

Size-Control and Size-Selection at the Nanosize Level: Production of CoFe_2O_4 Nanoparticles of Unusual High Coercivity at Room Temperature

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ABSTRACT

Among the various ferrite materials, cobalt ferrite (CoFe_2O_4) is well known to possess excellent chemical stability and good mechanical hardness. Furthermore, the large positive first order crystalline anisotropy constant has made this ferrite a promising candidate for magneto-optical recording media. However, applications of CoFe_2O_4 are often limited due to the lack of a synthesis technique capable to achieve a suitable control over particle size distribution, with particle diameters between the superparamagnetic and single domain sizes range. This control would permit to attain high coercivity and moderate magnetization at room temperature, which is critical for application of this material in actual devices. Here, we introduce a solution chemistry technique that involves a 'seeding step' followed by a size-selective particles separation that permits a fine size classification of single domain CoFe_2O_4 nanoparticles. The size-selected 40-nm particles reported room temperature coercivity as high as 4.6 kOe and a squareness ratio of 0.66.

Keywords: Cobalt ferrite, high coercivity, nanoparticles, seeding, size-selection.

1 INTRODUCTION

Nanometer sized magnetic particles are the subject of intense research because of their potential applications in high-density magnetic recording, magnetic fluids, etc. Among the various ferrite materials, cobalt ferrite (CoFe_2O_4) is well known to possess remarkable magnetic properties such as strong anisotropy, moderate saturation magnetization, M_s , and high coercivity, H_c , along with good chemical stability and mechanical hardness. At room temperature the critical single domain size and superparamagnetic threshold of cobalt ferrite are 70 and 10 nm, respectively [1]. On the other hand, the theoretical M_s and H_c and squareness ratio values at 300K [2] for a random system of spherical, non-interacting single domain particles with cubic anisotropy, are 80.8 emu/g, 5.3 kOe and 0.83, respectively. In other words, by increasing the size of the cobalt ferrite crystals within the single domain size range it should become possible to achieve high coercivity at the nanosize level.

Although a number of methods have been developed to synthesize cobalt ferrite nanoparticles, the reported values are far below the above cited maximum. The low coercivity

values are attributed to the lack of a fine control over particle size and size distribution, which should also have promoted the production of large fraction of superparamagnetic particles. Therefore, any synthesis approach capable to restrict the growth of CoFe_2O_4 nanoparticles in the range between superparamagnetic and single domain sizes range will be desired.

In the present paper we describe a solution-based approach that satisfies the mentioned requirements. It involves a 'seeding step' under conditions where supersaturation and growth rates of particles are controlled to produce single domain well-crystallized CoFe_2O_4 nanoparticles. Furthermore, by taking advantage of the size-selective methods developed for polydispersed nanoparticles [3, 4], it was possible to remove the superparamagnetic fraction in the bulk powder and get nearly monodispersed cobalt ferrite single crystals of various sizes. The size-selected ferrite particles exhibited unusual high coercivity at room temperature.

2 EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salts were dissolved in distilled water to achieve a Fe/Co mole ratio of two. NaOH was used as the alkaline precipitant agent.

In the size-selection tests, the ferrite particles were coated with the anionic surfactant Na-oleate, $\text{C}_{17}\text{H}_{33}\text{COONa}$. Toluene was used as the dispersing medium. Acetone or ethanol was used to promote the size sensitive phase separation from starting polydispersed ferrite suspensions.

2.2 Synthesis of Cobalt Ferrite Seeds

The cobalt ferrite seeds were produced by conventional coprecipitation method. The 800 ml of a 0.11 M Fe(III) and 0.055 M Co(II) solution was continuously added into the reaction vessel containing 1.5 l of a boiling 0.725 M NaOH aqueous solution under mechanical stirring at 500 rpm. The contact time of 2 hours was long enough to permit the dehydration and atomic rearrangement involved with the conversion of the precursor hydroxide into the ferrite

structure. The seeds were polydispersed and exhibited an average grain size of 16 nm.

2.3 Seeding-Assisted Ferrite Synthesis

In order to promote the growth of the CoFe_2O_4 particles seeds of the same material, synthesized as described in section 2.2, were used as pre-existing nuclei. Then, cobalt ferrite particles were prepared by adding the mentioned seeds into the starting solution containing the metal ions and sodium hydroxide. Other conditions were the same as detailed for the seeds preparation. Seeds were added at different seeds/ferrite, w/w ratios. The reaction time was fixed at 2.5 hours.

