Synthesis and Characterization of Copper Ferrite Nanoparticles

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Abstract
Copper ferrite CuFe₂O₄ nanoparticles were synthesized by sol-gel method with different annealing temperatures (200, 450, 650 and 850 °C). Structural, morphological, magnetic and electrical properties were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR), vibrating sample magnetometer (VSM) and LCR meter. The XRD patterns showed the system structure in Cu-ferrite had deformed at 650 °C from a cubic to a tetragonal system with apparent a secondary phase CuO. Lattice constant decreases with increasing annealing temperatures, while crystalline volume increases. The FT-IR spectrum of sample under investigations shows two significant absorption bands, which refer to the formation of a single-phase cubic spinel. Magnetization revealed a soft ferromagnetic behavior for the composition sintered at 850 °C. The saturation magnetization, remnant magnetization, and coercivity were 32 emu.g⁻¹, 11.64 emu.g⁻¹, 517.16 emu.g⁻¹, respectively. The electrical measurement of sample shows decrease in the real and imaginary part of dielectric constant with increasing frequency while and AC conductivity increasing.

Keywords: Copper ferrite, Magnetic properties, dielectric properties

1. Introduction

Spinel ferrite nanoparticles with the general formula MFe₂O₄ (M= Cu, Mn, Mg, Zn, Ni, Co, and other metals) are commonly used in high-density storage media, ferromagnetic fluids, catalysts, magnetic drug delivery systems, magnetic separation, magnetic resonance tomography, gas sensors, and other applications[1]. Copper ferrite (CuFe₂O₄) is a very effective ferrite like the other spinel ferrites. CuFe₂O₄ is one of the most important magnetic materials with regular spinel structure with tetrahedral A- occupied by Cu²⁺ ions and Fe³⁺ ions occupied by B- of nanoparticles [2]. Copper spinel ferrites were prepared by self-high-synthesis (HTS) [3], polymer matrix precipitation[4,5], citrate ecomposition [6], coprecipitation [7], hydrothermal
crystallization [8], low solid state reaction [9] sol–gel processing [10], microwave synthesis [11]. These studies showed that, in the synthesis of CuFe2O4, the crystallite size, morphology and phase composition of the final product depended to a large extent on the synthesis process, which often failed to provide the desired result. Due to its simplicity and control over the product properties, sol–gel and gel combustion technology appears as a promising choice in this paper. This is why numerous researchers have used this approach recently in their work. In this research, CuFe2O4 ferrite nanoparticles were prepared using sol–gel auto combustion process, and the results of the structural ,magnetic and electrical analysis are recorded in the manuscript.

2. Experimental

2.1 Synthesis of CuFe2O4 nanoparticles

The chemical materials used for the synthesis of CuFe2O4 samples are Iron nitrate Fe(NO3)3.9H2O, copper nitrate Cu(NO3)2.3H2O, Citric acid C6H8O7H2O and ammonia NH3OH were used as raw materials for preparing the compound CuFe2O4 nanoparticles. The equivalent amount of nitrates and citric acid are dissolved in deionized water separately then mix the nitrate solution with the acid solution. pH value of the solution mixture was maintained at 8 by ammonia solution. The mixing process continues to ensure mix the solution and a good distribution of the components at room temperature. After that the temperature is gradually raised and then fixed at 90°C with the stirring process continuing until the gel form is reached. After a period of time the gel begins to burn out to form a dry gel (Xerogel). The final burnt powders were then thermally calcined at 200, 450, 650, and 850 °C for 3h to obtain well-crystallized CuFe2O4.

2.2 Characterization

The X-ray diffraction patterns of the sample was identified using X-ray Diffractometer (XRD-6000 from SHIMADZU) using Cu Kα radiation (λ = 1.5406 Å), using (2θ) = 10°- 80° in steps of 5deg/s. The Fourier transform infrared (FT-IR) spectra of the powders were recorded using FTIR spectrometer (FTIR 8400S from Shimadzu) in the wave number range (400-3500 cm⁻¹) to confirm the spinel structure of the samples. The surface morphology was analyzed through field emission scanning electron microscope (FE-SEM) with QUANTA 400, (0.5- 30) KV type and TEM (CM120 Philips). The magnetic properties of CuFe2O4 was investigated using the vibrating scanning magnetometer (VSM) (Cryogenic Limited PPMS) under the applied field of ±1 (T). LCR meter (GW INSTEK LCR-8105G) was used to measure dielectric properties.

3. Results and discussion

3.1 XRD and FT-IR Analysis
Fig. 1a show XRD pattern of the CuFe$_2$O$_4$ nanoparticle annealed at (200, 450, 650, and 850) °C for 3 h. The XRD patterns confirmed that of the sample was converted to the required ferrite. The value calculated experimentally of d-spacing and relative intensities of all reflection peak is fully compatible with the standard JCPDS Card no (34-0425) for copper ferrite, respectively. For of the sample prepared and annealing at different temperatures, it was noticed that when the temperature increased, the peak of the reflections became sharp. This indicates an improvement in the crystal when the annealing temperature increases. Additionally, it is noticed that as the annealing temperature increases, the width of the central maxima decreases. This is due to the grain size increase with an increase in the annealing temperature.

