NOVEL PROPERTIES OF NANOSTRUCTURED COPPER FERRITE

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ABSTRACT

In this work, copper ferrite nano crystalline powder was prepared by sol gel method. The nitrate-citrate gel was prepared from metal nitrates and citric acid solution of ratio 1:3. The result showed that nitrate citrate gels exhibit a self propagating behaviour after ignition in air at room temperature. The as-prepared powder was annealed at 550^{0}C for 6 hrs. The phase composition and structural properties of sample was investigated by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The result shows single phase of tetragonal structure with the reflection the sample planes (220), (311), (400), (422), (440) and (511). The D.C. electrical conductivity decreases with increase of temperature ensuring the semiconducting nature of the ferrite.

Keywords: *Copper ferrite; Sol-gel auto combustion; nitrate-citric acid fuel; d.c. electrical conductivity.*

Introduction

Ferrites have broad range of applications depending upon their properties. The fundamental properties of ferrites such as structural, electrical and magnetic etc have been the subject of tremendous interest to Physicist, Chemists. The academic interest in the study of ferrites is due to the fact that they are the most important electronic and magnetic ceramics. The potential applications of ferrites in electronics, computer and microwave technologies have focused the curiosity of many research workers on these materials. The benificial properties of the spinel ferrites mainly depend upon the chemical composition, preparation methods, sintering temperature, nature of the additives and their distribution [1]. Ferrites have been need extensive study due to their wide range of application and their importance. They exhibit interesting structural, electrical and magnetic properties which depend upon the nature of ions and their charge, the preparation method and its associated parameters [2].

Nickel ferrite is an inverse spinel ferrite and has a very high electrical resistivity and very low eddy current losses [2]. Cobalt ferrite is a hard magnetic material. Cobalt ferrite has been widely studied due to its high electromagnetic performance, mechanical hardness, excellent chemical stability, high coercivity and moderate saturation magnetization, which make it a very importance for the electronic components used in computers, recording device scards [3–5]. Zinc ferrites (ZnFe2O4) have a normal spinel structure with the space group Fd3m, and they have opened up a new frontier area of material science and technology. Copper ferrite ($CuFe_2O_4$) is one of the most important spinel ferrites because it exhibits phase transitions, changes semiconducting properties, chemical and thermal stabilities, tetragonality variation when treated under different conditions. It is used in electrical switching [6]. It is used in the wide range of applications in gas sensing [7], catalytic applications [8–9], lithium- ion batteries [10] high density magneto-optic recording devices, bio-processing, color imaging, ferrofluids and magnetic refrigeration [11, 12].

Moreover, $CuFe_2O_4$ assumes great significance due to its high electric conductivity, high thermal stability and high catalytic activity for O_2 evolution from alumina–cryolite system used for aluminum manufacture [13]. $CuFe_2O_4$ is to exist in tetragonal and cubic structures. Under slow cooling Copper ferrite crystallizes in a tetragonal structure with c/a lattice parameter ratio of about 1.06. Tetragonal phase of Cu^- ferrite has inverse spinel structure with almost all Cu^{2+} ions occupying octahedral sublattice, whereas Fe^{3+} ions divide equally between the tetrahedral and octahedral sublattices [14]. The stable tetragonal structure is at room temperature and convert to cubic phase only at a temperature of 360^{0}C and above due to Jahn–Teller distortion. The cubic structure possesses a larger magnetic moment than that of the tetragonal one due to more cupric ions (Cu^{2+}) at tetrahedral sites in cubic

structure as compared to in the case of tetragonal structure [15,16].

There are rarely reported the synthesis of tetragonal copper ferrite powders. The correlation between the magnetic, catalytic properties and the microstructure of the produced tetragonal copper ferrite need intensive work.

Experimental Materials

Copper nitrate ($Cu(NO_3)_2.9H_2O$), ferric nitrate ($Fe(NO_3)_3.6H_2O$), citric acid ($C_6H_8O_7).H_2O$ all 99% pure analytic reagent grade are used as received.

Synthesis

Nanostructured copper ferrite was synthesized using sol-gel process.

Preparation of fine powder of copper ferrite

Copper nitrate and ferric nitrates were taken in desired ratio and dissolved in deionized water at room temperature. The solutions were constantly stirred at 90^0C for 2 hours in order to get homogenous solution. An aqueous solution of citric acid was mixed in metal nitrates solution. The mixed solution is then heated at 90^0C for 2 hours. The ammonia was also added in the mixed solution to maintain pH at 9. The temperature of the mixed solution was again increased to 110^0C, which results in the gel formation. After some time, the self ignitions starts and dried gel burnt in a self propagating combustion process to obtain fine particles of copper ferrite[17]. The powder was washed with distilled water and dried at 100^0C. The fine powder of copper ferrite was further annealed at 550^0C for 6 hours.

