The Effect of Substituting Fe with Co on the Phase Behavior and Magnetic Anisotropy of FePt Nanoparticles

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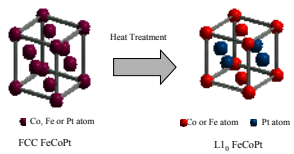
Project Objectives

- Discover new chemistry to prepare FeCoPt nanoparticles
- Convert the particles to the $L1_0$ phase
- Determine the effect of added Co on the magnetic properties

The Phase Transformation Problem



X-ray Diffraction Curves

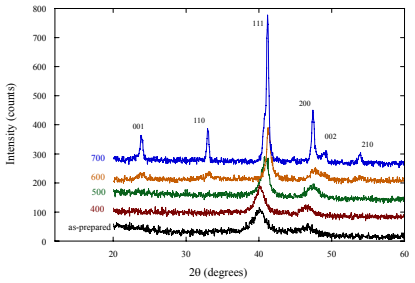


Fig. 1. Effect of annealing temperature on the x-ray diffraction curves for the particles prepared using the hydrazine route

Nanoparticle Synthesis

The Carbonyl Route

$Pt(acac)_2$ (0.50 mmol) + $Co(acac)_2$ (0.25 mmol)

+ 1,2-hexadecanediol (1.50 mmol) + phenyl ether (30 mL)

↓ heat to 120ºC

Add $Fe(CO)_5$ (0.25 mmol), oleic acid (0.5 mmol) and oleylamine (0.5 mmol)

↓ heat to reflux and reflux for 30 min

Black Dispersion

↓ cool to room temp., add ethanol, centrifuge

$Co_{31}Fe_{34}Pt_{34}$ Nanoparticles

The Superhydride Route

$Pt(acac)_2$ (0.50 mmol) + $Co(acac)_2$ (0.25 mmol) + $Fe(acac)_3$ (0.25 mmol)

+ 1,2-hexadecanediol (1.50 mmol) + phenyl ether (25 mL)

↓ heat to 100ºC

Add oleic acid (0.16 mL) and oleylamine (0.17 mL)

↓ heat to 200ºC

Add 2.5mL of a 2 molar solution of lithium triethylborohydride in tetrahydrofuran

↓ heat to reflux and reflux for 20 min

Black Dispersion

↓ cool to room temp., add ethanol, centrifuge

$Co_{16}Fe_{22}Pt_{63}$ Nanoparticles

The Polyol Route

$Pt(acac)_2$ (0.50 mmol) + $Co(acac)_2$ (0.25 mmol) + $Fe(acac)_3$ (0.25 mmol)

+ 1,2-hexadecanediol (1.50 mmol) + phenyl ether (25 mL)

↓ heat to 105ºC

Add oleic acid (0.5 mmol) and oleylamine (0.5 mmol)

↓ heat to reflux and reflux for 30 min

Black Dispersion

↓ cool to room temp., add ethanol, centrifuge

$Co_{20}Fe_{22}Pt_{58}$ Nanoparticles

The Hydrazine Route

$H_2PtCl_6 \cdot 4H_2O$ (0.4 mmol) + $FeCl_2 \cdot 4H_2O$ (0.2 mmol) + $Co(OAc)_2$ (0.2 mmol)

+ sodium dodecylsulfate (0.8 mmol) + water (20 mL)

↓ stir to dissolve

Add hydrazine hydrate (8 mmol)

