MICROSTRUCTURAL CHARACTERIZATION OF CO-DOPED IRON OXIDE NANOPARTICLES

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Aqueous suspensions of cobalt doped ferrites ($Co_xFe_{3-x}O_4$, x=0; 0.25; 0.5; 0.75; 1) nanoparticles synthesized by chemical co-precipitation were investigated by microstructural and liquid state methods: Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), capillary tension and dynamic viscosity coefficient measurements respectively, to reveal particle size and composition. The content of cobalt influence on doping the particle size in the studied samples was emphasized. The morphology of $Co_xFe_{3-x}O_4$ particles, studied by SEM indicated mostly regular quasi-spherical shape while EDX analysis was focused on Co incorporation. The ferrophase variable content appears to have no significant influence on the rheological properties of the corresponding nanoparticle suspensions.

Keywords: cobalt doped ferrites, nanoparticles, granularity, suspension properties

1. Introduction

The study of cobalt ferrite nanopowders is subjected to a continually increasing attention due to various applications in engineering and biomedical science [1-4]. The large scale of uses of ferrites, from permanent magnets, ferrofluids, storage devices, targeted drug delivery etc. makes them a subject of intensive experimental investigations, in order to better control and properly tailoring the magneto-granulometric properties.

Co doped nano-ferrites are of particular interest due to the large anisotropy, moderate magnetization, chemical stability and high Currie temperature. These special properties are most usefully in medical sciences for experimental cancer treatment by tumor hyperthermia [5]. In the case of $Co_xFe_{3-x}O_4$, magnetic properties vary as function of the cobalt concentration. However, not only chemical composition is important for the overall properties of the final

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powder substance. It is well known that magnetic properties are also dependent on the size, morphology and purity of the particles. Studies on nanocrystals from the perspective of the effect produced by the precursors of nanomaterial synthesis on magnetic properties, shape, and morphology characteristics to these nanomaterials were presented in [6-8]. Synthesis of cube-shaped $Co_xFe_{3-x}O_4$ nanocrystals which could be finely tuned in terms of nanometric size (from 15 to 27 nm) with high specific absorption rate values as well as cobalt stoichiometry realization (from 0.1 to 0.7) are reported in [9]. As inverse spinel structure is characteristic both for magnetite and cobalt-ferrite, intermediate $Co_xFe_{3-x}O_4$ nanocrystals are supposed to be similar in this respect as reported for such powders yielded by co-precipitation method [10], based on X-ray diffraction investigation, that showed no supplementary crystallization phase. However when ceramic method was applied by other authors [11] unexpected oxidization of magnetite was detected for several *x* values, that appears to be responsible for the difference between target stoichiomery of those cobalt ferrites compared to actual ones.

Cobalt ferrite is also a suitable dispersible phase for magneto-sensitive systems. A fast change in the rheological properties of such suspensions in response to a magnetic field offers the possibility to use such nanofluid in various medical applications. The influence of the annealing temperature on the structure, magnetic properties, and magnetorheological effect was investigated in [12].

In this paper, we present the preparation of $Co_xFe_{3-x}O_4$ nanoparticles in stable suspensions for increasing ratio of doping Co ions. The influence of the Co levels on the physical microstructure and the rheological properties of the samples were investigated.

2. Preparation of Cobalt ferrites ($Co_xFe_{3-x}O_4$)

Cobalt ferrite ($Co_xFe_{3-x}O_4$) is a cubic ferrite with a spinelic inverse structure where the Co cations occupy part of the octahedral coordination sites [6]. The cobalt ferrite nanoparticles were yielded by us by chemical route based on Massart's method, known as highly versatile, low cost and availability [13]. Iron source were hydrated crystalline powders of ferric chloride and ferrous sulfate while cobalt ions were provided by cobalt sulfate - all purchased as high purity reagents from Sigma-Aldrich and used without further purification. Progressive cobalt doping for each sample and the quantity of each component used for preparation of cobalt ferrites are presented in Table 1.