2.4 Size-Selection Procedure

Fixed amounts of cobalt ferrite synthesized by the seeding-assisted method were contacted with aqueous solutions of sodium oleate (surfactant/ferrite, w/w ratio of 30%) at 90°C for 1 hour. The suspension was left overnight to facilitate phase separation. The sediment, containing the larger particles, was separated from the stable suspension by decantation. The stable suspension of sodium oleate coated cobalt ferrite particles was contacted with controlled volumes of acetone or ethanol and sonicated to homogenize the mixture. After a suitable 'settling time' a size-sensitive phase separation became evident. The supernatant, containing suspended particles smaller in size than the ones in the sediment, was poured gently into another container. The recovered supernatant was treated again with acetone and the phase separation cycle was repeated for several times. The suspension coming from the last cycle was the final product of this size selection method.

2.5 Products Characterization

Bulk polydispersed powders, size-selected fractions produced in each cycle and the final suspension of ferrite nanoparticles were analyzed using high-resolution transmission electron microscopy (HRTEM) to determine the particle size and energy dispersive spectroscopy to verify the chemical composition. The magnetization measurements were carried out at room temperature by the vibrating sample magnetometer technique, VSM, under a maximum field of 15 kOe.

3. RESULTS AND DISCUSSION

3.1 Seeding –Assisted Ferrite Synthesis

The production of well grown crystalline precipitates requires that the supersaturation (defined from the saturation ratio $S = C/C_{\text{eq}}$, where C and C_{eq} are the concentrations of the precipitating metal in the actual solution and at equilibrium, respectively) must be

controlled below a critical value and seeds to be available. Under those conditions crystal growth (heterogeneous nucleation) will be predominant over homogeneous nucleation.

XRD analysis of powders produced under our experimental conditions showed the presence of spinel CoFe_2O_4 phase only and the average grain size was estimated between 23-25 nm irrespective of the seed /ferrite weight ratios. The room temperature H_c of the samples synthesized at various seed/ferrite weight ratios are shown in figure 1. In this figure the seed/ferrite ratios were replaced by their equivalent seed concentrations.

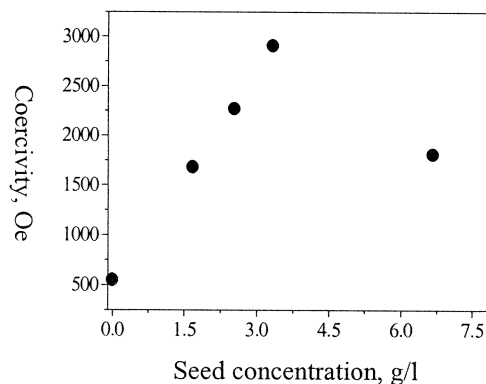


Figure 1. Coercivity at room temperature of seeded cobalt ferrite versus seed concentration.

The H_c increased from 560 Oe for the 'naked' seeds up to 2.91 kOe for the powders produced at a seed concentration of 3.33 g/l (w/w ratio 0.5). When the seed concentration was low, the fraction of the particles that were formed onto pre-existent seeds was considered to be small. In turn, when the weight fraction of the seeds was 0.5, a remarkable rise in the coercivity was achieved suggesting that a large percentage of single domain particles were produced; i.e. a suitable compromise was attained between the supersaturation conditions and the available surface area provided by the seeds. However, when the seed concentration exceeded 3.33g/l, the coercivity drastically decreased from 2.9 kOe to less than 2 kOe. This fact suggests that when the seed population is too high only some of them will effectively act as nucleating agent and promote the incorporation of Co and Fe atoms into the crystal. The excess of seed particles that are not taking place in the seeding process will contribute with the rise in the percentage of superparamagnetic particles and the consequent drop in coercivity. The HRTEM analysis confirmed that the particle size range was between 15 and 40 nm for the powders produced at a seed concentration of 3.33 g/l.

3.2 Size-Selection at the Nanosize Level

The unusual high coercivity of cobalt ferrite particles was attributed to the presence of an increased fraction of

particles with sizes close to the upper limit of the single domain region. To determine the relation between particle size and coercivity, the sample synthesized at a seed/ferrite weight ratio of 0.5 was size separated according to the procedure described in section 2.4. The HRTEM micrographs of figure 2 confirmed the effective size selection of the seeded CoFe_2O_4 particles. As observed, the latter fractions only contained highly monodispersed nanoparticles in the range from 2 to 4 nm (figure 2-c). Intermediate fraction contained medium size nanoparticles with a size averaging 15 nm whereas the biggest particles were reported in the first fraction.

