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Short communication

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# Microwave absorbent properties of nanosized cobalt ferrite powders prepared by coprecipitation and subjected to different thermal treatments

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## Abstract

Cobalt ferrite nanopowders were produced by means of two methods using a common precipitating agent. After precipitation, in the first method the cobalt ferrite was calcined, whilst in the second method the precipitation was followed by a hydrothermal treatment. Characterization of the obtained powders was achieved by X-ray diffraction and scanning electron microscopy / energy dispersive X-ray analysis. Frequency dependence of the complex dielectric permittivity and complex magnetic permeability, over the frequency range 0.1 GHz to 6 GHz, was also studied. By means of the above mentioned investigations, the structure, morphology and microwave absorbent properties of the powders obtained by both methods were compared.

## Keywords:

C. Nano materials; E. Electrical; E. Magnetic.

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## 1. Introduction

Two ferrite nanoparticle systems were investigated, both from a fundamental point of view and as promising materials to be used in various applications. Currently, due to the multiple applications of microwaves, the problem of electromagnetic interference has become a matter of serious concern. Consequently, there is increasing demand for the development of microwave absorbers. For instance, in Refs. [1-4] various ferrite nanoparticle systems were analyzed from the microwave absorbent properties point of view.

Cobalt ferrite is a part of the spinel ferrite group; it has cubic magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient [5, 6] and has been proven to have photomagnetic properties [7].

Different synthesis methods, such as coprecipitation [8], electrochemical [9], hydrothermal [10], combustion [11] or mechanical alloying [12] are used to produce cobalt ferrite. Among the reported methods, the coprecipitation method is an efficient and economical way to mass production of ultrafine cobalt ferrite powder.

In Ref. [13] it is shown that cobalt ferrite particles obtained by precipitation from an aqueous solution can crystallize in the normal spinel form, whilst in Ref. [14] it is reported that cobalt ferrite has mixed spinel structure (both normal and inverse spinel). Changes in the cation distribution over the tetrahedral and octahedral sites lead to changes in the magnetic properties of the ferrite, even if the ratios of the constituent ions of the ferrite do not change. Since the structure of cobalt ferrite depends on the preparation conditions, its magnetic properties should also depend on these conditions.

From an economical point of view, it is important to obtain materials as fast as possible, with low energy consumption and with the best possible properties. In this paper we analyze cobalt ferrite nanopowders obtained by two synthesis methods. Both methods have a common coprecipitation stage. After precipitation, in the first method the cobalt ferrite was calcined, whilst in the second method the precipitation was followed by a hydrothermal treatment. The calcination and hydrothermal treatments were made at the same temperature and over the same time period. The objective of this work is to compare the structure and microwave absorbent properties of cobalt ferrite nanopowders obtained by the coprecipitation-calcination method (CC method) and by the

coprecipitation-hydrothermal treatment method (CHT method). This paper reports, for the first time, on such a comparative study, underlining the benefits of the hydrothermal treatment on the microwave absorbent properties of cobalt ferrite nanopowders as opposed to the usual coprecipitation – calcination method.

## 2. Preparation methods

With both methods the same starting raw materials have been used in order to obtain  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$  powder (i.e. ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in a molar ratio of 2.2:0.8, with 5M NaOH aqueous solution as precipitation agent). In the CC method, the reactants solution was mixed under continuous stirring for two hours, at a temperature of 80-90°C. The precipitation was made in an alkaline medium, using a 5M NaOH aqueous solution, at a pH value of 11. After decantation and filtration, the obtained precipitate was washed with water and alcohol on a filter paper and then laid out to dry in an air oven, at 105°C. The obtained powder was then annealed at 200°C for 4 hours. The sample was denoted by sample A.

In the CHT method, the precipitation was made as in the CC method and then the colloidal suspension was transferred to a Teflon-lined stainless steel autoclave and tightly sealed. The autoclave was introduced in an air oven and maintained at 200°C for 4 hours. After decantation and filtration, the obtained precipitate was washed and dried as in the case of the CC method. The sample was denoted by sample B.

