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CHARACTERIZATION AND MAGNETIC PROPERTIES OF CAPPED $CoFe_2O_4$ NANOPARTICLES FERRITE PREPARED IN CARBOXYMETHYLCELULLOSE SOLUTION

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Inverse-spinel oxide, cobalt ferrite $CoFe_2O_4$, has been synthesized by co-precipitation method, using as capping agent Carboxymethylcelullose (CMC) solution. The cubic structure (S.G. Fd-3m) was determined from X-ray diffraction (XRD) using a X-ray diffractometer The average crystallite size (13 nm) were calculated by using (311) peaks and Scherre`s formula. The particle size, chemical composition and external morphology of the annealed powders were characterized by scanning electron microscopy, SEM. The IR spectra of as-prepared, annealed at 300 and 500 ^oC of cobalt ferrite show the broads bands assigned to the stretching vibration of the water, organic bonds C-H, C=O from CMC. This indicates that the CMC molecules are present on the surface of nanoparticles and do not undergo chemical change, such as oxidation of the double bond or molecular decomposition during the heat treatment. The shifted peaks from 610 and 460 cm^{-1} to 584 and 446 cm^{-1} indicate the migration of metallic cations from the octahedral to the tetrahedral sites. The magnetic properties at room temperature of fine particles were investigated using a vibrating sample magnetometer, VSM. From the obtained hysteresis loops, the saturation magnetization (Ms), remanance magnetization (Mr) and coercivity (Hc) where determined. The obtained values are: Ms= 52.151 emu/g), Mr= 18.544 emu/g, Hc= 634.66Oe.

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1. Introduction

The magnetic materials are playing a crucial role in many devices of every-day life: ac and dc motors which perform many operations (a top-of-the-range car has more than 20 dc motors); power distribution systems, based on power transformers, which deliver energy for home and industrial use etc [1]. Ferrites nanoparticles have attracted an increasing interest because of their wide area of applications, magnetic recording [2], storage [3], catalysis [4], biotechnology [5]. In the last years, the interest in the use of nanoparticles in biomedical applications has greatly increased [6, 7].

The size and composition of nanoparticles influence the bio-application of the magnetic nanoparticles [8]. Small particles (<10 nm) are suitable for applications angiography and tumour permeability. These nanoparticles can be obtained by precipitation of metallic salts in different media as polymers [9], organic acid or alcohol [10], sugars [11] etc., to ensure their colloidal stability, physiological condition and enhanced functionality. Medium size particles (10-30 nm)

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were obtained by heating (annealed) at high temperature of metallic salts with organic precursors. The size range depends on the precursors, surfactants and salts. For hyperthermia treatment particles with size below 50 nm in diameter are preferred because these have been found to produce the maximum specific absorption rate [12,13]. Herget and colab. have reported that the SAR of 35 nm magnetite nanoparticles is twice that of 10 nm particles [14].

The magnetic properties of MFe_2O_4 ferrite are significantly influenced of their bulk counterparts [15]. Various synthesis methods have been employed to obtain ferrites nanoparticles with superior and electrical properties. These synthesis routes include chemical auto-combustion route [16] sol-gel [17] conventional ceramic process [18] RF sputtering [19].

Among ferrite, cobalt ferrite, $CoFe_2O_4$ is especially interesting owing to its magnetic properties such as strong anisotropy, high coercivity at room temperature, moderate saturation magnetization and photomagnetic material [20, 21]. Its properties are very dependent on synthesis technique. Simple methods and cost effective routes to synthesis of nanocrystalline $CoFe_2O_4$ by utilization of cheap, nontoxic and environmental benign precursors are still the key issue. These methods use fungi, actinomycetes, plants extract as aloe vera [22].