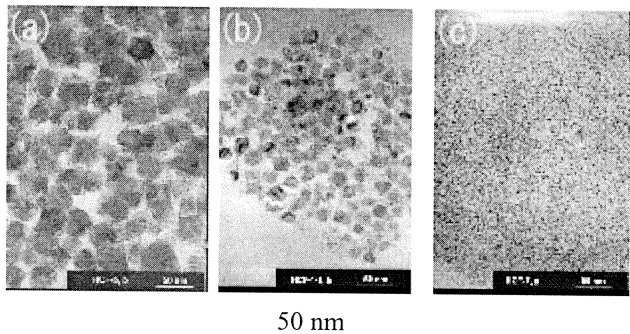


Figure 2. CoFe_2O_4 particles obtained after size-selection. (a) Settled particles at the end of the first separation cycle, (b) after 2 separation cycles, (c) last suspension.

Figure 3 shows the hysteresis loop measured at 300K corresponding to the size-selected cobalt ferrite particles of figure 2-(a). Figure 4 summarizes the variation in room temperature coercivity with size for size-selected CoFe_2O_4 nanoparticles. There is a gradual increase of coercivity with increase in particle size and reaches a maximum value of 4.6 kOe at 40 nm. The coercivity then decreases for any further increase in particle diameter. When the particle sizes are within the single domain size, the magnetization proceeds by reversible rotation at high applied fields and thus display Stoner-Wohlfarth behavior [5]; i.e., the dominant magnetization process is due to spin rotation and not by the domain wall displacement. Then, the magnetization reversal of nanoparticles is only related to the magnetic anisotropy.

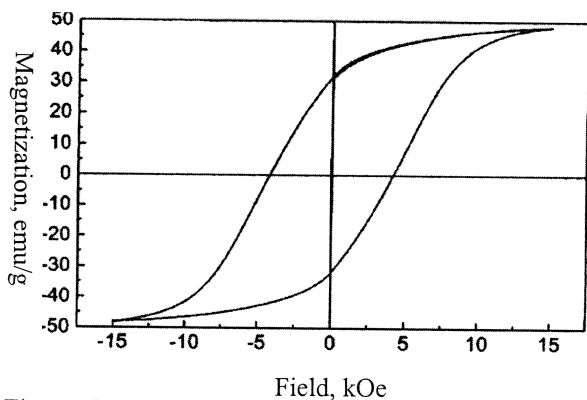


Figure 3. Hysteresis loop measured at 300K of size-selected 40-nm fraction cobalt ferrite nanoparticles.

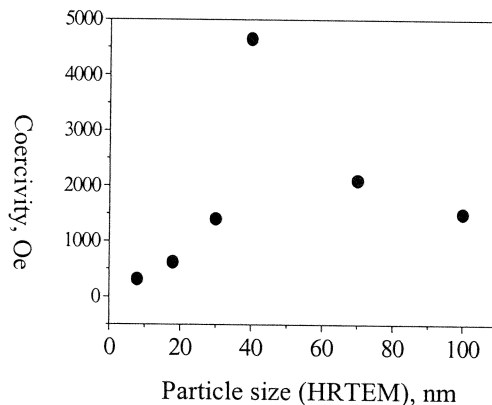


Figure 4. Coercivity for the various size-selected CoFe_2O_4 nanoparticles.

On the other hand, since the H_c of the 70-nm particles was less than the coercivity of the 40-nm ones, it can be suggested that the upper limit for the single domain size of produced cobalt ferrite nanoparticles could be around 40 nm and not 70 nm as reported by Berkowitz et al. [1]. When the particle size exceeds 40 nm it falls within the multidomain size range and the magnetization process takes place by domain wall displacement causing the drop in coercivity.

4 CONCLUDING REMARKS

The developed seeding assisted-size selection synthesis procedure permitted to produce well-crystallized cobalt ferrite nanoparticles within single domain size range. After size-selective separation of the products, several fractions ranging from 2 nm up to 100 nm in average size were produced. The room temperature coercivity and magnetization values reached a maximum of 4.6 kOe and 50 emu/g, respectively, for the size-selected 40-nm fraction. These cobalt ferrite nanoparticles can be considered as a potential candidate for high-density recording material.

Furthermore, the present approach can also be extended to the size-controlled synthesis of different functional materials in the nanometric size level.

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