Magnetic properties of nanoparticles of CoxFe(3−x)O4 (0.05 x 1.6) prepared by combustion reaction

Adolfo Franco Júnior, Vivien Zapf, and Paul Egan

Magnetic properties of nanoparticles of Co$_x$Fe$_{(3-x)}$O$_4$ (0.05 ≤ x ≤ 1.6) prepared by combustion reaction

Adolfo Franco Júnior[a)]
Departamento de Matemática e Física, Universidade Católica de Goiás, Caixa Postal 86, 74605-0101 Goiânia-Go, Brazil

Vivien Zapf
National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Paul Egan
Oklahoma State University, Stillwater, Oklahoma 44679

Nanoparticles of Co$_x$Fe$_{(3-x)}$O$_4$ with x ranging from 0.05 to 1.6 were synthesized by a combustion reaction method using iron nitrate, cobalt nitrate, and urea as fuel. X-ray diffraction patterns of all systems showed broad peaks consistent with the cubic inverse spinel structure of cobalt ferrite. The absence of extra reflections in the diffraction patterns of as-prepared materials, with x=0.6, 0.8, and 1.0, demonstrates the phase purity. Magnetization measurements show that the saturation magnetization (M_s), coercivity (H_c), and remanent magnetization (M_r) depend on the molar cobalt concentration and the temperature as well. At 4 K, the reduced remanence, M_r/M_s, are equal to 0.66 and 0.63 for x=0.8 and 1.0, respectively, indicating that cubic-type magnetic anisotropy is significant in these nanoparticles. These observations are discussed in terms of a model in which it is assumed that each crystallite consists of a ferromagnetic core surrounded by a magnetically disordered shell. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2711063]

Cobalt ferrite, CoFe$_2$O$_4$, crystallizes in a partially inverse spinel structure and space group $Fd3m$-O_h^7. In the bulk, it is ferrimagnetic with a Curie temperature, T_C, of 790 K, and exhibits very high cubic magnetocrystalline anisotropy [(2.1–3.9)×10^5 J/m^3],[1] high coercivity (13–14.1 kOe),[2,3] moderate saturation magnetization (80 emu/g),[3] remarkable chemical stability, wear resistance, and electrically insulating behavior.[3] These properties make cobalt ferrite good candidate for many applications in commercial electronics such as video, audio tapes, high-density digital recording media,[4] and as photomagnetic material due to an interesting light-induced coercivity change.[5,6] Most of these physical properties depend strongly on both the size and shape of the nanoparticles,[3,7,8] which are closely related to the method of preparation.

In the last decade, many synthetic methods to prepare highly crystalline and uniformly sized magnetic nanoparticles of cobalt ferrite have been reported.[9–13] However, most of these methods cannot be applied economically on a large scale because they require expensive and often toxic reagents, complicated synthetic steps, high reaction temperatures, long reaction times, and precisely controlled stoichiometric compositions.

As an alternative, the combustion reaction method is a simple, fast, and inexpensive approach to synthesizing these ferrites since it does not involve intermediate decomposition and/or calcining steps.[14–16] In addition, it is easy to control the stoichiometric composition and crystallite size, which have important effects on the magnetic properties of the ferrite.[3] This method exploits an exothermic, usually very rapid and self-sustaining chemical reaction between the desired metal salts and a suitable organic fuel, usually urea. A peculiar characteristic of this method is that the heat required to sustain the chemical reaction is provided by the reaction itself and not by an external source.[14,16] The resulting product is a dry crystalline powder agglomerated into very fragile foam with high chemical homogeneity and purity.

In the present study, we report the magnetic properties of a series of nanoparticles of cobalt ferrite Co$_x$Fe$_{(3-x)}$O$_4$ with x ranging from 0.05 to 1.6 synthesized by the combustion reaction method without subsequent calcinations steps. Further detail of sample preparation is available in the literature.[16]

The as-prepared samples were characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The full widths at half maximum (FWHMs) of three prominent diffraction peaks and Scherrer's equation[17] were used to estimate the crystallite diameter of all samples.

