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Structural and magnetic properties of $CuFe_2O_4$ ferrite nanoparticles synthesized by co-precipitation

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Abstract

Copper ferrite nanoparticles have been synthesized using a co-precipitationmethod. The samples are annealed at different temperatures 600, 800 and 1000°C. The structural, morphological and magnetic properties of the nanoparticles arecharacterized by thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction, scanning electron microscopy and Mössbauer spectrometry. The annealing temperature effect on the grain size, the lattice parameter, the degree of inversion, the cationic distributionis studied. TG-DTA measurements show a crystallization temperature of about 520°C. The X-ray diffraction measurements show that the average grain size increases from 10 to 90 nm when the annealing temperature ranges from 600 to 1000°C. For its part, scanning electron microscopy shows that the particles have spherical shapes but not homogeneous sizes. Mössbauer spectra recorded at room temperature show a paramagnetic behavior of iron atoms for the un-annealed sample, while for the samples annealed at 600, 800 and 1000°C, the iron atoms are magnetic and the inversion parameter x ranging from 0.77 to 1.

*Keywords:*Copper ferrite, Chemical co-precipitation method, Nanoparticles, XRD, magnetism, Mössbauer spectrometry.

1. Introduction

Ferrite nanoparticles have attracted considerable attention because of their particular properties [1-10]. So, they are intensively studied and developed for industry as information storage, high frequency devices, ferrofluid [1,11]and transformers but also in biological applications[12].The changes in the properties of the nanoparticles are mainly attributed to crystallite size due to the fraction of atoms on the surface compared to the bulk [13]. The copper ferrite bulk belongs to the inverse spinel structure [14,15] with 8 Cu^{2+} ions occupying octahedral B-site while 16 Fe^{3+} ions occupy equally the tetrahedral (A-sites) and octahedral (B-sites) site of the unit cell [13], this configuration is shown by $(Fe^{3+})_A[Cu^{2+}Fe^{3+}]_BO_4^{2-}$.The most widely used methods for synthesis offerrite nanoparticles,with range of crystallite size between 1 to 100nm,are sol-gel, co-precipitation and solid state methods [16].

In this work, we present the results obtained on nano-ferrite $CuFe_2O_4$spinels synthesized by co-precipitation method. The structural properties were investigated by X-ray diffraction and by scanning electron microscopy. The magnetic properties were characterized by Mössbauer spectrometry on ^{57}Fe. The obtained results are discussed in terms of the annealing temperature and grain size.

2. Experimental procedures

Copper ferrite nanoparticles were synthesized by co-precipitation method using $Cu(NO_3)_2.6H_2O$ and $FeCl_3\cdot 6H_2O$ in stoichiometric proportion as starting materials.

The mixture was dissolved in 100 ml of distilled water and thoroughly mixed using a magnetic stirrer and heated to a temperature of 40°C. The precipitation was performed by adding NaOH (1M) until pH equal to 12. The resulting product was washed several times by distilled water and dried at 80°C for 24h. The sample was annealed at different temperatures 600, 800 and 1000°C for 2h.

Thermo-gravimetric analyzer (LabSys EVO Setaram 1600) was used to investigate the thermal changes in the samples.Phase identification of the samples were investigated by an X-ray diffractometer (Bruker, D8-Advance) in the reflection mode, using CuK_{α} radiation (λ = 1.5406Å). The diffraction patterns were collected in the 2θ range from 15 to 70°. Mean crystallite sizes of the samples were estimated by using Scherrer's formula [17]$D= k\lambda/\Delta(2\theta)\cos\theta$ where D is mean crystallite size, k is an instrumental and form factor and 0.9 is usually used for spherical particles, θ is Bragg angle and Δ(2θ) is broadening of the diffraction peaks, measured at half their maxima intensities, due to purely crystallite size. The XRD data were also used for refining the lattice parameters by using the Bruker EVA software.Morphology of the powders was investigated by a scanning electron microscope(VEGA-3 SBH TESCAN).

Room ^{57}Fe Mössbauer spectra were collected using a 25 mCi^{57}Co source in Rh matrix in constant acceleration mode using standard transmission configuration of Mössbauer spectrometer (Wissel). The velocity scale was calibrated using anα-Fe foil at 300K. Theestimated isomer shifts (δ) are given relative to this standard. The fitting of the spectra was carried out with a set of Lorentzian lines, determined by least squares fitting programme NORMOS.