Characterizations

The XRD pattern of the sample was measured in a Philips diffractometer using CuKα radiation. The morphology of the particles was observed using scanning electron microscope. IR measurements were carried out at room temperature in the range from 200 up to 1000 cm^{-1} by using an infrared spectrophotometer (Perkin Elmer, Model 883).

Result and Discussion

XRD Analysis

The X-ray diffraction pattern (XRD) of the synthesized material was found to be a tetragonal spinel structure similar to that of bulk copper ferrite [13]. The X-ray diffraction patterns for copper ferrite was sintered at 550 ^{0}C are shown in fig.1. The X-ray pattern show sample is existence of the single phase of tetragonal structure with the reflection the sample planes (220), (311), (400), (422), (440) and (511).

It is observed that all the peaks corresponds to the tetragonal structure of copper ferrite and indicates the single phase of the particles. The reflections characteristics of the spinel phase are not intensive, which may indicate low crystalliniety or small particle size.

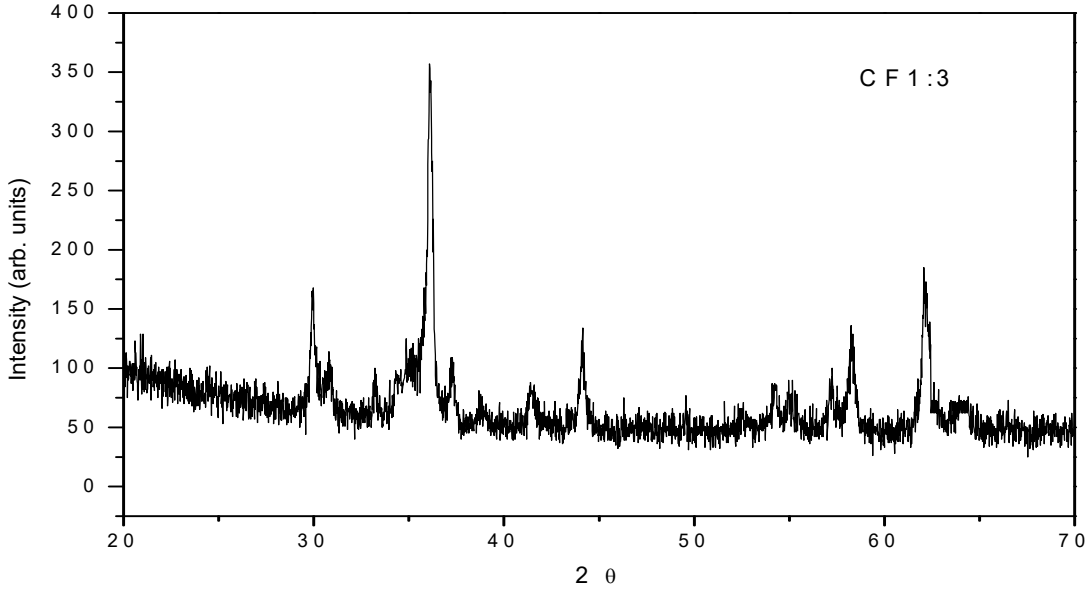

Fig.1: X-ray diffraction patterns for CF 1:3

Besides the spinel phase, reflection characteristics of phase αFe_2O_4 copper in the XRD spectrum. Similar XRD pattern was observed by Irena Szczygiel and his colleague [14]. Table 1 gives the values of interplanar spacing obtained from XRD data. The values of interplanar spacing 'd' and Millar indices (h, k, l) were used to determine the lattice parameters of the sample under investigation.

Table 1 Interplanar spacing (d) for CF 1:3

Plane (h k l)	d
(220)	2.979
(311)	2.486
(400)	2.049
(422)	1.690
(440)	1.451
(511)	1.582

The average crystalline size for sample can be estimated by Sherrer equation i.e.

$D_{h, k.l} = k\lambda / (B_0 - b_0) \cos\theta$

Where, k is a constant, about l, generally considered as 0.89;

λ- Wavelength of X-ray radiation,

B_0 - full width at half height of XRD peaks,

b_0 - natural width of XRD spectrometer, generally replaced by full width at half height of standard sample and

θ - Diffraction angle.

Table 2: Lattice constant (a), X-ray density (dx), Bulk density (d), Porosity (P) For CF 1:3

Ferrite	Lattice Constant (A^0)		dx (gm/cm^3)	d (gm/cm^3)	p %
	a	b			
CF1:3	8.225	8.712	5.399	4.426	18.02

The experimental density was found using Archimede's principle, given by

Ferrite	G (nm)	T (nm)
CF1:3	27.77	31.66

$$\rho_{exp} = \frac{\text{Weight of sample in air}}{\text{loss of weight in distilled water}}$$

The X-ray density was determined using the following relation;

$\rho_{X\text{-}ray} = 8M / Na^3$

Where, M- is molecular weight of the sample, N is Avogadro's number and a -is the lattice parameter.