Measurements of the temperature and field dependence of the dc magnetization were carried out using an induction technique in a physical property measurement system (PPMS) by Quantum Design in magnetic field up to 6 T at 4, 72, 272, and 340 K.

The actual chemical compositions of all samples determined by atomic spectroscopy were found to be quite close to the target compositions, calculated based on the proportions of the starting materials (see Table I). X-ray powder diffraction patterns of all samples are shown in Fig. 1. Samples with x=0.6, 0.8, and 1.0 exhibited sharp and intense peaks that correspond to the cubic inverse spinel structure of CoFe$_2$O$_4$ (Ref. 16). Samples with other stoichiometries ex-

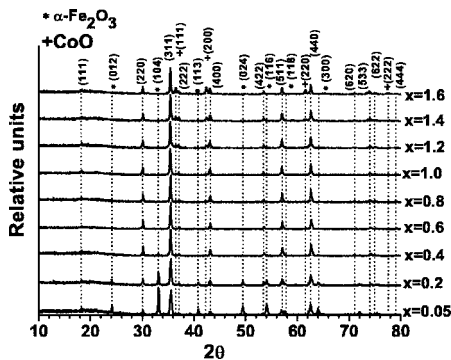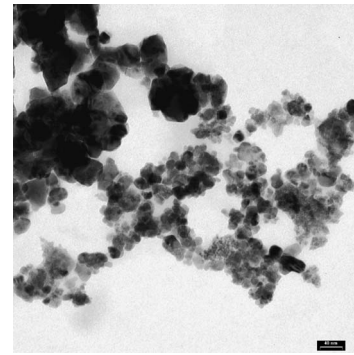a)Electronic mail: franco@ucg.br

101, 09M506-1

TABLE I. Some physical characteristics of $Co_xFe_{(3-x)}O_4$ powders prepared by combustion reaction.

Sample chemical composition		Lattice parameter (Å)	Particle size (nm)	
Calc.	Determined		$\langle d \rangle_{x\ ray}$	$\langle d \rangle_{TEM}$
$Co_{0.05}Fe_{2.25}O_4$	$Co_{0.06}Fe_{2.94}O_4$	8.342±0.001	29.90±7.99	24.93±7.11
$Co_{0.2}Fe_{2.8}O_4$	$Co_{0.18}Fe_{2.82}O_4$	8.365±0.003	29.28±8.09	25.03±5.31
$Co_{0.4}Fe_{2.6}O_4$	$Co_{0.39}Fe_{2.61}O_4$	8.378±0.007	29.65±4.68	24.93±8.45
$Co_{0.6}Fe_{2.4}O_4$	$Co_{0.57}Fe_{2.43}O_4$	8.390±0.006	41.12±8.09	39.58±9.21
$Co_{0.8}Fe_{2.2}O_4$	$Co_{0.78}Fe_{2.22}O_4$	8.395±0.003	54.85±9.93	43.97±9.69
$Co_{1.0}Fe_{2.0}O_4$	$Co_{0.96}Fe_{2.04}O_4$	8.396±0.001	52.74±6.01	41.37±7.12
$Co_{1.2}Fe_{1.8}O_4$	$Co_{1.15}Fe_{1.85}O_4$	8.391±0.002	46.76±8.59	42.07±8.11
$Co_{1.4}Fe_{1.6}O_4$	$Co_{1.26}Fe_{1.74}O_4$	8.389±0.004	48.67±11.51	42.58±7.17
$Co_{1.6}Fe_{1.4}O_4$	$Co_{1.46}Fe_{1.54}O_4$	8.385±0.001	56.30±10.59	49.97±9.12

FIG. 2. TEM image of the as-prepared $CoFe_2O_4$ samples.