In present work we report the synthesis of $CoFe_2O_4$ nanoparticles with crystalline size of 13 nm by a simple method using $CoCl_2 \cdot 6H_20$, $FeCl_3 \cdot 6H_2O$ and used for the first time of carboxymethylcelullose (CMC) solution as precursors. The samples were characterized by TG-DTG analysis, FT-IR spectrophotometry, X-ray Diffraction and Scanning Electronic Microscopy (SEM). The magnetic properties of prepared nanoparticles were investigated with a vibrating sample magnetometer (VSM).

2. Experimental Section

2.1. Materials

The reagents used, $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$ and NaOH were of analytical grade and were used without any further purification.

2.2. Synthesis of $CoFe_2O_4$ Nanoparticles

Nanocrystalline cobalt ferrite has been synthesized by a wet chemical route. The mixed aqueous solution containing 21.2 mL of 0.2 M $CoCl_2 \cdot 6H_2O$ and 21.2 mL of 0.4 M $FeCl_3 \cdot 6H_2O$ were stirred together for 30 min into the reaction vessel of 200 mL. A solution of 21.2 mL of CMC 1% was added into above solution as a capping agent, followed by the addition of an aqueous solution of 3M NaOH. The pH of the solution was continuously monitored and maintained in the range of 11-12. The solution was heated to 80 ºC and it was constantly stirred for 60 min. The solution was then cooled to the room temperature. A blackish precipitate was magnetically separated and washed several times with distilled water and ethanol. The precipitate was dried for 12 h at 110º C and appeared black in color. The samples were heated in the furnace, in air atmosphere, at 500º C for 6 h.

2.3. Structural Characterization

The thermal decomposition and weight loss of the precursor powders were characterized by means of thermogravimetric-differential thermal analysis (TG-DTG) that has been performed on a Paulik-Paulik-Erdey type derivatograph (MOM Bdapest) by varying the temperature from 25 ºC up to 710º C with a heating rate of 10º C/min. The particles were characterized for crystal phase identification by powder X-ray Diffraction (XRD) using the X-ray diffractometer (LabX XRD-6000) with CuKa radiation ($\lambda = 0.15406$ nm). Fourier transmission infrared (FT-IR) spectra of the powders (as pellets in KBr) were recorded using a Fourier transmission infrared spectrometer (FT-IR Spectrometer, Jasco 660 Plus) in the range 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The particle size, chemical composition and external morphology of the fine annealed powders were characterized by scanning electron microscopy, SEM (JEOL JEM-3010 SEM). The magnetic properties of fine particles were investigated using a vibrating sample magnetometer, VSM (AGM & VSM Magnetometer, Princeton Measurement Co.) at room temperature.

3. Results and discussion

Metal oxides are obtained by grinding solid metallic salts with sodium hydroxides. In the first step of the mechanism are obtained $Co(OH)_2$, $Fe(OH)_3$ with a higher reaction activity. When the solution was heated to 80º C, the sodium hydroxides are decomposed to produce CoO and Fe_2O_3 in the reaction process.

$$CoCl_2 \cdot 6H_2O + 2NaOH \xrightarrow[-2NaCl;\ -6H_2O]{} Co(OH)_2 \longrightarrow CoO + H_2O$$

$$2FeCl_3 \cdot 6H_2O + 6NaOH \xrightarrow[-6NaCl;\ -12H_2O]{} 2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\,H_2O$$

$$CoO + Fe_2O_3 \xrightarrow{500\ ^oC} CoFe_2O_4$$

Nanoparticles $CoFe_2O_4$ formation proceeding according this mechanism, has been easily and immediately formed when the powder is calcined in the furnance at 500°C for 6h. Also, other ferrite nanoparticles can be obtained by this procedure.

3.1. Thermal behavior of as-prepared precursors

Thermal analysis provides evidence for the removal of associated solvent, amorphous to crystalline phase transformation and an isochemical transformation. The thermal behaviour of the as-prepared $CoFe_2O_4$ precursor nanoparticles has been carried out in oxygen atmosphere. The results of TG-DTG curves are shown in Fig.1.

