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# Remanence of the interparticle interactions and its influence on the microwave absorption in Co-ferrite

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**Abstract**

Cobalt ferrite nanoparticles were obtained by the sol–gel method at several annealing temperatures: 400, 450, 500, 550 and 600 °C. X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed the formation of the spinel phase with a nanoparticle size in the 17–26 nm range as function of the annealing temperature. The Mössbauer spectra at room temperature showed the presence of a partial inverse spinel structure. Saturation magnetization and the coercive field are strongly dependent on the annealing temperature and they can be associated with variations of the nanoparticles size. Microwave power absorption (MPA) ($dP/dH$) measurements were carried out as a function of DC field ($H_{DC}$) in asymmetric sweeps in the $0\,\text{kOe} \leqslant H_{DC} \leqslant 9\,\text{kOe}$ range, at X-band (9.4 GHz), for all annealing temperatures. The large hysteresis in the MPA is due to interparticle interaction associated with its demagnetizing-like nature.


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*Keywords:* Henkel plot; Microwave absorption; Cobalt ferrite

## 1. Introduction

In recent years, the metal oxide nanoparticles have been a subject of intense research due to their applications in several technological fields: magnetic fluids, microwave devices, and high-density information storage systems [1,2]. Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material with a high coercivity and moderate magnetization. In soft-ferrites, a microwave power absorption (MPA) signal around zero field has been previously observed [3,4], and it is clearly distinct to ferromagnetic resonance (FMR), since it shows hysteresis and is very far from the Larmor conditions. Recently, we published a preliminary study on the MPA in nanoparticles of cobalt ferrite as a function of the particle size [5]. In particular, in our system FMR cannot be detected; however, it presents the novel aspect of an extended hysteresis-loop in all the interval of magnetic field (0–9 kOe). On the other hand, the usual method for measuring the strength and the kind of interactions between particles is based on the use of the so-called Henkel plot or $\delta M$ plot. First, Henkel [6] plotted the demagnetization remanence curve $M_d(H)$, versus the isothermal remanent magnetization curve $M_r(H)$ which, in accordance with the fundamental Wohlfart relation [7] in the case of no interactions, should give a linear plot with a slope of $-2$. Any deviation from the idealized straight line is attributed to interactions. A variation of the Henkel technique is the use the first derivatives of the remanent magnetization curves for investigation of the interaction effects. In this work, we focus on the phenomenon of hysteresis in the MPA in cobalt ferrite nanoparticles.

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An investigation of the role of interparticle interactions as a function of particle size is presented through the Henkel plot and is analyzed in order to investigate the nature of MPA signal in nanoparticles of cobalt ferrite.

## 2. Experimental procedure

### 2.1. Synthesis

Stoichiometric amounts of $Co(CH_3CO_2)_2 \cdot 4H_2O$ (1/200 mol) and $Fe(NO_3)_3 \cdot 9H_2O$ (1/100 mol) were first dissolved in 2-metoxyethanol (100 mL) and water (15 mL) for 30 min with the help of ultrasonic cleaning. The solution was refluxed for 24 h at 80 °C to allow gel formation, and then dried at 60 °C in air. The dried amorphous precursor powder was heated at temperatures ranging from 400 to 600 °C with intervals of 50 °C for 3 h, at heating rates of 10 °C/min.