hibited extra peaks that correspond to either the hematite phase (α-Fe_2O_3) or the cobalt oxide (CoO) phase. The mean particle diameter increases linearly with the cobalt molar content, being approximately 29.99±7.99 and 56.30±10.59 nm for $x=0.05$ and $x=1.6$, respectively, in irregular and rough spherical morphologies, as shown in Fig. 2. The lattice parameters are slightly dependent on cobalt molar concentrations having the largest value (8.396±0.001 Å) for the inverse spinel structured $CoFe_2O_4$ (see Table I). This suggests that the lattice parameter of these compounds is closely related to the cation distribution as reported by Lee *et al.*[18]

At 4 K, all samples exhibited typical magnetic hysteresis loops, indicating the presence of an ordered magnetic structure in the spinel system, as shown in Fig. 3. In addition, it is clear that the samples do not saturate at applied magnetic field up to 6 T at 4 K. In the region of high applied field of the magnetization curve, Fig. 3, the domain rotation predominates and a considerably large increase in applied field is required to produce a relatively small increase in magnetization. The fact that the samples could not be magnetized sufficiently close to saturation is an indication that the anisotropy has become so high that creates a barrier of the orientation of the total magnetic moments toward the applied field. However, at 272 K samples with $x=0.8$ and 1.0 exhibited the hysteresis loop while the other samples exhibited typical superparamagnetic behavior, i.e., no remanence and coercivity, as shown in the inset on Fig. 3.

The values of M_s obtained for samples with $x=0.8$ and $x=1.0$ are 79 emu/g and 74 emu/g, respectively, which is lower than the $CoFe_2O_4$ bulk value of 80.8 emu/g at 340 K.[3] This reduction of the saturation magnetization for each particle in the nanocrystalline $CoFe_2O_4$ powders may be attributed to structural distortions in the surface compared to the bulk.[19] It is possible that the cation site occupancy in nano-sized $CoFe_2O_4$ is different from the bulk, resulting in a reduced magnetic moment. In addition, a "dead" surface layer may exist in the nanoparticles, in which magnetic moments do not contribute to the magnetization. In fact, the thickness of this dead surface layer can be estimated[3] by $V_m/(V_m+V_s)=M_s/M_{bulk}$, where V_m is the effective "magnetic volume" of the particle, V_s is the dead surface layer, M_s is the saturation magnetization, and M_{bulk} is the bulk magnetization expected for the same temperature and magnetic field. Thus we found a surface layer thickness of approximately 5.3 Å for the $x=1.0$ sample, as shown in the inset on Fig. 4. This value is much lower than the published values of 10–16.9 Å (Ref. 20) and much higher than 1.0 Å (Ref. 21) found for similar nanostructured $CoFe_2O_4$ but having smaller particle sizes and synthesized by different methods.

However, for samples that have off-stoichiometric compositions (samples either rich on Fe^{3+} or on Co^{2+}), the low value of M_s for a given temperature may be attributed to the fact that these samples are not in the pure cobalt ferrite phase, having hematite and/or cobalt oxide impurities as shown by the x-ray diffraction patterns in Fig. 1. Also these samples have a dead surface layer much thicker than those samples that have stoichiometric compositions, as shown in