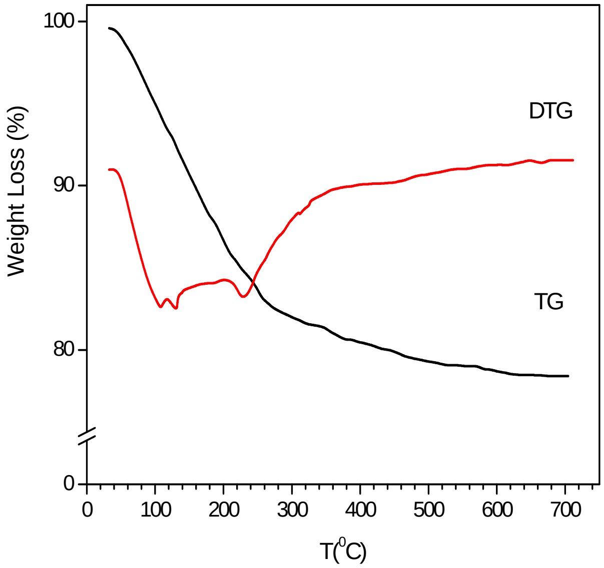


Fig.1. TG-DTG curves of as-prepared $CoFe_2O_4$ precursors powders.

The DTA curves show exothermic peaks at around 100-130ºC and 220-240 ºC which correspond to sharp weight losses on the TG curve. The TG curves show three stage of the weight loss. The first weight loss up to 125 ºC and correspond to removal of adsorbed water on the powder surface. The second stage in the temperature region 125-265 ºC is due to the decomposition of CMC surfactant. The third stage over 260 ºC corresponds to gradual elimination of organic molecules capped on nanoparticles [22].

3.2. FTIR spectra

The FT-IR spectra are a very useful technique to deduce structural investigation of chemical compounds. For ferrite particles, FT-IR spectra can offer information about redistribution of cations between octahedral and tetrahedral site of the inverse spinel structure in $CoFe_2O_4$. Fig.2 shows the FT-IR spectra of $CoFe_2O_4$ nanoparticles (a) as prepared, (b) annealed at 300ºC for 6 h, (c) annealed at 500 ºC for 6h.

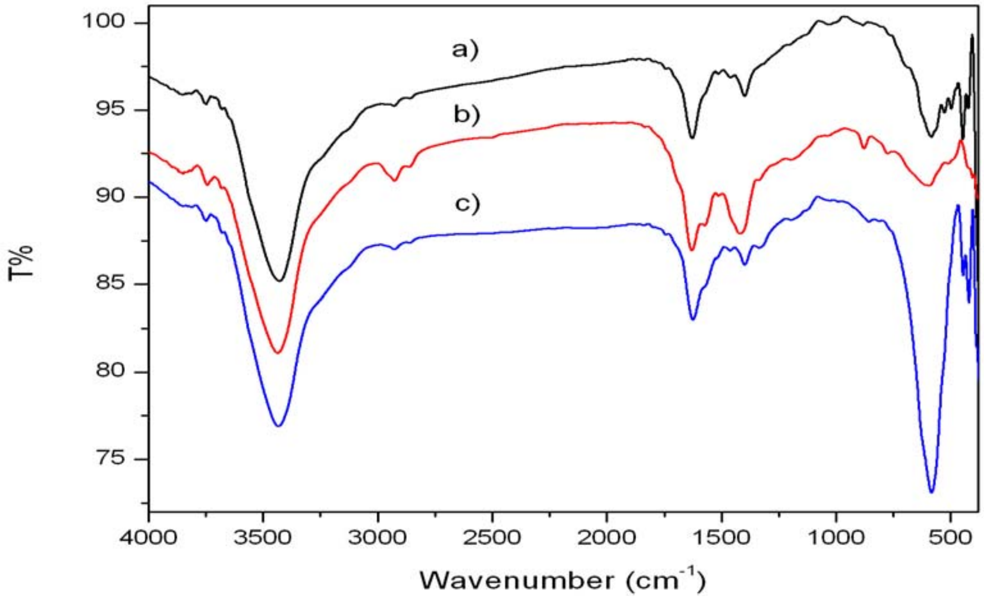


Fig.2. FT-IR spectra of $CoFe_2O_4$ nanoparticles (a) as prepared,
(b) annealed at 300ºC for 6 h, (c) annealed at 500 ºC for 6h

