Synthesis and characterization $CuFe_2O_4$ nanoparticles prepared by the hydrothermal ultrasonic assisted method

S. F. RUS[a], P. VLAZAN[b] , S. NOVACONI[b], P. SFIRLOAGA[b], I. GROZESCU[b]
[a]*"Politehnica" University of Timisoara, Piata Victoriei 2, 300006, Timisoara, Romania*
[b]*Institute for Research and Development in Electrochemistry and Condensed Matter, P. Andronescu Street, No.1, 300224 Timisoara, Romania*

Copper ferrite nanoparticles were synthesized by hydrothermal ultrasonically assisted method using iron nitrate and copper nitrate as precursors in aqueous alkaline solution. Mixing process was performed using an immersed sonotrode in synthesis environment. Ultrasonic treatment was performed at 100 W/40 kHz during the hydrothermal synthesis at 200°C and 40 barr for 2 hours. The synthesized nanoparticles were characterized by X-ray diffraction (XRD) that shows a high crystallization of degree for $CuFe_2O_4$ nanoparticles and their dimension is about 16 nm. The scanning electron microscopy analyses evidenced the presence of agglomerated quasi spherical nanoparticles of the copper ferrite and particles are almost spherical shape. The surface morphology of $CuFe_2O_4$ was performed by atomic force microscopy which revealed a clear topographic image of the nanosized $CuFe_2O_4$ powder and illustrates the particles with a narrow size distribution in the range of 15-18 nm. The magnetic measurements showed a superparamagnetic behavior of $CuFe_2O_4$ nanoparticles at room temperature. The specific magnetization values of the as-obtained powders are reached 29emu/g and the initial magnetic susceptibility is 0.04.

(Received January 17, 2012; accepted April 11, 2012)

Keywords: Copper ferrite, Hydrothermal synthesis, X-ray diffraction, Magnetic, Scanning electron microscopy measurements, Ultrasonication

1. Introduction

Nanomaterials have brought many great changes and new research opportunities in chemistry, physics, biology, material science and others [1]. Ferrites are very important materials due to the large number of technological applications, as well, they can be used as model materials and provide an opportunity for better understanding of the magnetic interactions in nanoscale [2, 3]. Development of ferrite nanoparticles has been intensively investigated because of their fundamental scientific and technological importance. In all areas of research (basic and applied), it is of fundamental importance to have precise control of the nanostructure. This challenge is currently being faced in order to allow various applications, from magnetic recording to medicine [4]. Ferrite nanoparticles with interesting magnetic properties [5] have been synthesized which may exhibit superparamagnetic behavior[6] with a number of innovative potential applications such as image contrast agents in magnetic resonance imaging [7], bioseparation as sensors [8,9], enzyme protein immobilization, high frequency applications[10]: cell separation and quantification in biomedicine [11,12]. Methods as hydrothermal [13], reverse micelle synthesis [14], co-precipitation [15, 16], microemulsion [17, 18], microwave-hydrothermal reaction [19], sol gel and auto-combustion methods [20] aerosol and by mechanochemical [21] routes have been studied. Among special preparation methods, hydrothermal synthesis is a very promising process since the particles prepared by this procedure are pure, ultra fine, relative strain free, with narrow size distribution and has therefore attracted much attention in recent years [22]. The nature of the precursors plays an important role in the synthesis of nanoferrites. However the properties of the obtained ferrite nanoparticles deviate considerably as regard to the average particle size [23], surface areas, magnetic properties, sintering characteristics, as well as their dependency on the ferrite composition [24].

In the present work a copper ferrite ($CuFe_2O_4$), is synthesized by a hydrothermal ultrasonically method, from metal chloride solutions, using aqueous ammonia as precipitating agent. The prepared powders are characterized and their behavior is investigated.

In the present work we report obtaining $CuFe_2O_4$ nanostructure by assisted ultrasonic hydrothermal method from metal chloride solutions using aqueous ammonia as precipitating agent and sodium hydroxide as pH regulator. The prepared powders are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDAX), atomic force microscopy (AFM) and magnetic measurements.