### 2.2. Characterization

The X-ray diffraction (XRD) pattern of the as-prepared sample and the patterns for samples annealed at various temperatures were recorded in the $2\theta = 10–70$ range in steps of 0.04 $min^{-1}$ on a Siemens D-5000 diffractometer using $CuK_\alpha$ radiation. MPA ($dP/dH$) measurements were carried out as a function of magnetic field ($H_{DC}$), in a JEOL JES-RE3X spectrometer at X-band (9.4 GHz) in the range 0–9 kOe. For this purpose, a JEOL ES-ZCS2 Zero Cross Sweep unit was used to digitally compensate for any remanence in the electro-magnet. Magnetization measurements were carried out using a LDJ 9600 vibrating sample magnetometer, VSM, to obtain the $M$–$H$ loops and Henkel plot at room temperature. Mössbauer spectra were obtained at room temperature by using a conventional constant acceleration Mössbauer spectrometer, placing the sample holder in a γ-ray beam from a $^{57}Co$ source. A high purity natural iron foil was used as the standard. The spectra were analyzed by using a program that fitted the curves with Lorentzian functions. The Mössbauer parameters were obtained by analyzing the spectra. A JEOL JSM-5600LV transmission electron microscope (TEM) was used to observe the nanoparticles.

The isothermal remanent magnetization curves were obtained by measuring the remanent magnetization as a function of increasing positive applied field. First, a field $H = 300$ Oe was applied and then it was removed; the magnetization obtained when the system reached zero applied field was $M_r(H)$. This procedure was done in steps of 300 Oe, until positive saturation was obtained (12 kOe). The remanent magnetization for the remanence curve started from the saturated state, with the remanent magnetization being measured as a function of decreasing applied fields. As above, a $H = -300$ Oe was applied and then removed to obtain the magnetization value, $M_d(H)$. This procedure was carried out with similar increments, until the negative saturation was obtained (−12 kOe).

## 3. Results and discussion

XRD patterns of the annealing powder at 400, 450, 500, 550 and 600 °C show that the final product corresponds to cobalt ferrite with the expected spinel structure. The Mössbauer spectrum exhibited two sets of sextets corresponding to $Fe^{3+}$ in occupying tetrahedral (A) and octahedral (B) sites of the inverse spinel structure, and also a doublet due to superparamagnetic nanoparticles (SPM). The hyperfine field and isomer shift are listed in Table 1. The area ratio $I_B/I_A$ of the Mössbauer patterns indicated that $CoFe_2O_4$ was not completely inverse.

The superparamagnetic particles decreased from 17.8% to <3% when the annealing temperature increased from 440 to 600 °C.

The size distribution of the particles was determined using TEM images for each annealing temperature. Fig. 1(a) shows the TEM images of nanoparticles annealed at 500 °C for 3 h. In general, most of the particles in all samples appear spheroidal. The particle size depended on annealing temperature and, as observed in Fig. 1(b), the average size increased with the annealing temperature. This increase was slow between 400 and 500 °C, and appeared to be rapid above 500 °C. The magnetic properties are strongly dependent on particle size variations. Coercive field and saturation magnetization are summarized in Table 1. The coercive field goes through a maximum at 2120 Oe for an average particle size of 19 nm. A further increase in particle size above 22 nm decreases the coercive field. Therefore, the system of particles obtained can be considered as a system of interacting spheroidal particles due to partial agglomeration with cubic anisotropy resulting from the crystalline phase. The magnetic contribution of SPM is negligible.

Table 1
Cation distribution and magnetic parameters of cobalt ferrites

| $T$ (°C) | IS (mm/s) | $H_{hf}$ (kOe) | Intensity ($I$) % | $H_c$ (Oe) | $M_s$ (emu/g) |
|---|---|---|---|---|---|
| 400 | B 0.389 | 516 | 31.9 | 655 | 21.5 |
| | A 0.286 | 488 | 50.3 | | |
| | SPM 0.370 | – | 17.8 | | |
| 450 | A 0.401 | 515 | 37.3 | 2120 | 49.2 |
| | B 0.298 | 488 | 59.7 | | |
| | SP 0.354 | – | 2.9 | | |
| 500 | B 0.399 | 513 | 36.0 | 1978 | 49.7 |
| | A 0.290 | 487 | 62.3 | | |
| | SPM 0.280 | – | 1.7 | | |
| 550 | B 0.430 | 513 | 40.3 | 1867 | 61.0 |
| | A 0.296 | 488 | 59.7 | | |
| | SPM –0 | – | – | | |
| 600 | B 0.380 | 515 | 40.8 | 1506 | 48.2 |
| | A 0.280 | 486 | 56.2 | | |
| | SPM 0.310 | – | 2.9 | | |