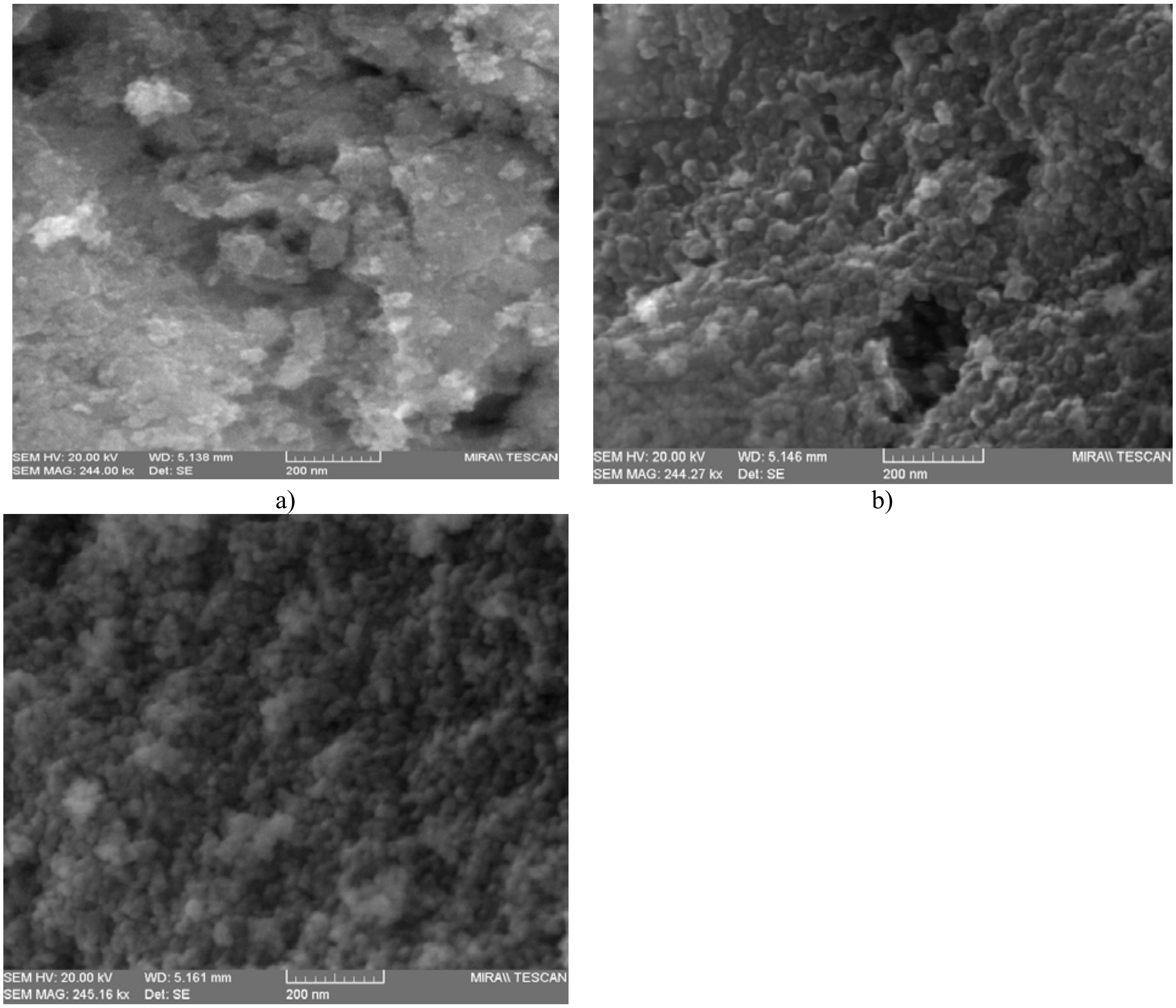
The FT-IR spectra of the as-prepared $CoFe_2O_4$ show a board bands at 3426 cm^{-1} which are assigned to the streaching vibrations of the free and absorbed water on the surface of nanoparticles. The C-H streatching bands observed at 2928 and 2867 cm^{-1} confirm the presence of CMC on the surface of as-prepared $CoFe_2O_4$ nanoparticles. The bands at 1624 and 1398 cm^{-1} are assigned to keto(C=O) streatching vibration from CMC and bending vibration from the absorbed water.