## 3. Structural characterization of the samples

The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy- energy dispersive X-ray analysis (SEM-EDAX). The XRD patterns for the investigated samples are presented in figure 1.

The X-ray diffraction pattern of the cobalt ferrite obtained by the CC method confirms a very poorly crystalline ferrite phase, as the XRD peaks are weak and broad. In the case of the cobalt ferrite obtained by the CHT method, the diffraction pattern indicates a higher degree of crystallinity of the sample, displaying the characteristic XRD peaks of the cobalt ferrite spinel as reported in the literature [15].

Fig.1. X-ray diffraction patterns of cobalt ferrite nanopowders obtained by the CC and CHT methods

The average crystallite size,  $D$ , of the cobalt ferrite powder in sample B was calculated from the diffraction peak of the [311] plane using the Debye-Scherrer formula [15]:

$$D = \frac{0.89\lambda}{\beta \cos(\theta)} \quad (1)$$

where  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum of the main diffraction peak expressed in radian, and  $\theta$  is the Bragg angle. In our case, for Cu-K $\alpha$  radiation,  $\lambda=0.15418$  nm, the computed  $D$  value was found to be 26 nm.

a) b)

Fig.2. SEM image of sample A (a) and of sample B (b)

a) b)

Fig.3. EDAX quantification of sample A (a) and of sample B (b)

The morphology of the ferrite powders was observed by Scanning Electron Microscopy (SEM) and is presented in figure 2. The SEM image of sample A (figure 2(a)) shows large particle agglomerations (with mean diameter in the order of 600 nm), whilst the SEM image of sample B (figure 2(b)) shows that the sample consists of smaller particles, with a mean diameter of 28 nm. Based on the XRD patterns and on the SEM images of the samples, one can assert that the CC method leads to the formation of large

clusters having a small degree of crystallinity, whilst the CHT method leads to the formation of clusters consisting of crystalline domains.

The compositional analysis of the samples was determined by EDAX (figure 3). Assuming that the obtained powder consists of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  type molecules, the atomic fraction Co/Fe is given by,  $x/(3-x)$ . From the EDAX quantification of the samples, the atomic fraction Co/Fe, (denoted by *At-ratio*), was determined. Solving the equation,

$At-ratio = x/(3-x)$ , one gets a cobalt content of,  $x_A=0.886$  (for sample A) and  $x_B=0.884$  (for sample B). These values obtained for the cobalt content are larger than would be expected (for the molar fraction of cobalt in the mixture of the raw materials,  $x=0.8$ ). Bearing in mind the 5% measurement error in the EDAX quantification, as given by the apparatus manufacturer (FEI Company), the difference between the intended atomic fraction ( $x=0.8$ ) and the values obtained by EDAX ( $x_A=0.886$  and  $x_B=0.884$ ) lead to the conclusion that a small portion of the Co atoms are not chemically bounded in  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$  type molecules. On the other hand, the EDAX quantification can be influenced by the surface crystalline defects of nanoparticles. This can also be taken into account to explain the difference between the values of the atomic ratio as determined by EDAX and the expected value.

A similar result was reported in Ref. [16] for cobalt ferrite obtained by coprecipitation.

