

Effect of high-energy ball milling time on structural and magnetic properties of nanocrystalline cobalt ferrite powders



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ABSTRACT

Cobalt ferrite nanocrystals synthesized by conventional and size-controlled coprecipitation methods were treated by high-energy ball milling, HEBM, in order to study the effect of crystal size reduction and/or strain on the resulting magnetic properties. Processed nanocrystals were characterized by X-ray diffraction, Brunauer, Emmett, and Teller surface area analysis, transmission electron microscopy (TEM), and vibrating sample magnetometry. The cobalt ferrite nanocrystals exhibited crystal size reduction from initial values (average crystallite sizes of 12 ± 1 nm and 18 ± 3 nm, respectively) down to 10 nm after HEBM for 10 h. The specific surface area was decreased by milling (from 96.5 to 59.4 m²/g; for the 12 nm cobalt ferrite nanocrystals), due to particles aggregation. TEM analyses corroborated the aggregation of the nanoparticles at such long milling times. The same cobalt ferrite nanocrystals exhibited a rise in coercivity from 394 to 560 Oe after 5 h ball milling which was attributed to the introduction of strain anisotropy, namely point defects, as suggested by the systematic shift of the diffraction peaks towards higher angles. In turn, the magnetic characterization of the starting 18 nm-nanocrystals reported a drop in coercivity from 4506 Oe to 491 Oe that was attributed predominantly to size reduction within the single domain region. A correlation between particle size, cationic distribution, and HEBM processing conditions became evident.

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1. Introduction

The selection of suitable synthesis and processing conditions of nanometric ferrites will affect their crystal size, morphology, cation distribution and hence, the resulting magnetic properties. Although coercivity is mainly governed by the magnetocrystalline anisotropy energy, contribution from surface anisotropy, strain anisotropy and/or shape anisotropy also affect the magnetic anisotropy, particularly at the nanoscale. High-energy ball milling (HEBM), so-called mechano-chemical processing, has emerged as a technique to produce nanomaterials capable to achieve a remarkable particle size reduction from a previously synthesized materials [1–4], or induce solid-phase transformations [5]. HEBM has also been widely used in the preparation of ferrites from metal oxides [6]. In HEBM, powdered samples are placed inside metallic jars containing suitable proportion of grinding media, usually ceramic balls, and contacted at extremely high rotational speeds to promote the impact and abrasion of the powder with the

grinding media, which in turn will induce the generation of defects and strain along with particle size reduction [7]. The advantage of this processing technique relies on the use of inexpensive and environment-friendly solvents and low temperatures, when compared to wet-chemistry-based routes or conventional solid-state processing (e.g. sintering).

The mechano-chemical synthesis or activation of spinel structured oxides by HEBM has been reported with the resulting final outcome depending on the type of material and grinding conditions. For instance, the use of inert grinding materials are reported to only impact structural disorder due to change in degree of inversion as was reported in the case of MgFe₂O₄ [8]. On the other hand, the formation of NiFe₂O₄ was observed when solid NiO and α-Fe₂O₃ solid precursors were ball-milled [9] using stainless steel grinding media.

Cobalt ferrite nanocrystals were selected for this study because its magnetic properties are easily tunable when composition, size, shape, and cation distribution are modified. Nanometric cobalt ferrite exhibits a strong size-dependent coercivity; therefore, any change in the ferrite synthesis and/or processing conditions will affect the crystal size and hence, the magnetic properties [10]. Besides, the high-energy impacts inside the milling apparatus should induce strain anisotropy in the crystal lattice, thereby modifying the corresponding coercivity.

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On this basis, the present work is focused on the study of the dependence of specific surface area, structural (average crystallite size and lattice parameter), and magnetic (coercivity and maximum magnetization) with HEBM processing conditions of cobalt ferrite nanocrystals of different average crystallite sizes.

2. Material and methods

2.1. Materials

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (ACS, 98–102%, Alfa Aesar), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (ACS, 97–102%, Alfa Aesar), and NaOH (pellets, 98%, Alfa Aesar) were used without further purification, as precursor for the synthesis of cobalt ferrite nanocrystals.

2.2. Synthesis of cobalt ferrite nanocrystals

Cobalt ferrite powders were synthesized using the conventional and the size-controlled coprecipitation methods. The later considered the synthesis under fixed flow-rate (0.71 mL/min) of reactants addition according to the method developed by Cedeño-Mattei et al. [11]. A micro-peristaltic pump was used for this purpose. Control on flow-rate leads to the formation of nanocrystals with larger size due to modification in oversaturation conditions that promotes heterogeneous nucleation [12]. A 0.315 M NaOH boiling solution was the precipitant agent. The reaction time was set to one hour based on our previous works [11].