FIG. 1. X-ray diffraction patterns of powders of $Co_xFe_{(3-x)}O_4$ prepared by combustion reaction.
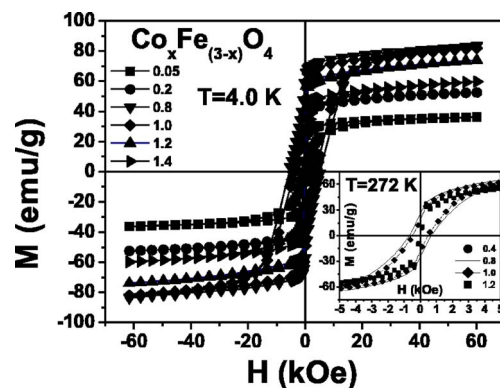
FIG. 3. Typical hysteresis loops of the $Co_xFe_{(3-x)}O_4$ samples (as prepared) obtained at room temperature. Inset on the right lower corner is the typical hysteresis loop for specimens at 272 K. Notice that for the sample with $x=1.2$, M_r and H_c are zero.
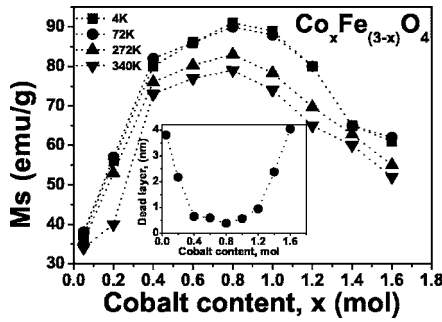
FIG. 4. Saturation magnetization (M_s) vs cobalt content of $Co_xFe_{(3-x)}O_4$ samples at various temperatures. The inset is the "dead" surface thickness vs cobalt content. The dotted lines are to guide the eye.

FIG. 6. Coercivity (H_c) vs cobalt content of $Co_xFe_{(3-x)}O_4$ samples at various temperature. The dotted lines are to guide the eye.

the inset on Fig. 4. In addition, samples rich in Fe^{3+} (for example, $x=0.05$, 0.2, and 0.4) may have more Fe^{3+} ions in the A site, making this material less ferrimagnetic and thus lowering the saturation magnetization.[22]

The temperature dependences of remanence (M_r) and coercivity (H_c) for all samples are plotted in Figs. 5 and 6, respectively. At 272 K, samples that have very off-stoichiometric compositions (samples either rich in Fe^{3+} or in Co^{2+}), M_r, and H_c are equal to zero, which is a characteristic behavior of superparamagnetism. This is a rather interesting result since the critical size of cobalt ferrite showing superparamagnetic relaxation at room temperature is not theoretically known. Empirical results show that cobalt ferrite in the size range of 10–30 nm (Ref. 23) shows no superparamagnetic relaxation up to room temperature. Furthermore it is reported[24] that the critical size of cobalt ferrite for superparamagnetic relaxation is roughly between 4 and 9 nm. The particle sizes of our samples are significantly larger than that, yet showing superparamagnetism. One interpretation is that our samples have wide particle size distribution, and the smallest particles may be dominant, thereby enhancing superparamagnetism. At temperatures as low as 4 K our samples did not exhibited superparamagnetism as expected since their particle sizes are larger than 9 nm.[23,24]

The remanence versus saturation magnetization ratio M_r/M_s drastically decreases with temperature for samples with $x=0.8$ and 1.0, as given in the inset on Fig. 5. At 4 K, M_r/M_s are approximately 0.63 and 0.66, for samples $x=1.0$ and 0.8, respectively, indicating that these nanoparticles of cobalt ferrite are characterized by cubic anisotropy, for
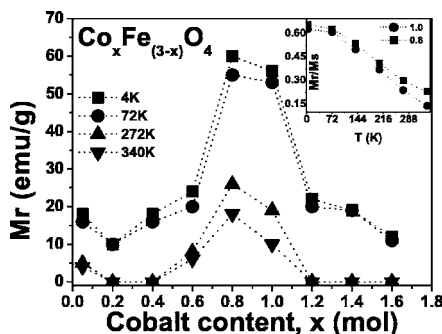
which theoretical M_r/M_s ratio is 0.83.[25] On the other hand, at 272 K, M_r/M_s are approximately 0.24 and 0.30 for sample $x=1.0$ and 0.8, respectively, which are lower than that for uniaxial particles, 0.5.[25] It may be attributed to the fact that saturation is not attained and also that the very small particles may form agglomerates (Fig. 2) consisting of closed magnetic circuits reducing the remanence. However, as saturation is not reached at 6 T in these particles, especially at higher temperature, the value of remanence to saturation ratio is not easy to interpret.