3. Results and discussion

Coupled DTA-TGA analysis is carried out to study the systematic weight loss and subsequent transformations during heat treatment of the un-annealed sample. TG-DTA curves are shown in figure1. The first stage is reached at 30–120°C, which is attributed to the loss of water physisorbed. The second stage corresponding to the total loss of about 22% of weight between 120 and 400°C, which is due to the departure of nitrate residue. After 400°C no significant weight loss was observed and the exothermic peak at 520°C was attributed to crystallisation of sample.

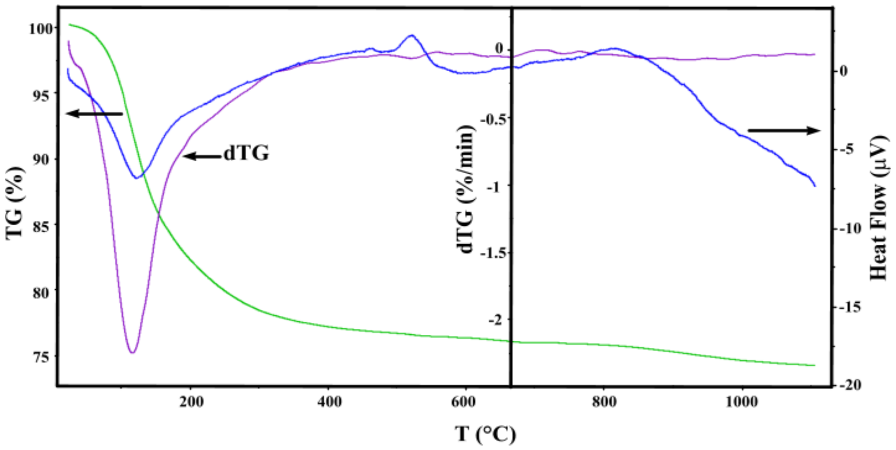

Figure1:TG-DTA curves for theun-annealed sample.

Figure2 shows the XRD patterns of the annealed samples. These patterns are indexed using DIFFRACT.EVA software according to hkl value of the standard pattern withFd-3m space group. The peaks are indexed to the plans (111), (220), (311), (222), (400), (422), (511) and (440)of pure spinel cubic structure. No impurity was detected on the spectra. The width of the strongest peak (311) decreases with the annealing reflecting an increase of the average grain size.Note that the spectrum corresponding to the un-annealed sample shows a broad peak indicating its amorphous nature.

By using the Debye-Scherrer's formula, we estimated the average grain size to10, 30 and 90 nm respectively for samplesannealed at 600, 800 and1000°C. The evolution of the grain size versus the annealing temperature is shown in figure 3.

The lattice parameter, a, was calculated from the diffraction peak using the formula: $a^2=d^2.(h^2+k^2+l^2)$ where d is the inter-reticular distance and hkl are the Miller indices of the plan.For an accurate calculation of the lattice constant, the lattice parameter was calculated for each peak of the XRD pattern and then the average of these values is determined, a = (8.384±0.005)Å which is in agreement with the previously reported results [4].

Typical Scanning Electron Microscopy micrographs of copper ferrite nanoparticles annealed at 1000°C are shown in figure4. They show the formation of multigrain agglomerations consisting of fine crystallites with irregular shapes and sizes.

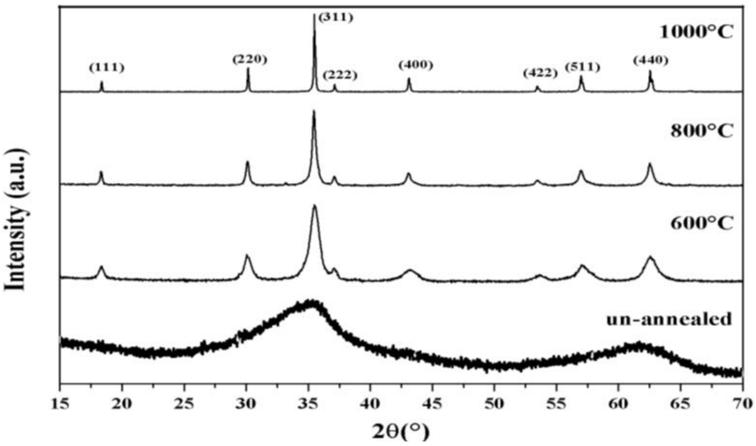

Figure2:XRD patterns for the annealed samples.