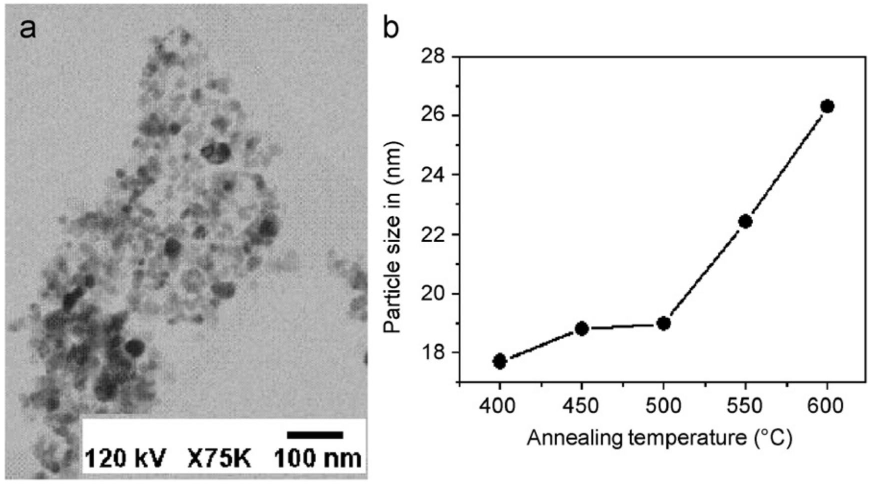


Fig. 1. (a) TEM micrograph of cobalt ferrite nanoparticles annealed at 500 °C for 3 h with average crystallite size of 19 nm. (b) Particle size (nm) as a function of annealing temperature (°C) for cobalt ferrite nanoparticles.

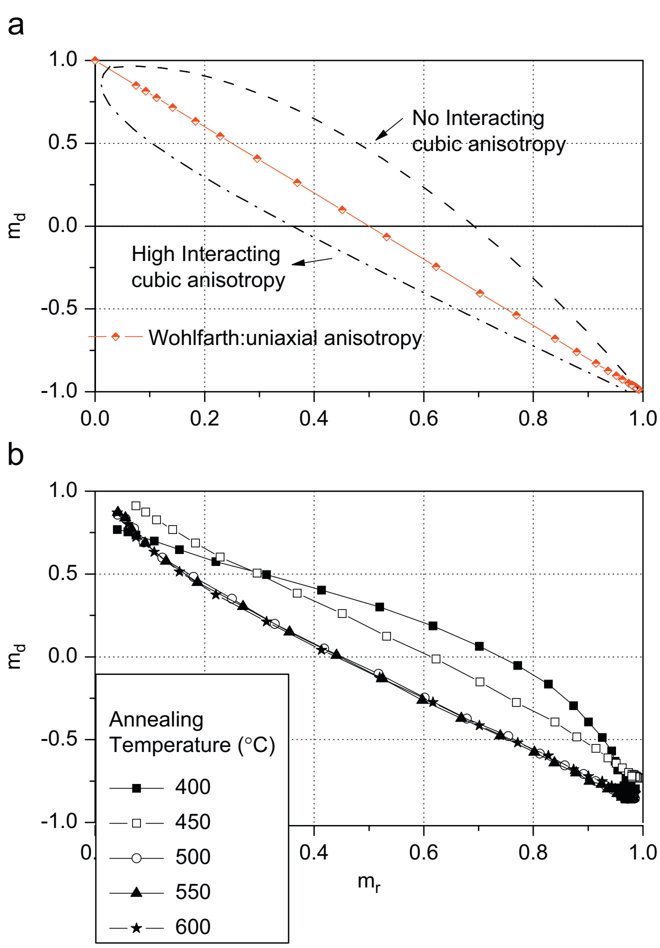


Fig. 2. (a) Theoretical Henkel plot [10]. (b) Henkel plot of experimental data on annealed cobalt ferrite at different temperatures; solid lines are guides to the eye.