2. Methods

Analytical pure chemicals (Aldrich) used for obtaining copper ferrite particles were iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), copper nitrate ($Cu(NO_3)_2{\bullet}3H_2O$), 1M NaOH solution and distilled water. Iron nitrate and copper nitrate were mixed in a 2:1molar ratio and were added over the distilled water. This precursor were mixed and continuous stirred for 15 minutes for a better homogeneity, adjust pH to 11 with 1M NaOH, and introduced in a teflon lined steel autoclave with an immersed sonotrode. The recation is described by:

$$Cu(NO_3)_2 + 2(Fe(NO_3)_3 + 8NaOH \longrightarrow CuFe_2O_4 + 8NaNO_3 + 4H_2O$$

The synthesis is made under a fill degree of autoclave about 80%, at pH 11 for 2 hour at 200°C under continuous ultrasonic at 100W and 40 KHz. For this temperature the auto generate pressure in hydrothermal process is about 40 Barr. Sonication was performed using a power high voltage amplifier (connecting to computer via NI USB-6008 (National Instruments) equipped with an immersion ultrasonic sonotrode, which was made of titanium alloy, and with the tip diameter of 7 mm. The variable power output control allows the ultrasonic vibrations at the probe tip to be set to any desired amplitude and controlled by computer. After the reaction, the autoclave was cooled to room temperature and then opened.

Ultrasonation was an important factor in this assisted hydrothermal synthesis of $CuFe_2O_4$ nanostructures. Firstly, the ultrasonation accelerate the reaction. When the reaction was performed without ultrasonation, large quantity of unreacted precursors remained in the product. Secondly, ultrasonation was helpful to obtain relatively small and uniform particles.

The cavitation in liquid–solid systems produces mechanochemical effects, in addition to the homogeneous cavitation observed in pure liquids. Liquid jets and/or shock waves formed under ultrasound irradiation can cause surface damage of the solid and/or produce high velocity interparticle collisions. These effects, can produce particle breakage, thus favored its dissolution and accelerated the reaction, and also can prevent the aggregation of the resulting nanocrystals. In addition, cavitation accelerates mass transport, and makes the repassivation by reaction products less important or even avoidable.

The reaction product, a dark brown powder was filtered, washed with distilled water, ethanol and acetone several times, and dried to 60°C for 4 hours. More than 80% of the theoretical material amount was obtained after the drying.

The phase structures of the prepared samples was investigated by X-ray diffraction (XRD) using PANalytical X'PertPRO MPD Diffractometer with Cu $K\alpha$ radiation $\lambda = 1.5406$Å, 2θ-step of 0.01° from 20 to 90. Powder morphology was observed using an Inspect S PANalytical model scanning electron microscopy (SEM) and a Nanosurf Easyscan 2 atomic force microscopy (AFM). The semiquantitative elemental analysis was analyzed through EDAX facility of SEM. The magnetic measurements are performed by conventional AC method.

3. Results

3.1. X-ray diffraction (XRD) results

XRD analysis show that we have obtained crystalline MFe_2O_4 sample with the expected cubic spinel structure (Fd3m) with lattice 8.39Å identified as $CuFe_2O_4$ (01-077-0010). XRD analysis revealed a high degree of crystallinity with diffraction peaks correspond to the cubic spinel structure. In the XRD pattern of that sample we observe the presence of one little peak which correspond to the diffraction of CuO(00-001-1117). Crystallite sizes were determined from the full-width at half maximum (FWHM) of the strongest reflection the (311) peak using the Scherrer equation:

$$D = K\lambda/\beta cos\theta_\beta \quad [25]$$

Where K is the shape factor with a typical value about 0.9 for spherical form, λ is the x-ray wavelength (CuKa=0.154178 nm), β is the line broadening at half the maximum intensity (FWHM) in radians and θ is the Bragg angle. The dimension of crystallite for (3 1 1) peak using the Scherrer equation is about 16 nm.