#### 4. Microwave absorbent properties

The complex temporal expressions of the electric and magnetic components of an electromagnetic plane-wave propagating through a medium on the  $oz$  axis are given by [17]:

$$\vec{E} = \vec{e}_x E_0 e^{-\alpha z} e^{j(\omega t - \beta z)} \quad (2)$$

$$\vec{H} = \vec{e}_y \frac{E_0}{Z_m} e^{-\alpha z} e^{j(\omega t - \beta z)} \quad (3)$$

where  $\vec{e}_x$  and  $\vec{e}_y$  are the unit vectors on the  $ox$  and  $oy$  axes,  $E_0$  is the amplitude of the electric component of the electromagnetic wave at  $z=0$  (where the propagation through the medium is assumed to begin),  $\omega$  is the angular frequency of the electromagnetic wave and  $j = \sqrt{-1}$ . The parameters  $\alpha$ ,  $\beta$  and  $Z_m$  are respectively the attenuation constant, the phase constant and the intrinsic impedance of the propagation medium and they depend on the effective complex dielectric permittivity,  $\epsilon_{r,eff} = \epsilon' - j\left(\frac{\sigma}{\omega\epsilon_0} + \epsilon''\right) = \epsilon' - j\epsilon''_{eff}$  and on the complex magnetic permeability,  $\mu_r = \mu' - j\mu''$  of the propagation medium as given by Eqs. (4), (5) and (6) [18].

$$\alpha = \pi f \sqrt{\mu_0 \epsilon_0} \sqrt{2 \left[ \sqrt{(\mu'^2 + \mu''^2)(\epsilon'^2 + \epsilon''_{eff}{}^2)} - (\mu' \epsilon' - \mu'' \epsilon''_{eff}) \right]} \quad (4)$$

$$\beta = \pi f \sqrt{\mu_0 \epsilon_0} \sqrt{2 \left[ \sqrt{(\mu'^2 + \mu''^2)(\epsilon'^2 + \epsilon''_{eff}{}^2)} + (\mu' \epsilon' - \mu'' \epsilon''_{eff}) \right]} \quad (5)$$

$$Z_m = \sqrt{\frac{\mu_0}{\epsilon_0}} \sqrt{\frac{\mu_r}{\epsilon_{r,eff}}} \quad (6)$$

In the above equations,  $f$  is the frequency of the electromagnetic wave,  $\mu_0$  and  $\epsilon_0$  are the magnetic permeability and the dielectric permittivity of free space,  $\mu'$  and  $\mu''$  are the real and the imaginary parts of the complex magnetic permeability, whilst  $\epsilon'$  and  $\epsilon''$  are the real and the imaginary parts of the complex magnetic permittivity of the propagation medium. Also,  $\epsilon''_{eff} = \epsilon'' + \frac{\sigma}{\omega\epsilon_0}$  is the imaginary part of the effective

complex dielectric permittivity of the propagation medium, including the conductivity,  $\sigma$ . The reflection coefficient,  $R$ , of the electromagnetic wave at the interface between two propagation media, for normal incidence, is given by equation (7) [18]. In Eq. (7) it is assumed that the electromagnetic wave comes from medium 1 and reflects on the surface of the medium 2.

$$R = \frac{|Z_{m2} - Z_{m1}|}{|Z_{m2} + Z_{m1}|} \quad (7)$$

Here  $Z_{m1}$  is the intrinsic impedance of medium 1 and  $Z_{m2}$  is the intrinsic impedance of medium 2.

The absorbent properties of the propagation medium are mainly given by the attenuation constant,  $\alpha$  (see Eqs. (2) and (3)) and by the reflection coefficient  $R$ . In order to determine these parameters, the frequency dependence of the complex magnetic permeability and of the effective complex dielectric permittivity of the two samples were measured, over the frequency range 0.1 – 6 GHz. Measurements were carried out by means of the coaxial line technique [19]. A Hewlett-Packard 50  $\Omega$  coaxial line incorporating a coaxial cell with 3 mm inner diameter and 7 mm outer diameter was used in conjunction with a HP 8753C network analyzer. The samples were placed in the coaxial cell and standard HP open-circuit (O/C) and short-circuit (S/C) test devices were used as terminations. The instruments, operating in the one-port mode, automatically measure the S11 scattering parameter and convert the S11 measurements to the complex components of the load impedance. The input impedance of the line was measured for the O/C and S/C cases. Using the complex components of the load impedance, the complex permeability and complex permittivity are determined as detailed in Ref. [19]. The results are given in figures 4 and 5.