Overall, the magnetic properties, M_s, M_r, and H_c, of samples either rich in Fe^{3+} or Co^{2+} are drastically smaller than for pure samples with $x=0.8$ and 1.0. Even though the particle size of these off-stoichiometric samples is larger than approximately 30 nm they seemed to be superparamagnetic at 272 K. It also appears that the superparamagnetic behavior is dominated by small particles, but the total magnetization is dominated by large particles. Further studies to confirm the existence of superparamagnetic behavior in these systems are in progress.

FIG. 5. Remanence (M_r) vs cobalt content of $Co_xFe_{(3-x)}O_4$ samples at various temperatures. The inset is the reduced remanence (M_r/M_s) vs cobalt content. The dotted lines are to guide the eye.
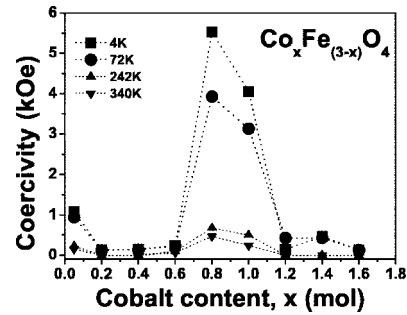
[1]H. Shenker, Phys. Rev. **107**, 1246 (1957).
[2]J. G. Lee *et al.*, J. Appl. Phys. **84**, 2801 (1998).
[3]M. Grigorova *et al.*,J. Magn. Magn. Mater. **183**, 163 (1998).
[4]L. Piraux *et al.* Appl. Phys. Lett. **65**, 2484 (1994).
[5]A. K. Giri *et al.*, Appl. Phys. Lett. **80**, 2341 (2002).
[6]K. E. Mooney *et al.*, Chem. Mater. **16**, 3155 (2004).
[7]R. T. Olsson *et al.*, Chem. Mater. **17**, 5109 (2005).
[8]M. Rajendran *et al.*, J. Magn. Magn. Mater. **232**, 71 (2001).
[9]V. Pillai and D. O. Shah, J. Magn. Magn. Mater. **163**, 243 (1996).
[10]C. Liu *et al.*, J. Am. Chem. Soc. **122**, 6263 (2000).
[11]Y. Ahn, E. J. Choi, S. Kim, and H. N. Ok, Mater. Lett. **50**, 47 (2001).
[12]S. R. Ahmed *et al.*, Mater. Res. Soc. Symp. Proc. **661**, KK 10.10.1 (2001).
[13]R. H. G. A. Kiminami and J. Kona, Powder and Particle **19**, 156 (2001).
[14]A. C. M. Costa *et al.*, J. Mater. Sci. **37**, 3569 (2002).
[15]S. R. Jain *et al.*, Combust. Flame **40**, 71 (1981).
[16]A. Franco Júnior *et al.*, J. Magn. Magn. Mater. **308**, 198 (2007).
[17]P. Sherrer, Nachr. Cöttinger Gesell. **2**, 98 (1918).
[18]D. H. Lee *et al.*, Solid State Commun. **96**, 445 (1995).
[19]J. Park *et al.*, Nature (London) **3**, 891 (2004).
[20]D. Lin *et al.*, J. Magn. Magn. Mater. **145**, 343 (1995).
[21]L. D. Tung *et al.*, J. Appl. Phys. **93**, 7286 (2003).
[22]R. A. McCurrie, *Ferromagnetic Materials: Structure and Properties* (Academic, London, 1994), pp. 132–139.
[23]Y. I. Kim, D. Kim, and C. S. Lee, Physica B **337**, 42 (2003).
[24]K. Haneda and A. H. Morrish, Appl. Phys. Lett. **63**, 4258 (1988).
[25]N. Moumen and M. P. Pileni, J. Phys. Chem. **100**, 1867 (1996).