Disproportionation of Cobalt Ferrite nanoparticles upon annealing

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Abstract. Size control of cobalt ferrite (CoFe$_2$O$_4$) nanoparticles is often achieved through annealing. To better understand the annealing process we have synthesized 5 nm CoFe$_2$O$_4$ nanoparticles using a co-precipitation technique. Characterization of the intrinsic magnetism of these nanoparticles using magnetometry and susceptometry shows typical CoFe$_2$O$_4$ nanoparticle behaviour [1]. The temperature evolution of the annealing process was examined using transmission Mössbauer spectroscopy. The Mössbauer data provide clear evidence for a disproportionation of the CoFe$_2$O$_4$ phase, beginning at around 500 K and continuing to evolve up to 800 K. Using a combination of Mössbauer spectroscopy and x-ray powder diffraction we show that annealing the CoFe$_2$O$_4$ nanoparticles not only results in a larger nanocrystallite size, 17 nm, but also a significant disproportionation into a mixture of residual CoFe$_2$O$_4$, CoO and α-Fe(Fe$_3$O$_4$) (the majority phase). Upon cooling back to room temperature from 825 K a magnetite-like component develops and by room temperature this phase accounts for 20% of the Mössbauer spectral area.

1. Introduction

Nanoscale cobalt ferrite (CoFe$_2$O$_4$) systems exhibit high coercivities due to a large cubic magnetocrystalline anisotropy. The typical saturation magnetization of CoFe$_2$O$_4$ nanocrystallites in combination with these high coercivities ($H_c \gtrsim 10$ kOe at 10 K) suggest that nanoscale CoFe$_2$O$_4$ could be a promising basis for permanent magnets, magnetic recording media, and even drug delivery applications. The eventual technological exploitation of CoFe$_2$O$_4$ nanoparticulate systems will require both a comprehensive understanding of the size dependence of the nanomagnetism and the ability to control the nanocrystallite size. A common method for preparing different sized nanocrystallites is thermal annealing which not only creates larger crystallites, but also results in dramatic changes in the nanomagnetism, such as unusual decreases in $H_c$ with increasing size [2, 3].

The altered magnetism of annealed CoFe$_2$O$_4$ nanocrystallites has been attributed to internal strain during the annealing process that creates an extra uniaxial anisotropy in addition to fanning modes of the magnetization [4]. Cation diffusion during the annealing process has also been postulated as a source of the unusual size-dependent trends in magnetic properties [5].

We have synthesized CoFe$_2$O$_4$ nanoparticles with an average crystallite diameter of ∼ 5 nm using a co-precipitation technique. Annealing these nanoparticles at 873 K...
Disproportionation of Cobalt Ferrite nanoparticles upon annealing for 10 hours in vacuum resulted in \( \sim 17 \) nm diameter particles. Magnetometry studies of the unannealed nanoparticles exhibited \( H_c \) ranging from \( \sim 13 \) kOe at 10 K to \( \sim 50 \) Oe at 400 K with a \( T \) dependence, and a saturation magnetization, \( M_s(T) \), that decreases linearly with increasing temperature. By contrast, the larger annealed CoFe\(_2\)O\(_4\) nanocrystallite system shows a linear \( H_c(T) \) with a reduced \( H_c \) of \( \sim 8 \) kOe at 10 K, a larger high temperature \( H_c \sim 400 \) Oe at 400 K and a Brillouin-like \( M_s(T) \) [1].

2. Experimental Methods

The CoFe\(_2\)O\(_4\) nanoparticles were synthesized using a co-precipitation method [6]. 0.4M of FeCl\(_3\)\( \cdot \)6H\(_2\)O (98% purity, Alfa Aesar) was mixed with a 0.2M solution of CoCl\(_2\) \( \cdot \)6H\(_2\)O (98% purity, Alfa Aesar). A 3M solution of NaOH (98% purity, Alfa Aesar) was then added dropwise to the metallic salt solution until a pH of 11.75 was reached. 50 \( \mu \)l of oleic acid (99% purity, Alfa Aesar) was added via rapid injection to coat the precipitate, thereby stopping nucleation and protecting against oxidation. The resulting solution was heated to 353 K while being stirred continuously for 1 h. After cooling to room temperature, the precipitate was separated and washed several times with water and methanol and then dehydrated for 10 h at 373 K. Cu–K\( \alpha \) x-ray diffraction on a PANalytical PW3830 was used to determine the phase composition of the nanoparticles. Refinement of the x-ray diffraction patterns was carried out using the FULLPROF/WinPlotr package [7, 8]. A Photocor Instruments static and dynamic light scattering (DLS) apparatus was used with a 25 mW Coherent solid state laser \((\lambda=632 \text{ nm})\) to measure the particle size and size distribution of a dilute suspension of nanoparticles in chloroform at room temperature. Magnetometry experiments were performed using Quantum Design PPMS and MPMS systems. Transmission Mössbauer measurements were made in constant acceleration mode with a 1 GBq \(^{57}\)CoRh source. The Wissel spectrometer was calibrated using \( \alpha \)-Fe at room temperature and all isomer shifts (IS) are quoted relative to the \( \alpha \)-Fe calibration. An ASA Mössbauer vacuum furnace was used to collect spectra at temperatures between 300 K and 830 K.