Two strong bands are observed around of 585 and around 450 cm^{-1} for all $CoFe_2O_4$ samples. These two vibrations bands are corresponded to the intrinsec lattice vibrations of octahedral and tetrahedral coordination compounds in the spinel structure, respectively [25]. The different frequency between the characteristic vibrations (ν_1 and ν_2) may be attributed to the long band length of oxygen-metals ions in the octahedral sites and shorter band length of oxygen-metals ions in the tetrahedral sites [24].

For $CoFe_2O_4$ heated at 300 and 500 ºC the skeleton bands are present at 446 and 584 cm^{-1}. The careful observation in the range 1300-400 cm^{-1} shows that the intensity of the octahedral sites decreases and that of the tetrahedral increases during the heat treatment. This shows that during the heat treatment cations migrate from octahedral site to the tetrahedral site in the inverse spinel structure of the cobalt ferrite nanoparticles. This observation is also supported by the DTG exothermic peaks observed between 260 and 400 ºC.

3.3. SEM

The morphology of the ferrite powders was investigated by SEM. In the Fig. 3 are presented the SEM micrographs which show that the morphology of the materials is affected by the annealed temperature.



a) b)

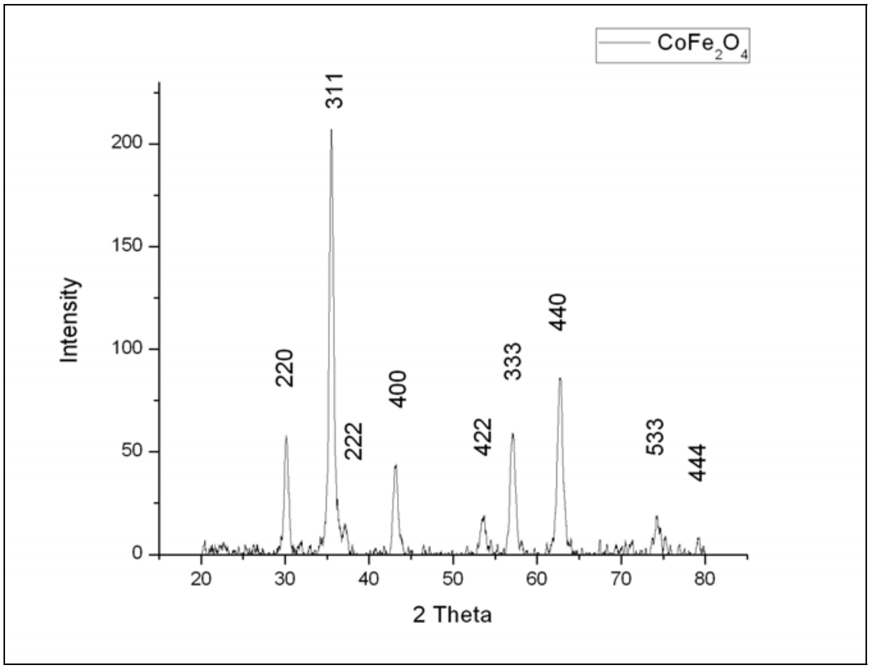
c)

Fig. 3. SEM micrographs of the $CoFe_2O_4$ nanoparticles:
a) as-prepared, b) annealed at 300 ºC, c), d) annealed at 500 ºC.