↓ heat at 70ºC for 3 hr

Black Dispersion

↓ cool to room temp., add ethanol (55 mL), centrifuge

$Co_{28}Fe_{34}Pt_{36}$ Nanoparticles

X-ray Diffraction Results

Carbonyl Route	a (pm)	c (pm)	<D> (nm)	S
As-prepared	387		3.5	
400ºC	390		3.5	
500ºC	392		4.0	
600ºC	386	384	11	0.66
700ºC	386	385	14	0.67
Superhydride Route	**a (pm)**	**c (pm)**	**<D> (nm)**	**S**
As-prepared	386		1.3	
400ºC	387		6.2	
500ºC	388		8.4	
600ºC	386		10	
700ºC	385	385	14	0.67
Polyol Route	**a (pm)**	**c (pm)**	**<D> (nm)**	**S**
As-prepared	387		1.1	
400ºC	389		7.2	
500ºC	387		12	
600ºC	386	386	21	0.54
700ºC	386	385	28	0.80
Hydrazine Route	**a(pm)**	**c(pm)**	**<D> (nm)**	**S**
As-prepared	390		3.7	
400ºC	389		5.0	
500ºC	383		6.5	
600ºC	382	372	12	0.77
700ºC	384	373	31	0.87

Effect of Heat Treatment Temperature on the Magnetic Properties

FePt

Carbonyl Route	H_c (kOe)	H_0 (kOe)	KV/kT
500ºC	2.8	9.0	90
550ºC	8.8	13	251
600ºC	13.3	16.0	598

FeCoPt

Superhydride Route	H_c (kOe)	H_0 (kOe)	KV/kT
400ºC		2.11 ± 0.01	45.0 ± 0.2
500ºC	1.0	4.10 ± 0.06	60 ± 2
600ºC	0.25	7.33 ± 0.03	145 ± 2
700ºC	2.9	4.14 ± 0.01	198 ± 3
Hydrazine Route	**H_c (kOe)**	**H_0 (kOe)**	**KV/kT**
400ºC		3.6 ± 0.2	26.8 ± 0.2
500ºC	1.2	6.63 ± 0.02	102 ± 1
600ºC	4.8	7.77 ± 0.01	269 ± 2
700ºC	3.2	4.12 ± 0.02	701 ± 44

Magnetic Characterizations

Magnetic hysteresis curves (plots of magnetization as a function of applied magnetic field) were obtained on an alternating gradient magnetometer. An example is shown in fig. 2. The values of coercivity reported below were obtained from the hysteresis curves. In a different experiment, values of remanence as a function of time were obtained. The data fit to Sharrock's Law (see fig. 3 and equation 1), where f0 is the attempt frequency (10^9 Hz). The fit to Sharrock's Law gave values intrinsic coercivity (H_0) and thermal stability factor (K_uV/kT).

$$H_{CR} = H_0\{1-[\frac{kT}{K_uV}\cdot\ln(f_0t)]^{2/3}\}$$

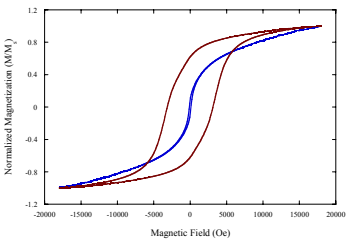


Fig. 2. Magnetic hysteresis curves for the particles made by the hydrazine route, as-prepared (black) or after annealing at 700ºC (red)

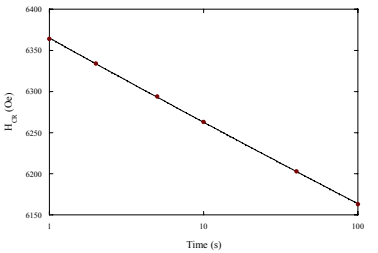


Fig. 3. Fit of remanence data for the film containing particles made by the hydrazine route and annealed at 600ºC

Conclusions

- We have four different procedures to make FeCoPt nanoparticles – the carbonyl procedure was reported earlier by Chen and Nikles (*Nano Letters* **2002**, 2(3), 211-214), the other three are new procedures.
- Adding Co lowered the order-to-disorder transformation temperature and heating at 700ºC gave some fcc phase in addition to the $L1_0$ phase
- Adding Co to $L1_0$ FePt lowered the anisotropy, giving films with much lower coercivity and lower values of intrinsic coercivity.

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