2.3. HEBM processing of cobalt ferrite nanocrystals

Cobalt ferrite samples were synthesized by the conventional and size-controlled coprecipitation routes. These two samples were processed by high-energy ball milling in a Fritch Pulverisette-4 milling apparatus with tungsten carbide (WC) balls and jars. The ball-milling assembly consisted of 2 jars of 45 mL each one bearing 17 balls of 10 mm diameter each. A ball to powder ratio (BPR) of 40:1, a milling speed of 1400 rpm, and milling times in the 20 min–10 h range, were used in all our experiments. The choice of BPR of 40:1 was based on previous studies on bulk cobalt ferrite which showed its effectiveness in particle size reduction [13]. Small amounts of sample were withdrawn at pre-selected milling times to monitor the progress of the size reduction/aggregation process and determine the corresponding structural and magnetic properties.

2.4. Nanocrystals characterization

The structural characterization of the nanocrystal ferrites was carried out by X-ray diffractometry using a Siemens D500 powder diffractometer with Cu K_α radiation. The average crystallite sizes reported were determined by XRD measurements and the Scherrer's equation.

The specific surface area of the powders was measured in a Horiba SA-9600 series surface area analyzer. The external specific surface area of spheres, SSA, with diameter 't' (or cubes with edge length 't') and density ρ can be estimated by [14]:

$$\text{SSA} = 6/\rho t \quad (1)$$

This formula does not take into account interparticle overlapping (aggregation) but only reversible agglomeration.

Morphological analyses of the samples were done in a JEOL 2011 transmission electron microscope.

A LakeShore 7400 series vibrating sample magnetometer was used to determine the magnetic properties of the powdered samples at room temperature.

A WEBRES spectrometer operating in the transmission mode, with a 50 mCi ^{57}Co source in a Rh matrix from Ritverc, GmbH was for Mössbauer measurements. The degree of Fe^{3+} distribution within the tetrahedral and octahedral sites was deduced via the following expression:

$$I_{\text{Tet}}/I_{\text{Oct}} = (f_{\text{Tet}}/f_{\text{Oct}})[\lambda/(2-\lambda)] \quad (2)$$

with, I_{Tet} and I_{Oct} , referring to the relative abundances associated with the tetrahedral and octahedral sites, and f , the recoilless fraction at the corresponding sites for the temperature of measurement (in our case, a room temperature value of 0.94 was used [15]). The inversion parameter, λ , translates to the following structural designation: $(\text{M}_{1-\lambda}\text{Fe}_\lambda)^{\text{Tet}}[\text{M}_\lambda\text{Fe}_{2-\lambda}]^{\text{Oct}}\text{O}_4$ and expresses the degree of departure of the cations ("M"=Co in our case, and "Fe") from their expected octahedral and tetrahedral occupations.

3. Results and discussion

3.1. XRD analyses

XRD patterns from the 12 ± 1 nm and 18 ± 3 nm as-synthesized cobalt ferrite powders before (0 min) and after 30 min, 60 min, and 300 min of milling times are shown in Figs. 1 and 2, respectively. Peak broadening became evident after prolonged milling time that suggested the decrease in crystallite size. The average crystallite size of the 12 nm powders showed a just minor decrease (10 nm) even after 10 h of milling, whereas a more noticeable diminution in the average crystallite size (from 18 nm to 10 nm) was exhibited at the end of the 10 h milling period by the sample synthesized under size-controlled conditions. Evidently, the impact and abrasion forces generated inside the milling jar must have broken up the crystals even at the nanoscale. Figs. 1 and 2 also evidenced the shift of the XRD peaks towards smaller diffraction angles. This shift in diffraction angle is attributed to strain which is also reflected by the increase of the corresponding increase of the interplanar distances [7,16], the interplanar distance between (440) planes was increased from 1.483 Å to 1.486 Å when the milling time was prolonged up to 10 h. An increase in the lattice parameter could be attributed to point defects, e.g. ferric ion occupies normally unoccupied sites [17]. In turn, it will cause a change in the degree of inversion of cobalt ferrite.

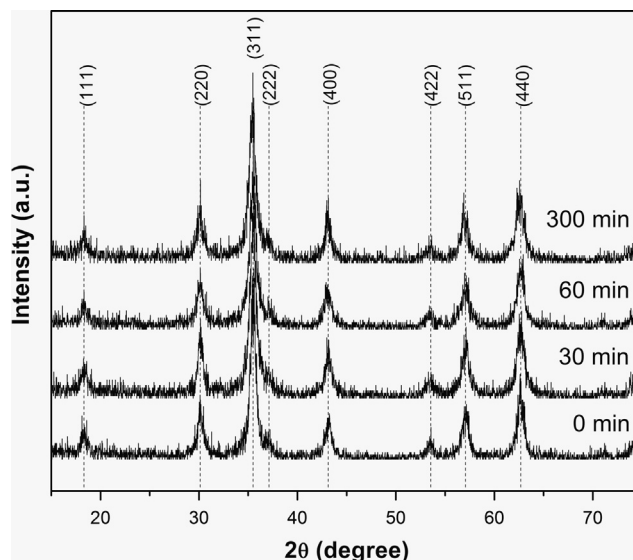


Fig. 1. XRD patterns of 12 nm-cobalt ferrite nanocrystals ball-milled at different times.

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