3. Results

In figure 1 (top) we show the x-ray diffraction pattern obtained at room temperature on a CoFe\(_2\)O\(_4\) sample which had been annealed at 550 K for 8 hours. The pattern shows that the annealing produces a mixture of the following phases: CoFe\(_2\)O\(_4\) (Space Group SG = Fd\(_3\)m #227), \( \alpha \)-Fe(Co) (SG = Im\(_3\)m #229), CoO (SG = Fm\(_3\)m #225) and an unidentified phase. The pattern is dominated by the two sharp peaks from NaCl formed during the co-precipitation process. In an attempt to identify the fourth phase we carried out a trial indexation using the DICVOL program [9]. The best match to the set of unidentified peaks was with an orthorhombic cell with lattice parameters \( a = 9.93 \text{ Å}, b = 3.04 \text{ Å, and } c = 2.92 \text{ Å} \). A tetragonal cell with lattice parameters \( a = 9.21 \text{ Å, and } c = 3.85 \text{ Å} \) was the second-best match to the observed peaks. We note that indexation programs such a DICVOL only return the minimum-volume cell which reproduces the peak positions. Consequently, we cannot rule out super-cells of these two possible cells. This fourth phase remains unidentified at present.

In figure 1 (bottom) we show a comparison of the \(^{57}\)Fe Mössbauer spectra obtained at room temperature before and after the annealing run. The pre-annealed spectrum...
is dominated by a doublet (IS = +0.33(2) mm/s; QS = 0.82(2) mm/s) which accounts
for about ∼ 80 % of the spectral area, assuming, for simplicity, the same f-factor for
all components. This doublet is due to the unblocked CoFe₂O₄ nanoparticles (In our
previous study we deduced a blocking temperature of 380(20) K [1]). The remaining
∼ 20 % of the spectrum is the still-blocked CoFe₂O₄ component with a hyperfine field
of 45.9(1) T, characteristic of the spinel-type structure of CoFe₂O₄.

The post-annealed room-temperature spectrum is markedly different from the
pre-annealed spectrum. The dominant component after annealing is now α-Fe(Co),
with an average hyperfine field of 35.9(1) T. We can estimate the Co content in this
α-Fe phase from the measured ⁵⁷Fe hyperfine field. The measured value of 35.9(1) T
is larger than the value of 33.0 T found in pure α-Fe and translates to a Co content
either about 15 at% Co or 38 at% Co [10]. Unfortunately, as pointed out by Johnson
et al. [10], the isomer shifts are small and unable to distinguish these two options.
The minor component in the post-annealed spectrum is most likely a maghemite-like
γ − (Co, Fe)₂O₃ phase or a magnetite-like (Co, Fe)₃O₄ phase with an average hyperfine
field of 50.5(2) T and an IS of +0.42(3) mm/s, consistent with iron oxide nanoparticles
with cobalt present. This phase develops at around 600 K during the cooling run from
825 K. At this stage, however, we cannot unambiguously identify this component due
to a variety of factors such as the nanoparticulate nature of the sample and the Co
content.

We can identify the temperature range in which disproportionation commences
by comparing the ⁵⁷Fe Mössbauer spectra obtained at 423 K and 573 K during the
heating run (figure 1 (bottom)). The development of the broad α-Fe(Co) component
is quite clear in the 573 K spectrum. The spectrum at 423 K shows that the CoFe₂O₄
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Figure 2. $^{57}$Fe Mössbauer spectra of CoFe$_2$O$_4$ obtained at various temperatures from 623 K to 823 K during the heating run, together with the corresponding hyperfine field distributions.

phase is virtually fully unblocked at this temperature.

In figure 2 we show the $^{57}$Fe Mössbauer spectra obtained at various temperatures between 623 K and 823 K during the annealing run. Due to the nanoparticulate nature of the samples and the significant solution of Co in the emerging $\alpha$-Fe phase, we fitted the spectra using the Le Caër-Dubois hyperfine field distribution method [11]. In figure 2 we also show the hyperfine field distributions for the $\alpha$-Fe(Co) spectral component. The peak in the $\alpha$-Fe(Co) field distribution is at 32.7 T at 623 K and decreases slightly to 32.1 T by 823 K. The sub-spectral area of the $\alpha$-Fe(Co) component is 59(4) % at 573 K and reaches a plateau of 92(3) % at around 770 K.

In conclusion, annealing of nanoparticulate CoFe$_2$O$_4$ leads to a disproportionation of the sample, commencing between 423 K and 573 K. The principal phase in the annealed sample is $\alpha$-Fe(Co).

Acknowledgments

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Canada Foundation for Innovation. JMC acknowledges support from the Canada Research Chairs programme.

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