Table 1

Synthetic illustration of precursor salts used for the preparation of cobalt doped ferrites stabilized with citric acid in aqueous suspensions

Sample	*x*	Ferric Chloride (g)	Cobalt Sulfate (g)	Ferrous Sulfate (g)	Sodium Hydroxide (g)	Citric Acid (g)
P1	0.00	3.62	-	1.86	3.4	1.7
P2	0.25	3.62	0.47g	1.40	3.4	1.7
P3	0.50	3.62	0.94	0.93	3.4	1.7
P4	0.75	3.62	1.41	0.47	3.4	1.7
P5	1.00	3.62	1.88	-	3.4	1.7

Alkali synthesis medium was ensured based on hot 24% sodium hydroxide pouring under continuous stirring while stabilization of nanoparticles in aqueous suspension was accomplished with citric acid as capping agent (5 g citric acid in 10 ml deionized water for each about 4 g of ferrophase sample).

3. Investigation methods

Microstructural and elemental analyses were carried out using Scanning Electron Microscope **(**Quanta 200**)** provided with EDX module at "Petru Poni" Institute of Macromolecular Chemistry in Iasi.

Dynamic viscosity coefficient versus distilled water as reference liquid (at 295 K; water dynamic viscosity: 1.020×10^{-3} N·m^{-2}·s; water density: 0.9982 g·cm^{-3}) was measured with an Ubbelohde device.

ROHR B type stalagmometer was used to measure surface tension using as reference liquid also the distilled water (water surface tension – 71.97×10^{-3} N·m^{-1} at 295 K).

The density was determined by gravimetric method with an accuracy of 0.0001 g using an ADAM PW254 analytical type balance.

Rheological measurements were repeated ten folds for each parameter in the same environmental conditions for each of the analyzed nanoparticle suspensions. Average values and standard deviations were taken into account for result discussion.

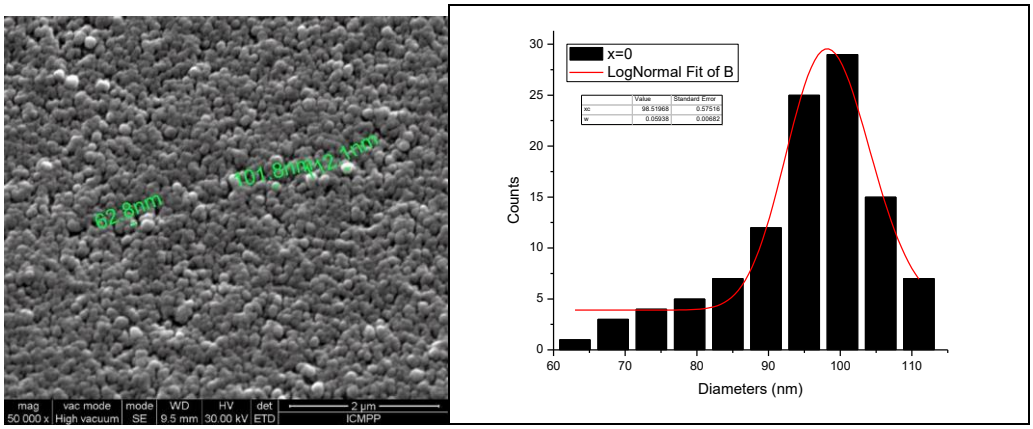
The SEM recorded images were analyzed with using ImageJ1 1.50b software. The mean particle diameter and the size distribution for each sample were obtained from statistical analysis.