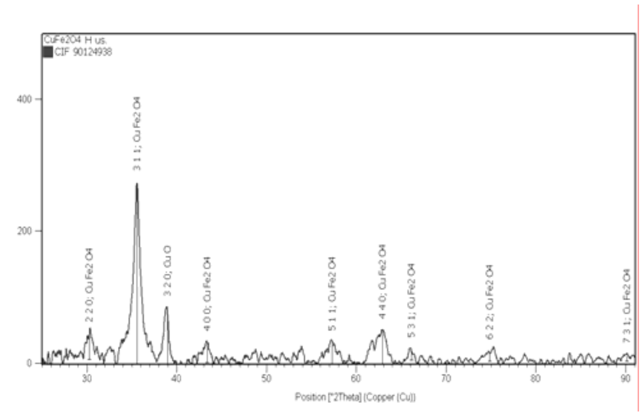


Fig.1. XRD spectrum of $CuFe_2O_4$: compound obtained by hydrothermal ultrasonically assisted method.

3.2. Scanning Electron Microscopy SEM-EDAX results

In Fig. 2 are shown the SEM micrographs and EDAX spectrum characteristic to the ferrite powders synthesized by ultrasonically assisted hydrothermal method. The micrographs show the particle surface morphology and dimensions (fig. 2.a.) The shape of powder obtained by ultrasonically assisted hydrothermal method is almost spherical agglomerated in bigger aggregates. The SEM micrograph shows that most of the particle size is between 15-18 nm. This value is in accordance with that obtained from XRD measurements. EDAX analysis that based on the strength of the emission energies characteristic to constituent elements was performed. The obtained EDX spectra (Fig. 2.b.) confirm the presence of Cu, Fe and O elements in the sample and a deviation from stoichiometry was observed Cu:Fe 1:1.82 (semiquantitative analysis).

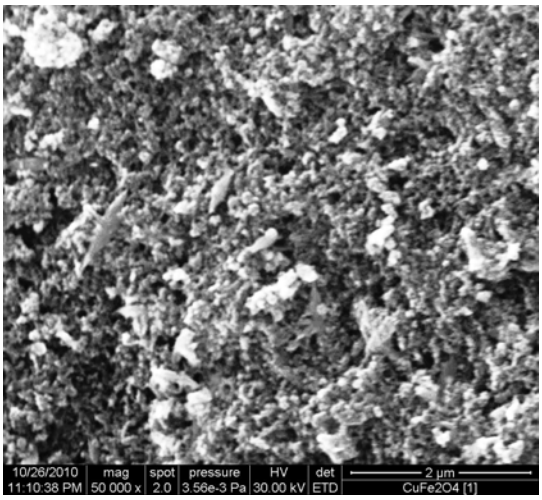
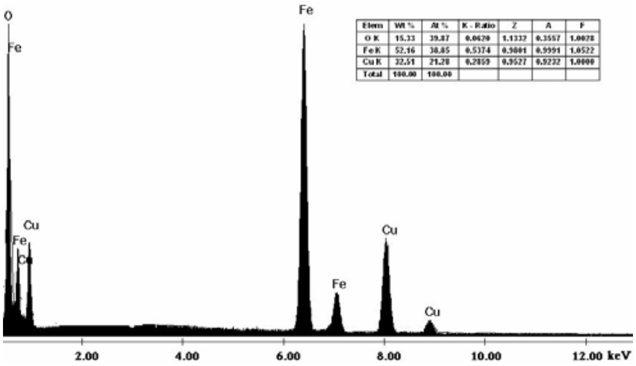


Fig.2.a. SEM image analysis of $CuFe_2O_4$ compound obtained by hydrothermal ultrasonic assisted method.