As can be observed from figure 4, the real part of the complex magnetic permeability,  $\mu'$ , of sample B is larger than that of sample A, a fact which can be correlated to the high degree of crystallinity of the cobalt ferrite powder obtained by the CHT method (see XRD patterns). Both samples exhibit more than one maximum in the imaginary part of the complex magnetic permeability,  $\mu''$ . This result may be due to the size dispersion and clusterization of the crystalline grains and to the possible presence of oxides other than  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ .

The cations of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  at their respective positions in the spinel structure form electric dipoles with the surrounding  $\text{O}^{2-}$  ions, contributing to the complex dielectric permittivity within a grain. Interfacial polarization and hopping electron relaxation can also contribute to the complex dielectric permittivity in both samples, because both



samples are powders. As a result, the frequency dependence of the  $\epsilon''$  component of the complex dielectric permittivity may display more than one peak, as can be observed from figure 5.

Fig.4. Frequency dependence of the complex magnetic permeability of samples A (CC method) and B (CHT method)

Fig.5. Frequency dependence of the complex dielectric permittivity of samples A (CC method) and B (CHT method)

Based on the measured frequency dependence of the complex magnetic permeability and the complex dielectric permittivity, the attenuation constant,  $\alpha$  and the reflection coefficient  $R$  were computed by means of Eqs. (4), (6) and (7), where medium 1 was considered to be air and medium 2 was the investigated samples. The results are presented in figures 6 and 7.

Fig.6. Frequency dependence of the attenuation constant of samples A and B

Fig.7. Frequency dependence of the reflection coefficient of samples A and B

From figure 6 one can observe that the attenuation constant of sample B is larger than that of sample A, for frequencies up to 2.7 GHz. For higher frequencies, the reverse is the case. For both samples, the frequency dependence of  $\alpha$  displays two local peaks, correlated to the  $\mu''$  and  $\epsilon''$  frequency dependence profile.

From figure 7 it is obvious that the wave reflection at the air – sample interface is more pronounced in the case of sample A, over the investigated frequency range.

A good absorbing material must have at least two characteristics [20]: 1) ideally no reflections at the interface air- absorbing material and 2) the electromagnetic wave

must get rapidly attenuated through the material layer. From this point of view, sample B is a better absorbing material than sample A in the frequency range 0.1 – 2.7 GHz, where its reflection coefficient,  $R$ , is smaller and  $\alpha$  is larger than that of sample A.

For frequencies larger than 2.7 GHz, the attenuation constant and reflection coefficient of sample A are both larger than those of sample B. Here only a double layer absorber (in a structure of air-sample B-sample A) may be considered as an absorbing structure.

## 5. Conclusions

Cobalt ferrite nanopowders were obtained by the coprecipitation-calcination (CC) method (sample A) and by the coprecipitation-hydrothermal treatment (CHT) method (sample B).

The XRD patterns have clearly shown that the sample obtained by the CHT treatment method has a higher degree of crystallinity than the sample obtained by the CC method, which has a rather amorphous structure.

EDAX analysis has revealed that the samples A and B have the same proportion of cobalt ( $x=0.88$ ), which is different from the molar fraction of cobalt in the mixture of the raw materials ( $x=0.8$ ), leading to the possible conclusion that a small part of the Co atoms are not chemically bounded in the intended  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$  type molecules.

Over the frequency range 0.1 to 6 GHz, the sample obtained by the CC method (sample A) has a smaller attenuation constant than that of the sample obtained by the CHT method (sample B), up to an approximate frequency of 2.7 GHz. This, correlated with the higher reflective characteristics of sample A, in comparison with those of sample B, makes sample B a better absorbent over this frequency range. In the approximate range of 2.7 to 6 GHz, the absorption is more pronounced in sample A than in the sample B but the reflection coefficient of sample B remains smaller than of sample A.

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