In order to determine the particle interactions, a Henkel plot analysis was made for each annealing temperature according to particle size. Non-interacting systems generally show a linear Henkel plot, while interacting systems show positive deviation plots, Fig. 2(a). A positive $\delta m(H)$ plot suggests that the interparticle interaction supports the magnetized state, and the exchange coupling interaction is dominant. A negative $\delta m(H)$ plot suggests that the interparticle interaction promotes a demagnetized state, and the magnetostatic interaction is dominant [6,8]. However, the model is valid only at 0 K and with uniaxial particles. Recently, some models have been developed which include a wide range of temperatures, cubic anisotropies, and interactions [9,10]. The Henkel plot ($m_d$ vs. $m_r$) is observed in Figs. 2(a) and (b); the demagnetization remanence is $m_d(H) = M_d(H)/M_r(H_{max})$ and the remanent magnetization is $m_r = M_r(H)/M_r(H_{max})$. The experimental plots of the systems of interacting particles with cubic anisotropy present a positive deviation for samples at 400 and 450 °C and small negative deviations for the rest of the samples. Comparing these results with theoretical Henkel plots (Fig. 2(a)) for systems with cubic anisotropy and high particle interaction, a similar behavior is observed between the experimental and the theoretical curves, indicating a demagnetized state for all samples annealed; therefore, strong magnetostatic interaction is expected. Particles' interaction increases with the annealing temperature.

Fig. 3 shows measurements of MPA for samples at 400 and 600 °C nanoparticles [5] as a function of annealing temperature. The MPA measurements show extended hysteresis loops obtained for DC magnetic field cycle in the 0 and 9 kOe interval. This behavior can be explained with a Henkel plots analysis, i.e. the particle interactions determine the MPA. In our case, in particular, the particle interaction originates the demagnetized state, and therefore a high magnetostatic interaction. In consequence, the saturation state is not reached and the resonance condition is not satisfied. This suggests that high magnetostatic interaction induces a high magnetic disorder, resulting in

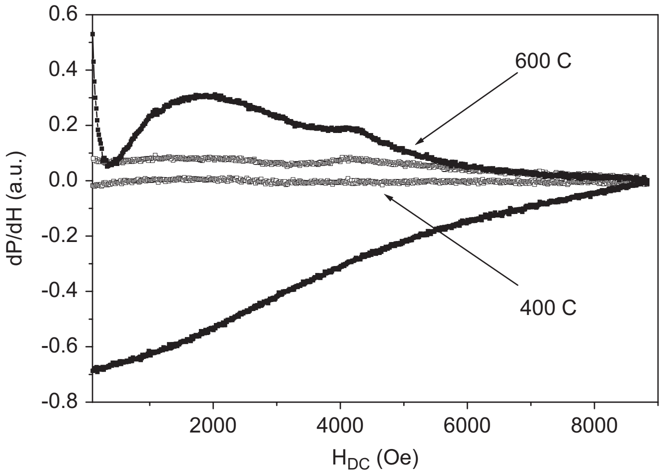


Fig. 3. X-band (9.4 GHz) microwave power absorption ($dP/dH$) measurements of the cobalt ferrite at different temperatures. The signal corresponds to cycling the DC magnetic field from 0 to 9 kOe.

an extended non-resonant absorption. This magnetic disorder is originating complex absorption processes such as spin curling, and so, in these materials, the resonance condition is satisfied at the high field due to high particle magnetostatic interactions. The area of extended hysteresis loop increases with the annealing temperatures, similar to increases in magnetostatic interactions with annealed temperature, suggesting that the magnetostatic interaction originates increases in area absorption.

## 4. Conclusions

The Henkel plot analysis is a good technique for determining particle interaction, and it can be correlated with microwave absorption features in the cobalt ferrite.

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