The percentage porosity of sample was calculated by using the following relation;

Porosity = $(\rho_{x\text{-}ray} - \rho_{exp.}) / \rho_{x\text{-}ray}$

The values of bulk density (experimental density), X-ray density and porosity are given in Table 2.

SEM Analysis

The scanning electron micrographs of copper ferrite sample is shown in Fig.2. The well defined microstructure can be observed from the photograph. The average grain size is about 27.77 nano-meter exhibiting a fine grained microstructure with respect to that of the ferrite powder prepared by conventional route. The value of grain size obtained from SEM image is presented in Table 3. **Table 3**: Grain size (G), Particle size (t) for CF 1:3

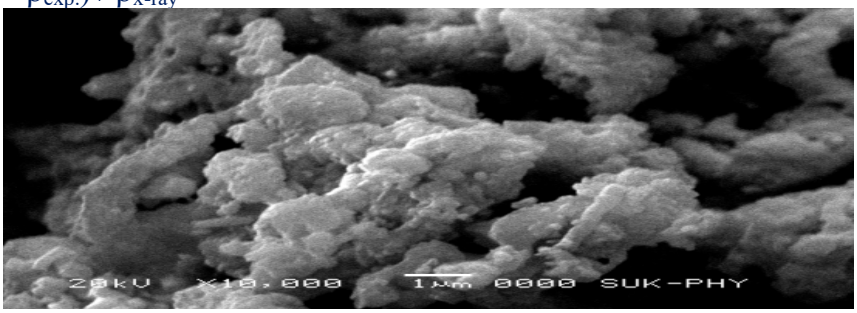

Fig. 2: SEM image of copper ferrite

D.C. Electrical Resistivity

The D.C. electrical resistivity measurements were performed on disc shaped palates of 10 mm diameter and 3 mm thickness using two probe techniques. The resistance 'R' of sample was measured using chromel-alumel thermocouple. The resistivity (ρ) was determined using pellet dimension resistance of the sample. Fig.3 depicts the variation of logarithm of resistivity as a function of reciprocal of temperature. The resistivity decreases with increasing temperature obeying Arrhenius relations. Similar behaviour of resistivity was reported in the literature [12]. The resistivity ρ decreases with increasing temperature exhibiting semiconducting behavior.

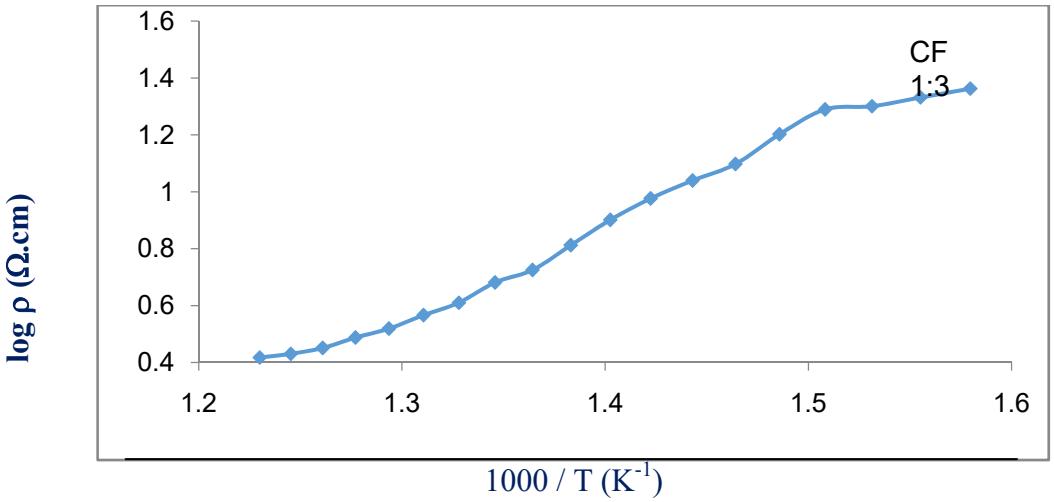

Fig.3: d.c. electrical resistivity

Conclusions

In order to prepare copper ferrite spinel system with good crystalliniety and stoichiometry, we investigated the structural and electrical properties are drew the following conclusions.

1) We successfully synthesized mono-phase spinel tetragonal structured copper ferrite
2) SEM observation showed that the product powder is nanocrystalline structured.
3) The D.C. electrical conductivity decreases with increase of temperature ensuring the semiconducting nature of the ferrite.

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