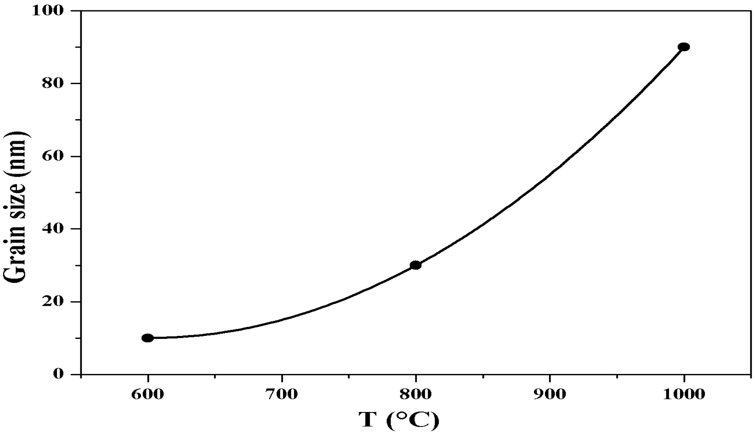

Figure3: Variation of grain size with annealed temperature. The curve between points is a guide to the eye.

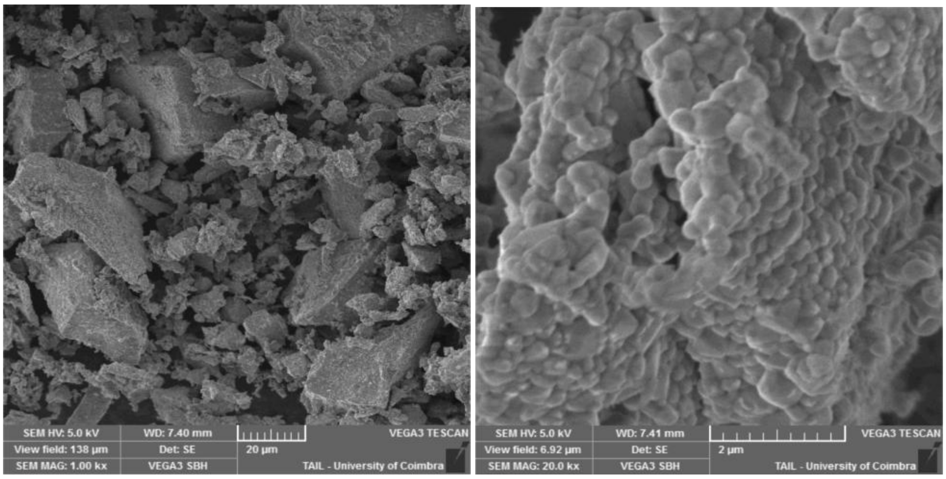

Figure4:SEM micrographsof$CuFe_2O_4$ annealed at 1000°C.

Room Mössbauer spectra of the un-annealed and annealed samples at 600, 800 and 1000°C, are shown in figure 5.For all the spectra, the points are experimental data and lines are the fitting data. As seen in this figure, the spectrum of the untreated sample is a doublet. This indicates that the iron atoms are in a paramagnetic environment. For the annealed sample, the shape of the Mössbauer spectra changed. The spectra are in the form of sextet reflecting a change of the magnetic behavior of the iron atoms, from the paramagnetic phase to the ferromagnetic phase. In agreement with the X-ray diffraction measurements the broadened Mössbauer lines are associated with the small crystallite size. The analysis of Mössbauer spectra is made possible by the superposition of three subspectra. Two subspectra with different hyperfine fields are Zeeman sextets due to Fe^{3+} ions in ordered magnetic state, and the third subspectrum is an additional doublet associated with Fe^{3+} ions in paramagnetic state are needed to get best fits to the experimental data. The Mössbauer hyperfine parameters including hyperfine magnetic field (H_{hyp}), isomer shift (δ), quadrupole splitting (*QS*), and fractional area subspectrum (*Area*) are given in table 1. We note that the values of the isomer shift and the quadrupole spilitting do not change significantly with the annealing temperature. The values of the hyperfine fields H_{hyp} increase (from454.4 to 473.8kOe for A-sublattice site and from483.7 to 504.3kOe for B-sublattice site) in accordance with increasing grains size[16, 18]. Using fractional area of each subspectrum, the Fe^{3+} ion ratio in both octahedral (B) and tetrahedral (A) sublattice site was calculated.