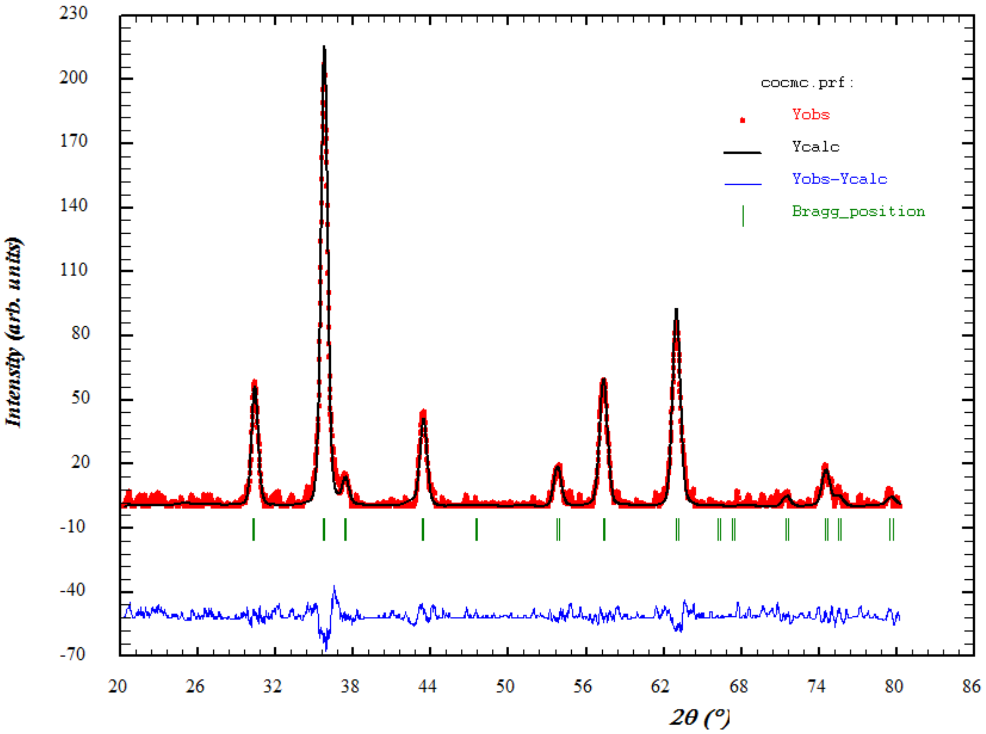
Regardless of their chemical composition, the ferrite nanoparticles are well-separated and quasi-spherical, suggesting that their surfaces are passived with a monolayer of organic molecules. These are confirmed by FT-IR spectra also. The average diameter calculated by counting 300 nanoparticles was found to be 13 nm. The average size obtained from SEM observation is in good agreement with the crystallite size calculated by the Debye-Scherrer formula from the broadering of the XRD patterns, indicates that the nanoparticle are single cristaline.

3.4. Crystal structure of $CoFe_2O_4$ nanoparticles

The XRD profiles of the $CoFe_2O_4$ ferrite nanoparticles precipitate in CMC solution under air are shown in Fig.4.