The crystallite size ($D$) has been calculated using the high intensity peak for the composition using Scherrer’s formula [12]. X-ray density and surface area of the ferrite sample was calculated by using the following formulas [13]:

$$\rho_{X-ray} = \frac{8M}{N_Aa^3} \quad (1)$$

$$S = \frac{6}{\rho_{X-ray}D} \quad (2)$$

$M$ is the molecular weight of the sample; $N$ is the Avogadro’s number and (a) is the lattice parameter. From Table 1, we can observe that x-ray density increases with increasing annealing temperature, while surface area decreases with increasing annealing temperature. The values of crystallite size, X-ray density and surface area are listed in Table 1. Fig. 1a show the XRD profile of the CuFe$_2$O$_4$ nanoparticles. The peaks appeared at 2θ range of 18.3°, 29.9°, 30.5°, 34.7°, 35.8°, 37.1°, 41.8°, 43.7°, 55.4°, 57.8°, 62.1°, 63.6° and 74.6° which corresponds to the reflection plane (101), (112), (200), (103), (211), (202), (004), (220), (105), (321), (224), (400), and (413) respectively. The XRD shows that the crystal structure had deformed at 650 c from the cubic into a tetragonal system, with secondary phase belonging to CuO at 38.7 (JCPDS Card no. (48-1548). On the other hand, the lattice constant decreases with increasing annealing temperature. The lattice constant was calculated using the formula [14]:

$$\frac{1}{d^2} = \frac{k^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (3)$$

where $d$ is inter planner spacing and $(hkl)$ are the Miller Indices. The crystallite size, lattice constant, unit cell volume, density, and surface area of the annealed samples are summarized in Table 1.

| Table 1. Structural parameters of CuFe$_2$O$_4$ |
Fig. 1. (a) XRD patterns and (b) FT-IR spectra of CuFe$_2$O$_4$

Fig.1b show the FT-IR spectra of CuFe$_2$O$_4$ at annealing temperatures 200, 450, 650, and 850 °C for 3 h. In the dry gel spectrum, a clear crystalline structure but rather a random compound did not appear, but at a temperature of 200°C, the phase beginnings of all samples were shown respectively. On the other hand, as the temperature increased, we observed a decrease in the intensity of the bands, indicating the disappearance of water molecules and organic groups from the sample. At 850°C, we observe in all spectra of samples the appearance of absorption bands at high frequency ($\nu_1$) due to the frequencies of the Fe-O bonds of the tetrahedral (A site) of 586 cm$^{-1}$. On the other hand, the absorption bands of low frequency ($\nu_2$) it returns to the frequencies of the M-O bonds of the octahedral (B-site) of 418 cm$^{-1}$ [15].

### 3.2 SEM and TEM Analysis

The morphology and surface structure of the material was examined through FE-SEM/EDX and TEM. Fig. 2 shows SEM micrographs, the respective energy-dispersive X-ray spectroscopy (EDX) and the particle diameter distribution of CuFe$_2$O$_4$ nanoparticle annealed at 850 °C. As can be seen from Fig. 2 show the SEM micrograph of CuFe$_2$O$_4$ nanoparticle. The image gave a polyhedron shape with few
agglomerations and negligible porosity. Fig. 2b shows a broad histogram of particle diameter distribution of CuFe$_2$O$_4$ with average size around 77.7nm. Additionally, the image showed the presence of gaps caused by the release of gases during the combustion process, such as CO$_2$, H$_2$O, etc.

The grain size of the sample was calculated by Image J software. The chemical composition of the synthesized sample was determined by EDX analysis. Fig. 2c shows the EDX spectrum of CuFe$_2$O$_4$ compound, we observe that the presence of Cu, Fe, and O peaks, which related to the CuFe$_2$O$_4$ nanoparticles. The Fe:Cu ratio was 2:1 which is consistent with theoretical calculations.