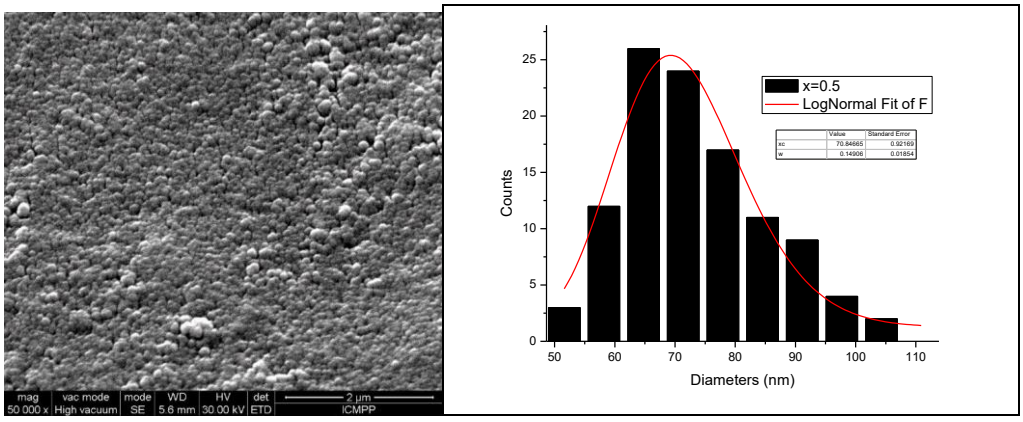
4. Results and discussion

The results of the microstructural and rheological analysis carried out on the samples of cobalt doped ferrites $Co_xFe_{3-x}O_4$ with different Co content are presented in the following.

Figure 1 shows the SEM images of the nanoparticles ferrites for the prepared samples with the specific fractions of cobalt doping: x = 0; 0.25; 0.5; 0.75; 1. As could be noticed from all images, the particle shape is characterized mainly by typical quasi-spherical geometry.

Most of the particle sizes ranges between 50 nm and 110 nm, however, SEM images show also a low percentage of smaller particles and the presence of rare conglomerates – that were excluded from our statistics.





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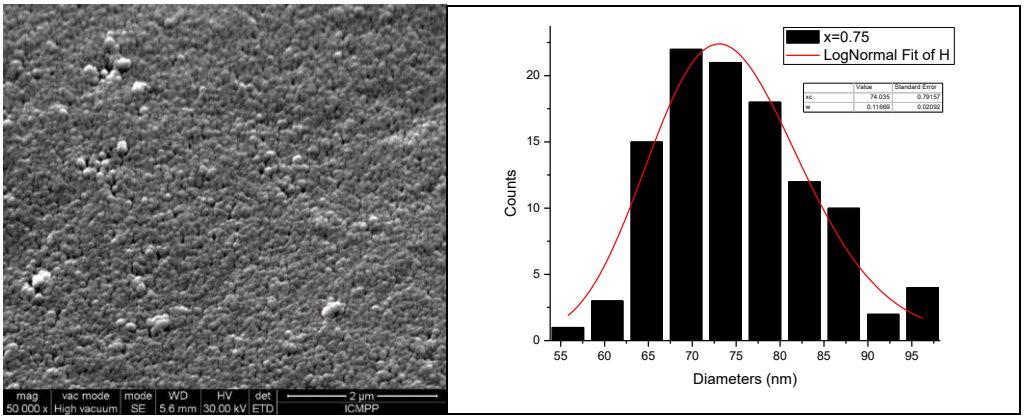

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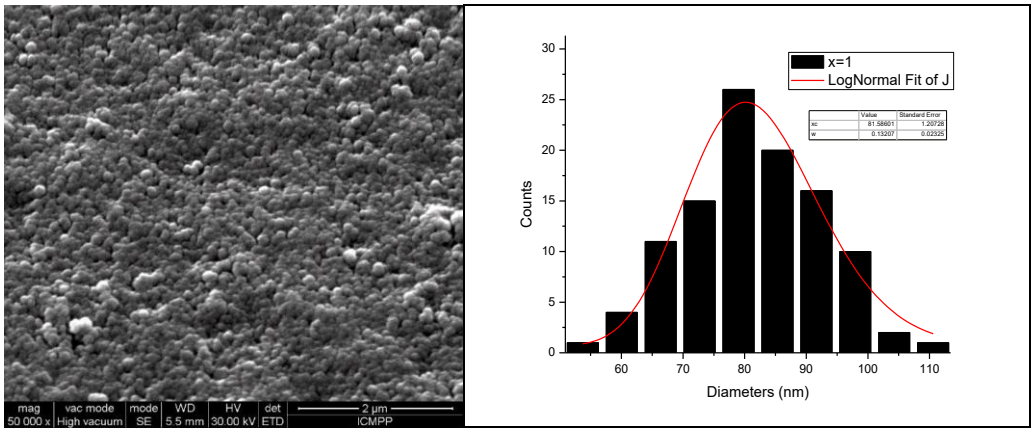


i j

Fig.1 SEM of cobalt ferrites $Co_xFe_{3-x}O_4$, (a, b) x=0; (c, d): x= 0.25; (e, f): x=0.5; (g, h): x=0.75; (i, j): x=1 and the corresponding histograms of particle diameters