Elem	Wt %	At %	K - Ratio	Z	A	F
O K	15.33	39.87	0.0620	1.1332	0.3557	1.0078
Fe K	52.16	38.85	0.5374	0.9801	0.9991	1.0522
Cu K	32.51	21.28	0.2859	0.9527	0.9232	1.0000
Total	100.00	100.00				

Fig.2.b. EDAX quantification of $CuFe_2O_4$: compound obtained by hydrothermal ultrasonical assisd method.

3.3 Atomic Force Microscopy (AFM)

The surface morphology of $CuFe_2O_4$ was performed by atomic force microscopy in tapping mode on 2.2/2.2 um of sample. Fig. 3 shows the AFM results of nanosized copper ferrite.

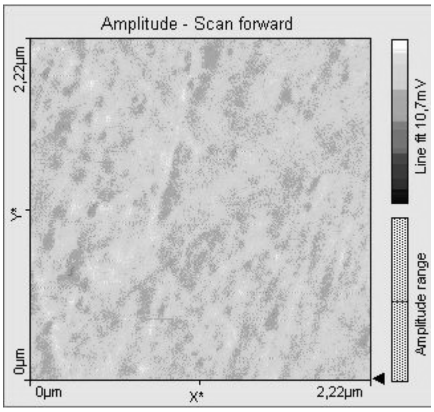


Fig. 3a Surface image of $CuFe_2O_4$ obtained ultrasonically assisted hydrothermal method

The AFM image (Fig. 3a) revealed a clear topographic image of the nanosized $CuFe_2O_4$ powder.

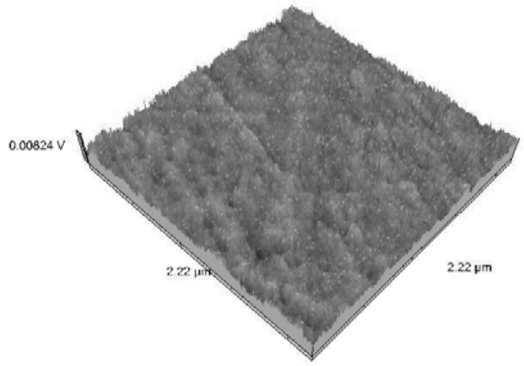


Fig.3b 3D image of $CuFe_2O_4$ obtained ultrasonically assisted hydrothermal method.

The three-dimensional view of the same sample (Fig. 3b) illustrates that the particles size of the $CuFe_2O_4$ powders were, with some little exception, in the range of 15-18 nm with a narrow size distribution.

3.4. Magnetic Measurements

The magnetic behavior was examined by means of the conventional AC method at room temperature.

We analyzed the magnetic behavior of the cooper ferrite obtained by hydrothermal ultrasonically assisted method by measuring the magnetization as a function of an applied magnetic field 50 Hz with amplitude up to 4000Oe [26].

The specific magnetization values of the as-obtained powders are comparable with those reported in the literature [27]. However, annealing in air of the powder prepared by hydrothermal ultrasonically assisted method at moderate temperature led to an increase of this quantity within the explored field range, presumably due to internal stress relaxation.

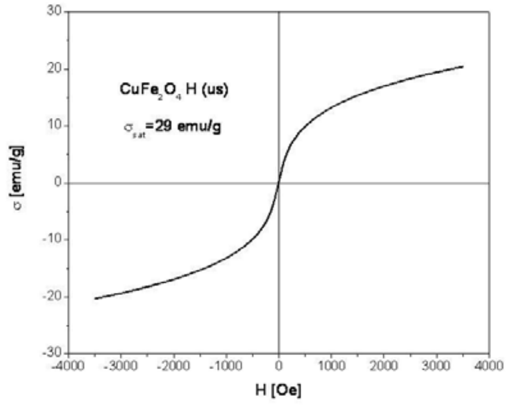


Fig.4.Variation of magnetization with applied magnetic field for $CuFe_2O_4$ nanoparticles obtained by hydrothermal ultrasonically assisted method.