Fig. 2 SEM-EDX micrographs and the particles diameter distribution of CuFe$_2$O$_4$

Fig. 3 (a-b) show the morphology of CuFe$_2$O$_4$ nanoparticle annealed at 850 °C by TEM. It is seen from the figure that most of the particle appear as spherical and polyhedron shape. these agglomerations cause an increase in particle size.
3.3 VSM Analysis

Fig. 4 shows magnetic hysteresis curve of CuFe$_2$O$_4$ annealed at 850 °C. It was seen from Fig. 4 that of synthesized sample has behavior soft superparamagnetic status. The saturation magnetization ($M_s$) value of the soft ferrite mainly depends upon the net magnetization of the spinel lattice. Magnetic parameters extracted from VSM data at room temperature are summarized in Table 2. a saturation magnetization ($M_s$) value of CuFe$_2$O$_4$ nanoparticles was 32 emu.g$^{-1}$. The experimental magnetic moment ($\mu_B$) was calculated using the following relation [16]:

$$\mu_B = \frac{M M_s}{5585} \quad (4)$$

As for remnant magnetization($M_r$) was 11.64 emu.g$^{-1}$. It is well known that CuFe$_2$O$_4$ has an inverted spinel, so Cu ion occupy eight-surface positions, and ions Fe$^{3+}$ are distributed on tetrahedral and octahedral sites [17]. On the other hand coercivity $H_c$ value of CuFe$_2$O$_4$ nanoparticles was 517.16 emu.g$^{-1}$.

The value of anisotropy constant (K) was evaluated using following relation [18]:

$$H_c = \frac{0.96 K}{M_s} \quad (5)$$
3.4 Dielectric Properties

Electrical properties represented by the real part of dielectric constant ($\varepsilon'$), the imaginary part dielectric constant ($\varepsilon''$) and the loss factor (tan$\delta$) in addition to the alternating conductivity ($\sigma_{ac}$) of the sample CuFe$_2$O$_4$ was studied as a function of frequency at room temperature in a frequency 20Hz -3MHz range. The real and imaginary dielectric constant have been calculated by the following equations [19]

\[
\varepsilon' = \frac{C \, d}{\varepsilon_s \, A} \quad (6)
\]

\[
\varepsilon'' = \varepsilon' \tan \delta \quad (7)
\]

Where C is the capacitance of the pellet, d is the thickness, A is the cross-sectional area and $\varepsilon_s$ is the permittivity of free space ($\varepsilon_s = 8.854 \times 10^{-12}$ Fm$^{-1}$). Fig. 5a and b shows the variation of real part and imaginary part of dielectric constant with
frequency for CuFe$_2$O$_4$ at 850°C. It is seen that the real and imaginary dielectric constant value of the sample decreases with increasing frequency and then it remains constant at high values, which is the normal behavior of most ferrites. The high values of the real dielectric constant at low frequencies are due to the polarization of the space charge due to the large mass of its dipoles compared to other types of polarization (electronic, ionic, directional) and when increasing the frequency, these dipoles cannot rotate with the electric field and thus the dielectric constant decreases. This behavior of ferrite has been observed by many researchers [20].

The loss factor is a measure of energy dissipation within the dielectric medium and is considered part of the primary loss in the frit; we notice from Fig. 5c that the maximum values of the loss factor and the loss tangent appeared at low frequencies while decreasing with frequency increase until it becomes constant and stable. Similar results have been observed in other research of ferrite systems [21]. This result of the distribution in the imaginary dielectric constant and loss factor is attributed to the Maxwell-Wagner theory of interpolarity [22]. As a result of this theory, the dielectric constant of ferritic materials consists of two layers. Grains and grain boundaries where the grains are considered regions with low electrical resistance, due to the ideal crystalline properties, while grain boundaries are regions with high resistance. According to Maxwell-Wagner polarization theory, the polarization between surfaces within the grain boundaries occurs due to the accumulation of charge in these high-resistance boundaries. This polarization occurs in all heterogeneous crystalline materials (which are more than one phase). Fig. 5d showed the alternating electrical conductivity, as this study provides important information about the alternating electrical conductivity and the effect of deformation on it. In general, the conduction process occurs in the frit materials as a result of the transfer of electrons between Fe$^{+2}$ and Fe$^{+3}$ located in eight-surface locations [23]. The values of AC conductivity ($\sigma_{ac}$) have been calculated using the following equation [24]:

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon' \tan\delta$$  \hspace{1cm} (8)

Where $\omega$ is the angular frequency. Fig. 5d show that AC conductivity decreases as electronic transitions between Fe$^{+2}$ and Fe$^{+3}$ decrease. On the other hand, grain boundaries in the low conduction operate in all samples at frequencies ($10^3$ - $10^4$ Hz) where the transmission of electrons between Fe$^{+2}$ and Fe$^{+3}$ decreases relatively, while electronic mobility increases in the larger frequencies $10^4$ Hz as the grain boundaries become more active and that enhances conductivity.
CONCLUSION

Copper ferrite nanoparticles were successfully prepared by citrate-gel auto combustion technique. The crystal structure of the copper ferrite is quadrangular, as infrared spectrum indicates the emergence of the absorption beams due to the vibration of the oxygen metal bond at the octahedral sites and tetrahedral sites. The prepared sample are soft ferrites have low hysteresis loss. Furthermore, real and imaginary part of dielectric constant decreases with increasing frequency while AC conductivity increasing. dielectric properties of copper ferrite which are useful in many device applications.

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