Detailed information on the particle size distribution is provided by the histograms placed next to each corresponding SEM image. One should take into account that SEM microscopy provides generally higher diameters than other imaging methods.

The distributions of the particle size (i.e. diameter D) are fitted by log-normal functions (solid lines drawn on each histogram). This function is known to properly describe the particle size distribution in ferrofluids [14,15]

$$f(D) = \frac{1}{\sqrt{2\pi}SD} \exp\left[-\left[\ln(D) - \ln(D_0)\right]^2 / (2S^2)\right] \qquad (1)$$

where D_0 is defined by $\ln(D_0)$ as the mean value of $f(D)$ while S is the mean deviation of $f(D)$ from its mean value.

The mean particle diameter D_m is computed using the relation:

$$D_m = D_0 \exp\left(S^2/2\right). \qquad (2)$$

The relevant parameters of the fitting are written inside each particular graph.

Fig. 2 shows the average values of nanoparticle diameter for each cobalt doping level.

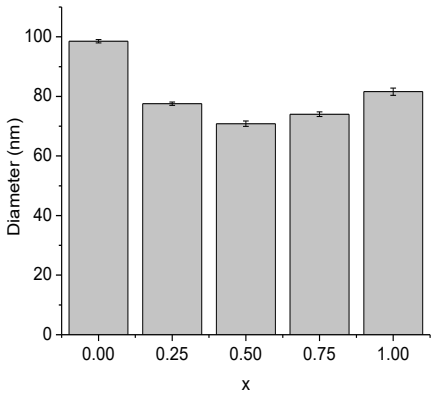


Fig. 2 Values of nanoparticle mean diameters for each sample characterized by the value of the cobalt doping parameter, x

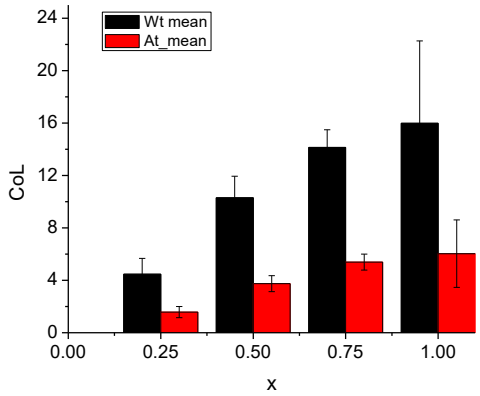
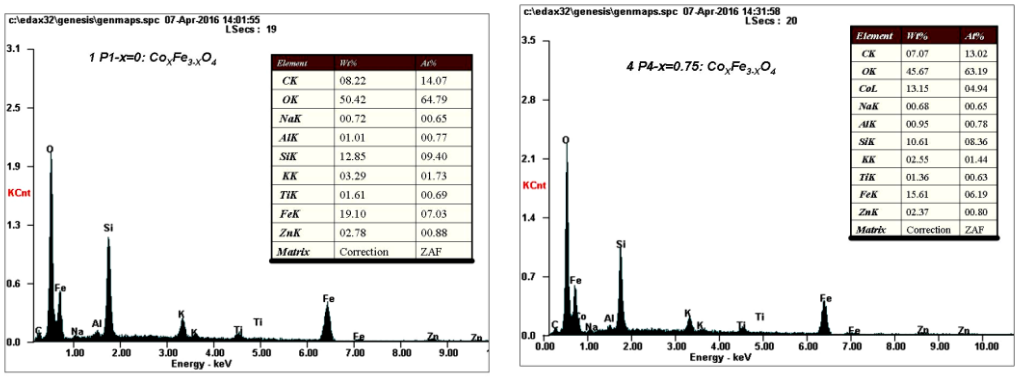