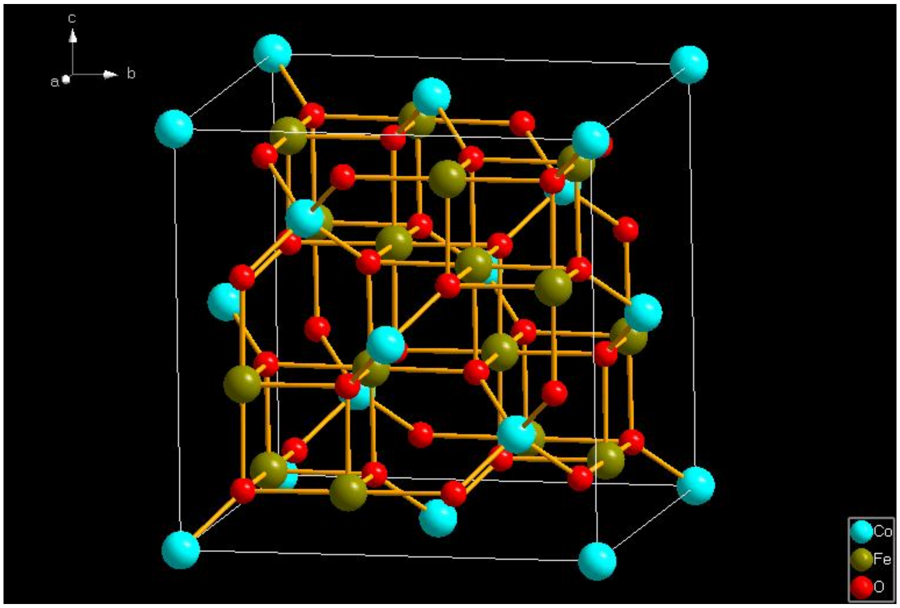
a)



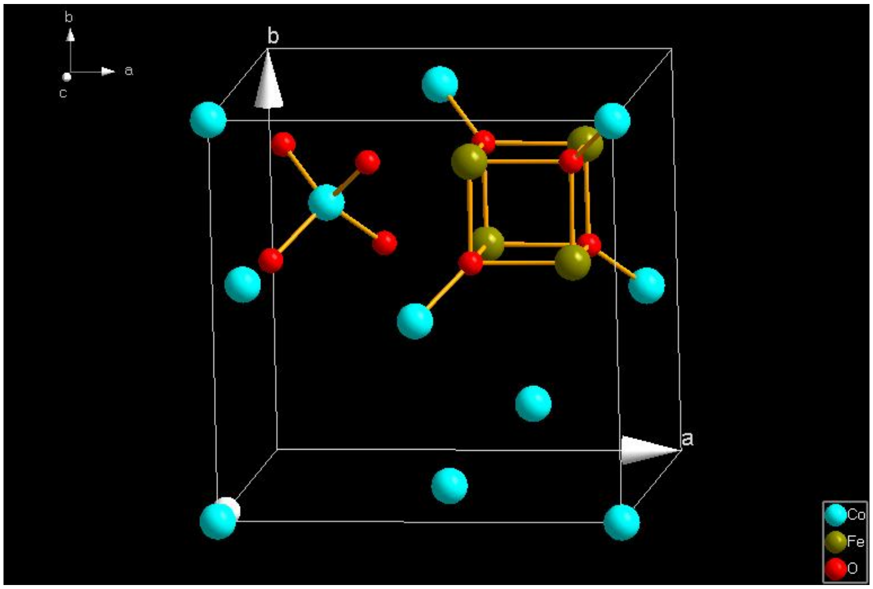
b)

Fig. 4. a) XRD diffraction pattern of $CoFe_2O_4$ annealed at 500°C;
b) XRD diffraction pattern of $CoFe_2O_4$ (calculated and observed) annealed at 500°C

Figure 4.a shows the x-ray diffraction patterns of the cobalt ferrite annealed at 500°C. The intensities and positions of the diffraction peaks in each phase correspond to the $CoFe_2O_4$ pure compounds and there are not extra diffraction peaks associated with the formation of any other phase during the processing. The x-ray diffraction patterns of $CoFe_2O_4$ samples (Fig. 4.b) at room temperature have been analyzed by the refinement method using FULLPROF program. The corresponding refined values of the lattice parameters are following a = 8.34628 Å, b = 8.34628 Å, c = 8.34628 Å, alpha = 90.000, beta = 90.000, gamma = 90.000, Direct Cell Volume = 581.41 Å^3. The patterns show Bragg reflection characteristics to the spinel structure (space group FD-3M) with relatively broad peaks due size of the crystalline domains. The XRD were indexed in the cubic system. Structure of $CoFe_2O_4$ is presented in Fig. 5.



a)



b)

Fig. 5. Structure of $CoFe_2O_4$: a) elementally cell; b) coordination of metallic ions.

