

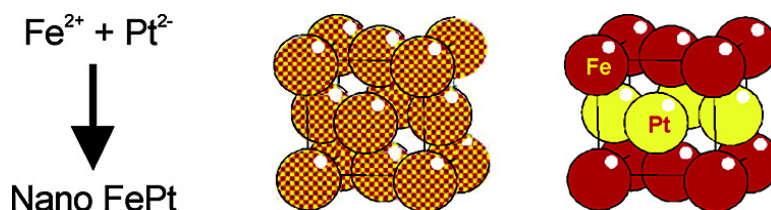
Communication

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A Synthetic Route to Size-Controlled fcc and fct FePt Nanoparticles

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Self-assembled L1₀ FePt nanoparticle superlattices have recently been identified as promising candidates for magnetic storage applications because of their large uniaxial magnetocrystalline anisotropy [$K_v \cong 7 \times 10^6$ J/m³] and good chemical stability.¹ Calculations indicate that particles as small as 2.8 nm have a sufficiently high *KV* product to be exploited for permanent data storage, leading to significant advances in hard disk drive areal densities over currently used materials.

Chemical routes using high-temperature solution-phase conditions are the most practical and widely chosen fabrication method to prepare monodisperse metal particles.² FePt nanoparticles are commonly synthesized by either the simultaneous decomposition of iron pentacarbonyl, Fe(CO)₅, and reduction of platinum acetylacetonate, Pt(acac)₂, in the presence of polyol reducing agents³ or by co-reduction of an iron and platinum salt.⁴ Both syntheses are performed in the presence of surfactant molecules to give particle size control. The as-synthesized particles are mostly reported to have an Fe/Pt disordered face centered cubic (fcc) structure and are superparamagnetic in nature. Due to its volatility at the synthesis temperature, an excess of Fe(CO)₅ is typically required to achieve materials with a 1:1 Fe:Pt ratio, and precise stoichiometry of materials under a certain set of reaction conditions can only be achieved empirically.

To obtain the magnetically interesting Fe/Pt ordered face centered tetragonal (fct) phase (the so-called L1₀ structure), the as-synthesized nanoparticles typically had to be heated to temperatures of 550 °C or more. At these annealing temperatures, however, the surfactants coating the particles break down, leading to a reduction in interparticle spacing, which eventually causes agglomeration of the particles, and a dramatic increase in particle size dispersion. This hinders their performance as high-density recording materials. Different methods have been attempted to lower the FePt phase transition temperature (*T_i*) and avoid particle sintering or to establish a direct route to fct nanoparticles. Introduction of a third metal, such as Cu,⁵ Ag,^{5,6} Zr,⁷ Au,⁵ and Al,⁸ into sputtered FePt alloys has lowered *T_i* to around 400 °C. Ag has also been doped into chemically produced nanoparticles, though these ternary nanoparticles have generally been shown to retain the problems of agglomeration or decomposition on further annealing at higher temperatures.⁶ Jeyadevan et al.⁹ suggested a first direct synthesis of fct FePt nanoparticles using a chemical route. The reduction of platinum and iron acetylacetonates in tetraethylene glycol at 300 °C has led to the formation of partial fct FePt alloys with a particle size of 5–10 nm. Recently, Kang et al.¹⁰ reported the preparation of partially ordered Fe₅₃Pt₄₇ nanoparticles by the simultaneous decomposition of Fe(CO)₅ and Pt(acac)₂ in hexadecylamine at 360 °C. These particles are only partially ordered, display small room

temperature coercivity, and little detail has appeared on their characterization to date.

To gain control over both the stoichiometry and internal structure of FePt nanoparticles, we have investigated the use of Collman's reagent,¹¹ Na₂Fe(CO)₄, as a reducing agent for Pt(II) in the preparation of FePt. This method has two potential advantages over other routes. First, as the reaction can be formally written as Fe²⁺ + Pt²⁺ → FePt, with the electrons required to reduce Pt(II) located on the Fe source rather than on an additional reducing agent, attainment of the ideal 1:1 stoichiometry is assured. Second, the reduction step that is key to alloy formation requires the simultaneous presence of Fe and Pt ions to occur, forcing the product alloy to be intimately mixed on an atomic scale. This is distinct to other methods requiring simultaneous reduction or reduction/decomposition of two metal sources where phase separation or the formation of core-shell particles could take place.

In a typical reaction, a 1:1 molar ratio of Pt(acac)₂, Na₂Fe(CO)₄, and an excess of surfactants was sonicated and then heated at reflux in hydrocarbon solvents at 330 °C or greater under an inert atmosphere. The phase type (fcc/fct) of FePt nanoparticles, their size, and their magnetic properties could be controlled by various parameters, such as solvent type, nature and concentration of surfactants and stabilizers, heating temperature, and purification process.

We find that long chain hydrocarbons, such as nonadecane, docosane, or tetracosane, are stable solvents for high-temperature reactions, allowing synthesis to be performed up to 389 °C; ether-type solvents, as used previously in FePt syntheses, are more easily decomposed at high temperatures. We note that attempting to follow conventional literature routes using Fe(CO)₅ in these hydrocarbon solvents can lead to violent/uncontrolled reactions.