Fig. 3 Quantitative result of the mean values for atomic percentage (At_mean) and for weight percentage (Wt_mean) of cobalt (CoL) versus x

The particle size is smaller when cobalt is incorporated but it is not mathematically correlated with the cobalt content. An optimum value around 70 nm for the physical diameter is obtained for an intermediate concentration of cobalt. Previous analysis (published as preliminary results [16]) showed smaller grains dimensions (suggested by TEM - known as the most accurate imaging method for nanoparticles since no covering shell is involved in sample

preparation). It was also found that magnetic properties were not linearly dependent on Co content. As reported by other authors, the highest values of magnetic anisotropy were revealed for intermediate Co content [17].



(a) (b)

Fig. 4 Illustration of EDX results of $Co_xFe_{3-x}O_4$ (a) x=0; (b) x= 0.75

EDX analysis allows the qualitative and quantitative identification of the elements in the samples emphasizing the progressive increase of cobalt ion concentrations. The results presented in Fig. 3 correspond to the average of the values given by the elemental analysis repeated five times for each sample. As shown in Fig. 3, the percentage of the proposed target levels of cobalt ions in the ferrite composition seems to be reached; this is based on the mean values of atomic percentage (At_mean) and weight percentage (Wt_mean), after removing the contributions of elements from the sample substrate. As illustration of EDX elemental analysis we present two examples in Fig. 4. However, the stoichiometry of cobalt ferrite samples - in the limits of evidenced standard errors for cobalt levels is subject of discussion since in co-precipitation method oxidization of magnetite could not be avoided totally so that haematite could partially be yielded affecting target stoichiometry as in the case of already mentioned literature [17].

In this context we have to mention that in literature it is specified that oxygen detection by EDX is not sufficiently accurate [11]. New analyses are needed to explain in detail the structure of the presented cobalt ferrite samples.

In order to characterize the rheological properties of cobalt ferrites suspension that makes them potentially good candidates in biomedical applications, we performed the measurements of viscosity and surface tension (Table 2).

Table 2

Rheological properties of cobalt ferrite nanoparticle suspensions

Co content (%)	0.00	0.25	0.50	0.75	1.00
Dynamic viscosity (*10^{-3}) $Nm^{-2}s$	2.09	2.11	2.02	2.40	2.29
Surface tension (*10^{-3}) Nm^{-1}	0.74	0.85	0.74	0.85	0.73

We found the values of dynamic viscosity around 2.18×10^{-3} $N\cdot s\cdot m^{-2}$ with a standard deviation of about 6.4% for all nanoparticle suspensions. This means that no dependence on the ferrophase composition could be revealed by this suspension parameter. The measured values of surface tension have slightly higher values than the reference liquid in all investigated suspensions: $0.78\times10^{-3}N\cdot m^{-1}$ with a standard deviation of about 6.1%. Since the density of nanoparticle suspensions was found of about 1.007 g cm^{-3} for the cobalt doped ferrite suspensions (standard deviation of 9%), the ferrophase variable content appeared to have no influence on the rheological properties of the corresponding nanoparticle suspensions.

5. Conclusions

We reported the synthesis and characterization of four cobalt ferrites $Co_xFe_{3-x}O_4$ with different Co doping levels (x=0; 0.25; 0.5; 0.75; 1).

The studied cobalt ferrites nanoparticles have generally typical spherical shapes and average particle size of 70 nm as resulted from SEM data. The particles physical diameter does not follow a mathematical dependence on the cobalt content, the smallest value being obtained for an intermediate cobalt doping sample. The content of cobalt ions was proved to be close to the target compositions accordingly to EDX data. Liquid state analyses showed very similar properties of nanoparticle suspensions from the viewpoint of dynamic viscosity and surface tension.

Further study of cobalt influence on the physical characteristics of such nanoparticle suspensions is planned aiming to reveal possible differential features related to their utilization in experimental tumor therapy by hyperthermia.

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R E F E R E N C E S

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