The magnetization of the produced $CuFe_2O_4$ powders using AC method was performed at room temperature under an applied field of 50 Hz with amplitude up to 4000Oe and the hysteresis loop of the ferrite powders was obtained. $CuFe_2O_4$ nanoparticles obtained by hydrothermal ultrasonically assisted method behaved superparamagnetically at room temperature comparable with those reported in the literature [28] and the highest saturation magnetization value reached 29emu/g.

Fig.5 is illustrate the variation of susceptibility with applied magnetic field

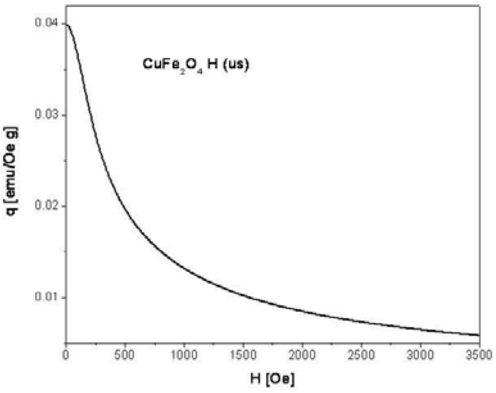


Fig 5. Variation of susceptibility with applied magnetic field for $CuFe_2O_4$ the nanoparticles obtained by hydrothermal ultrasonic assisted method.

Their initial magnetic susceptibility is 0.04 and varies with the intensity of magnetic field.

4. Discussions

Reported to hydrothermal classical method, ultrasonical assisted hydrothermal method offers serious advantages like obtaining of small nanoparticles with narrow size distribution. Also a processed time for sample is significantly reduced. The synthesis time for this method is a fraction of time from classical synthesis method (about 30-40%) because the ultrasonation is an important factor which accelerates the reaction. Also, when the reaction is performed without ultrasonation, large quantity of unreacted precursors remained in the product. As well ultrasonation is helpful to obtain relatively small and uniform particles.

XRD analysis revealed a high degree of crystallinity with diffraction peaks correspond to the cubic spinel structure of cooper ferrite. Crystallite size for (311) peak reflection is 16 nm. We observe a non allocated little peak attributed to CuO. In the future work we propose to eliminate this unwanted impurity in obtaining sample. One good method used to eliminate the copper oxide is adding besides precursors a determinate quantity of reducing agent.

The analysis of the morphology and structure by electron microscopy for cooper ferrites shows that the powders are composed of particles with diameters bellow 20 nm with quasi spherical shape.

From the hysteresis measurements for $CuFe_2O_4$ powders obtained in this study for a magnetic field up to 4000Oe, results a superparamagnetic behavior at room temperature, with high saturation magnetization value reached 29emu/g.

5. Conclusions

The nanostructures of $CuFe_2O_4$ were successfully synthesized by the hydrothermal ultrasonically assisted method using as reactants $(Fe(NO_3)_3{\cdot}9H_2O)$ and $(Cu(NO_3)_2{\bullet}3H_2O)$ salts which were dissolved in distilled water to produce an ionic solution with a mole ratio of 1:2 (Cu:Fe).

The reagent concentration and reaction medium have a particularly importance regarding hydrothermal synthesis.

Ultrasonation have a major importance in this synthesis regarding to reduce processing time and dimension of obtained powder.

The X-ray diffraction shows a high crystallization of degree for $CuFe_2O_4$ nanoparticles and their dimension, using Scherer equation, is about 16 nm.

SEM analyses suggest that particles are almost spherical shape.

The magnetic measurements show a super paramagnetic behavior of $CuFe_2O_4$ nanoparticles.

The specific magnetization values of the as-obtained powders are reached 29emu/g, comparable with those reported in the literature and the initial magnetic susceptibility is 0.04 and varies with the intensity of magnetic field.

Acknoledgements

This work is supported by the strategic grant POSDRU ID77265 (2010), co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013.

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[*] Corresponding author: rusflorinastefania@gmail.com