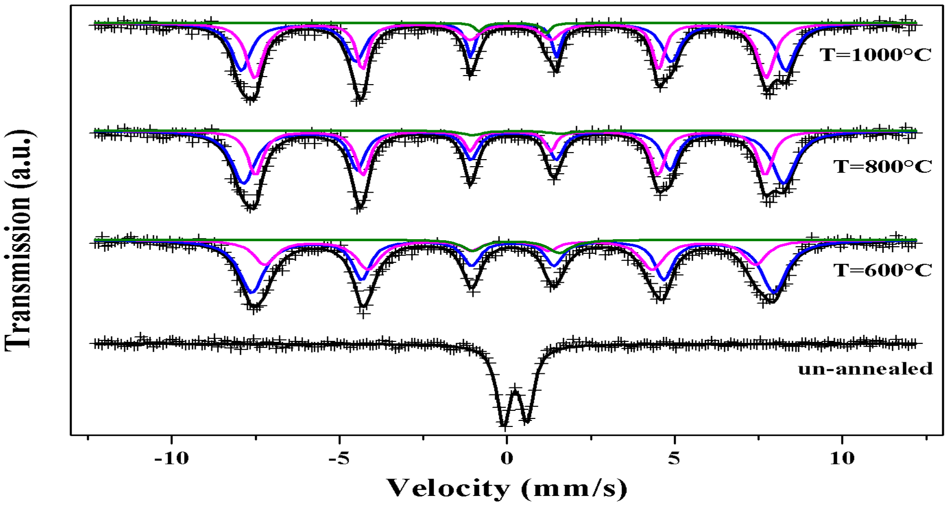

Figure5:Mössbauer spectra recorded at room temperature for the un-annealed and the annealed samples at 600, 800 and 1000°C.

Table1: Variation of the hyperfine parameters H_{hyp}, δ, *QS* and *Area* with annealing temperature.

Annealed temperature (°C)	Subspectrum	H_{hyp} (kOe)	δ (mm/s)	*QS* (mm/s)	*Area*(%)
Un-annealed	-	-	0.397	0.69	100
600	A	454.4	0.246	-	34.77
	B	483.7	0.326	-	59.02
	-	-	0.413	2.60	6.21
800	A	472.2	0.253	-	39.93
	B	500.4	0.349	-	58.03
	-	-	0.421	2.60	2.04
1000	A	473.8	0.259	-	47.84
	B	504.3	0.352	-	50.08
	-	-	0.326	2.00	2.08

The general formula of spinel ferrite is $M^{2+}Fe_2^{3+}O_4^{2-}$ where M^{2+} and Fe^{3+} are divalent and trivalent cations which occupy the tetrahedral sites (A) and octahedral (B) interstitial positions of the face centered cubic lattice formed by ions O^{2-}. However, these ferrites can be better represented by the expression $\left(Cu^{2+}\right)_{(1-x)}(Fe^{3+})_x\left[\left(Cu^{2+}\right)_x\left(Fe^{3+}\right)_{(2-x)}\right]O_4$, where the ions inside the brackets occupy the B sites and the others occupy A sites. In this expression, x represents the degree of inversion defined as the fraction of A-sites occupied by Fe^{3+} ions. Note that the change in the distribution of cations for this type of compounds confers their specific magnetic properties.

The relative number of irons in both A and B sites is determined from the relative subspectrum areas. The inversion parameter can be calculated using therelationabove [19]:

$$\frac{\text{Area(A-site)}}{\text{Area(B-site)}}=\frac{f_A}{f_B}\cdot\frac{x}{2-x}$$

where $\frac{f_A}{f_B}$ is the ratio of the recoilless fractions equivalent to 0.94 at room temperature [19]. From the calculated values for the areas, we estimated the values of x for the three calcination temperatures (see table 2). Also, the cations distribution for the samples is calculated and the results are listed in table2.It should be noted that the values of the inversion parameter x increases whenthe calcination temperature increases, this is attributed to cation exchange between the tetrahedral and octahedral sites.

Table 2:Inversion parameter x and cations distributions for 600, 800 and 1000°C.

Annealing temperature (°C)	x	Cations distributions
600	0.77	$\left(Cu^{2+}_{0.23}Fe^{3+}_{0.77}\right)\left[Cu^{2+}_{0.77}Fe^{3+}_{1.23}\right]O^{2-}_{4}$
800	0.84	$\left(Cu^{2+}_{0.16}Fe^{3+}_{0.84}\right)\left[Cu^{2+}_{0.84}Fe^{3+}_{1.16}\right]O^{2-}_{4}$
1000	1	$\left(Fe^{3+}\right)\left[Cu^{2+}Fe^{3+}\right]O^{2-}_{4}$

Conclusion

In this work, copper ferrite nanoparticles $CuFe_2O_4$ have been synthesized using co-precipitation method. The sample was calcined respectively at 600, 800, 1000°C. We have performed a study on structural and magnetic properties of the samples using complementary characterization techniques.XRD confirmed that the structure is the single-phase cubic spinel, with average lattice parameter of 8.384nm, and crystallite size in the range 10-90 nm. The Mössbauer measurements revealed that the degree of inversion of Fe^{3+} increases with the annealing temperature, the sample hasaninverse spinel structure for 1000°C.

Acknowledgements

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