Figure 1 shows X-ray diffraction patterns of FePt particles prepared using nonadecane as solvent at 330 °C and oleic acid as surfactant. Under these conditions, fcc FePt nanoparticles are formed with a particle size under 3 nm (see Supporting Information). Figure 1 also shows a series of in situ powder XRD patterns recorded under a 5% H₂/Ar atmosphere at different temperatures. Upon heating, the growth of the (001) and (010) superlattice peaks of the fct phase (at ~24 and ~33° 2θ) is observed. These peaks can be seen from temperatures as low as 703 K (430 °C), increase in intensity up to 903 K, and are a direct indication of Fe/Pt site ordering in the material. Rietveld refinement of the data of Figure 1 allow the degree of fcc → fct ordering to be followed as a function of temperature. By 903 K, the preferential site occupancy of Fe/Pt on an Fe site rises to 87/13% (50/50% for the initial fcc material). Some particle agglomeration occurs, as evidenced by decreasing X-ray peak widths with temperature. However, in our hands, the degree of particle growth that occurs is significantly less than that for materials prepared by previous literature routes; peak widths in Figure 1 suggest that particles remain under 4 nm at 903 K.

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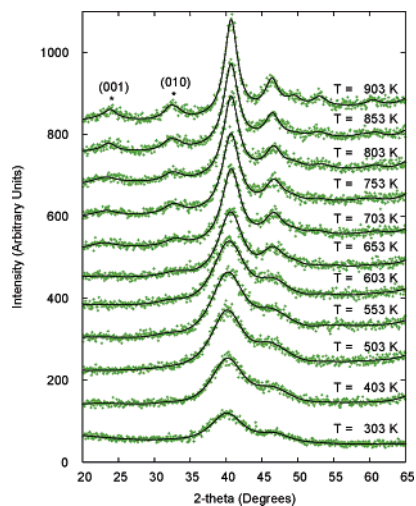


Figure 1. Eleven diffraction patterns recorded on a sample of as-synthesized fcc FePt as a function of temperature. Patterns have been offset vertically for clarity. Solid line is a Pawley fit to the experimental data and intended as a guide to the eye. Selected superlattice peaks indicating $L1_0$ ordering are labeled (relative to fcc cell) on the final scan. Indications of ordering are visible from 703 K. Diffraction patterns were collected on a Bruker D8 diffractometer using Cu $K\alpha$ radiation (1.5406 Å) with an Anton Paar htk1200 furnace under a flow of 5% H_2 in Ar.

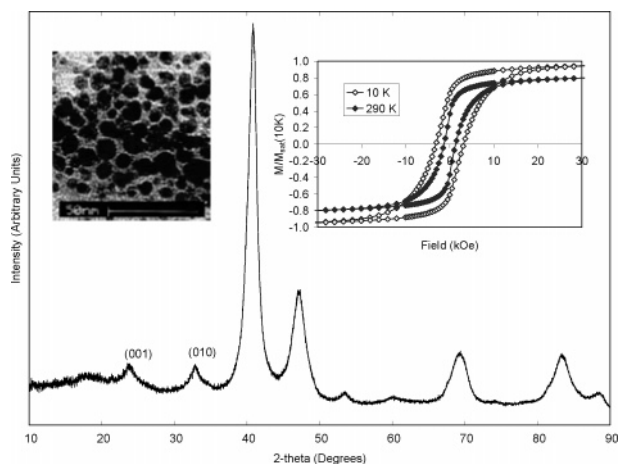


Figure 2. XRD pattern of directly synthesized fct FePt nanoparticles, which have had no postsynthetic heat treatment. (100) and (010) ordering peaks are clearly seen. Hysteresis loops of directly synthesized fct particles at 10 and 290 K and TEM image of particles shown as inserts. The TEM image shown represents a $\sim 85 \times 85$ nm region.

Magnetic measurements were performed on the as-synthesized nanoparticles using a Quantum Design SQUID magnetometer. The magnetic data indicated superparamagnetism ($H_c = 0$ Oe) with a blocking temperature of about 15 K, which is consistent with that expected from the size and structure of the particles as determined by X-ray diffraction.

Significantly, our synthetic methods have been extended to produce ordered fct particles directly in solution, allowing the direct preparation of the magnetically important phase without further processing. Figure 2 shows the X-ray diffraction pattern of an FePt sample prepared in tetracosane at 389 °C using an oleylamine surfactant (1:1 surfactant-to-metal ratio) without any postsynthesis annealing. Strong ordering peaks are present at ~ 24 (001) and 33° (010) 2θ , confirming Fe/Pt order. Selected area electron diffraction confirms that individual 6–8 nm particles show the same ordering peaks. Rietveld refinement confirms the Fe/Pt site ordering, with the material shown in Figure 2 showing 73% site ordering of metal cations. EXAFS experiments at the Fe edge also confirm local Fe/

Pt ordering. EDAX analysis of individual particles and clusters of particles and Rutherford Back Scattering of bulk samples confirm the Fe:Pt 1:1 stoichiometry within experimental error. Magnetic hysteresis loops of samples produced directly in solution (Figure 2) show a coercivity of ~ 1300 Oe at 290 K and 3100 Oe at 10 K.

By using high boiling solvents, such as tetracosane, one can also convert fcc particles previously synthesized by this route to the fct phase in solution in the presence of amine surfactants (Supporting Information Figure S2). A small growth in particle size is generally observed during this process.

The general synthetic route to FePt nanoparticles presented here provides a straightforward and stoichiometrically controlled synthesis. By using this route with nonadecane as the solvent, it is possible to produce fcc FePt nanoparticles which can be converted to the fct structure at low temperatures with minimal agglomeration/sintering. The size of FePt particles and their internal structure can be controlled by the variation of solvent, surfactant, and growth inhibitor used. Most significantly, FePt nanoparticles with the fct structure can be synthesized directly in tetracosane without the need to anneal the material to temperatures where sintering may occur; such particles can thus be manipulated in solution. We believe that this synthetic method can be readily extended to the preparation of a number of metal alloys of controlled size, stoichiometry, and physical properties.

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Supporting Information Available: Full synthetic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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