CF as-prepared sample (b) CF annealed at 600 °C (c) CF annealed at 800 °C

IV. CONCLUSION

V.

X-ray diffraction measurements have indicated the formation of a single-phase spinel cubic structure with the space group $Fd\bar{3}m$. The structural and morphological characteristics were analyzed using SEM technique. It concludes that the particle size of spinels depends on the nature of transition metal. In nickel ferrite nanopowders, the M_s reaches a maximum of 0.9932 emu/g at the annealing temperature of 800 °C and copper ferrite nanopowders, its magnetic saturation increases with increasing annealing temperature at 800 °C which is 1.0043 emu/g. The hysteresis curve for the nickel ferrite and copper ferrite spinel cubic structure were recorded at room temperature. These curve shows, the saturation magnetization (M_s) and the coercivity (H_c) values, which were calculated. These parameters depend on the microstructure and distribution of cations on the A and B-sites of the single phase spinel cubic structure. M_s and H_c are dependent on ferrite composition and annealing temperatures. The annealed samples exhibit superparamagnetic behaviour.

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