The values of the lattice parameters refined with de FullProf program are in good agreement with those of the bulk compound confirming that the annealing of the stoechiometric mixture of transition metal cloride in CMC solution lead to the stabilization of spinel-type structure. The average crystallite size of nanoparticles for the most intense peaks (220,311,400) was determined from the XRD using Debye-Scherrer formula: D= kλ / B cos Θ , where D is particle size, k is constant, λ for Cu is 1.54Å, B is full half wide and 2theta = 4degree [23].

3.5. Magnetic properties of the $CoFe_2O_4$ nanoparticles.

The magnetic properties of the ferrite annealed at 500°C were investigated by the VSM technique at the room temperature (20°C) under an applied field of >10 KOe. The field dependence of specific magnetization of $CoFe_2O_4$ nanoparticles is presented in Fig. 6.

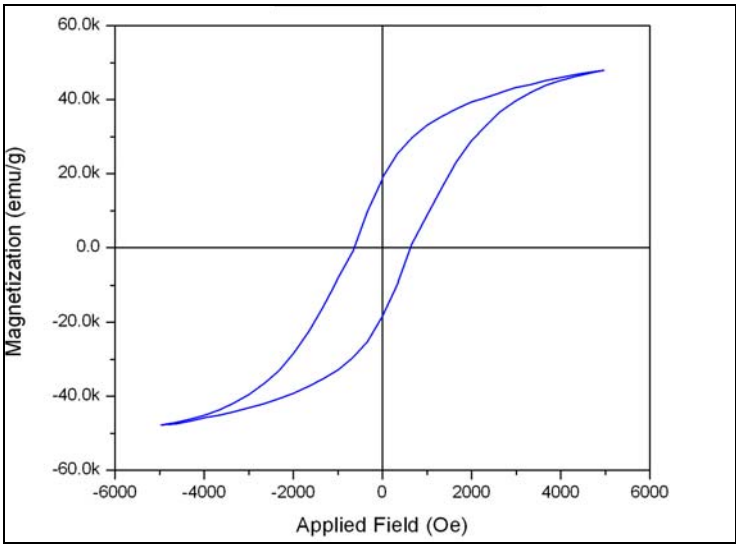


Fig. 6. Magnetic properties of the $CoFe_2O_4$ nanoparticles annealed at 500 C

The annealed $CoFe_2O_4$ nanoparticles have a magnetization value Ms = 52.2 (emu/g) obtained with 6 KOe magnetic field and the coercivity Hc = 634.7 Oe at room temperature. The hysteresis loops of the samples measured at room temperature show ferromagnetic behavior of sample. The saturation magnetization and coercivity are dependent of the annealed temperature and particle size [26]. The magnetic saturation values of the sample are around 52.2 emu g^{-1}, which is smaller than the corresponding counterpart material. Comparing this value with the researches, the lower value observed in our study should be a result of the pining of the surface spins and existence of surfactant on the surface of $CoFe_2O_4$ nanoparticles [27].

4. Conclusion

The studies show that by using CMC as a surfactant, nanoparticles of $CoFe_2O_4$ with small particle (13 nm) can be obtained. The XRD diffractions pattern confirms the purity phase of the nanocrystalite $CoFe_2O_4$. From VSM analysis we can conclude that the nanoparticles surface is activated with OH and C-O groups, that originate from the surfactant, which leads to a high coercitive field.

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