

Synthesis and structural study of L1₀-FePt nanoparticles*

Majid FARAHMANDJOU

*Islamic Azad University, Varamin Pishva Branch, Department of Physics,
Varamin-IRAN*

e-mail: farahmandjou@iauvaramin.ac.ir

Received 15.10.2010

Abstract

A comparison of the synthesis and structural properties of magnetic FePt nanostructures is presented. The FePt nanoparticle system is an excellent candidate for ultrahigh-density magnetic recording. Monodisperse FePt nanoparticles were synthesized by the superhydride method. The composition of nanocrystals was determined by energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) images showed monosized FePt nanoparticles with a diameter of 3.5 nm. The average distance between the monodisperse particles was nearly 2 nm. In order to determine the stability of nanoparticle colloidal solution, a measure of stability was defined via spectrophotometric analysis. The magnetic measurement showed that as-made FePt was first superparamagnetic at room temperature; after annealing at 600 °C for 4 h, the nanoparticles gained the ability to phase transition to L1₀-FePt, and the coercivity of the nanocrystals was raised to 6.5 kOe.

Key Words: L1₀ phase, FePt nanoparticles, superparamagnetism, coercivity, nanocrystals

Introduction

Hard magnetic nanoparticles have attracted much attention as future ultrahigh-density magnetic recording media (Nguyen, 2005). The FePt nanoparticles in the tetragonal L1₀ chemically ordered phase have high uniaxial magnetic anisotropy ($K_u \sim 8 \times 10^7$ erg cm⁻³) along the tetragonal *c*-axis, so the thermal stability criteria for magnetic recording media can be satisfied for magnetic nanostructures, resulting in an enormous areal storage density of about 50 Tbit in⁻² (Liu et al., 2006; Sun, 2006). However, one of the crucial parameters limiting the maximum achievable areal density is the size distribution in the array of magnetic nanostructures.

The FePt nanoparticles (NPs) have the ability to form a chemical order fct phase, L1₀, after heat treatment (Nguyen et al., 2005; Liu, 2006). In this phase, the coercivity is raised up to a tesla order of magnitude (Elkins et al., 2005; Sun, 2006). Fabrication of NPs by chemical method makes it possible to produce a self-organized, long-ordered superlattice on the substrate (Sun, 2006). For application purposes in increasing the density of magnetic recording, these nanoparticles eliminate 2 major limitations: exchange coupling and superparamagnetism (Wang and Taratorin, 1999).

*Paper presented at the 6th Nanoscience and Nanotechnology Conference (NanoTRVI), İzmir, Turkey, June 15-18, 2010.

In the thin films method, the nanolayers of Fe and Pt are sputtered on a carbon layer, and then, by annealing, the FePt nanoparticles are diffused into a carbon matrix (Christodoulides et al., 2003). In this approach, the particles have wide distributions of size and distance. A chemical synthesis leads to the forming of monosized metallic nanoparticles by adding superhydride in temperature reactions above 200 °C in the presence of oleic acid and oleylamine (Sun et al., 2003). The stable colloidal system of the NP suitable solution prepared by polymeric stabilizers can make ordered arrays of NPs on a single crystal substrate (Vazquez et al., 2004; Acet et al., 2005).

In regard to the magnetic movement of FePt nanoparticles, the agglomeration of the particles is important. To prevent agglomeration, nanoparticles should be covered by surfactants to stabilize the system and, therefore, eliminate the exchange coupling between them (Vazquez et al., 2004). When the FePt stable colloidal system is dried on a substrate, equal space between NPs is achieved as a result of the equilibrium condition (Scherer et al., 2005). For stabilizing the magnetic single domain particles in a nonpolar solvent, one can use a type of polymer molecule with a polar head and an apolar tail (Ahner et al., 2004; Shukla et al., 2007).

In the present work, FePt monosized NPs were fabricated with a 3.5 nm diameter. After purification, the NPs were dispersed in hexane with different amounts of oleic acid and oleylamine stabilizers. The structural and magnetic properties were studied by XRD and VSM analysis.

Experimental Details

FePt NPs were prepared by the following method, as reported by Sun et al (2003). The synthesis of NPs involves the reduction of Pt(acac)₂ (197 mg) and FeCl₂.4H₂O (139 mg) in the presence of 1,2-hexadecanediol (520 mg). By adding superhydride (LiBEt₃H) under a N₂ atmosphere at 200 °C, followed by refluxing at 245 °C, FePt nanoparticles were formed. The black reaction mixture was cooled to room temperature and then combined with ethanol to remove the impurity.

Afterwards, the product was precipitated and separated by centrifugation (6000 rpm, 10 min). The NPs were then dispersed in hexane in the presence of different values of renewed surfactant. Any undissolved material was removed by centrifugation. After the 2 stages of purification, 12 dispersion solutions of NPs, each in 7 mL of hexane, were prepared with 4 different values of surfactant.

A VARIN Cary 500 UV-Vis-NIR spectrophotometer system was used for comparing the concentration of colloidal solutions as a measure of the stability of the NPs. For this purpose, transmission was measured for colloidal solutions. Energy dispersive spectroscopy (EDS) (15 kV) was used to determine the composition of the NPs. The specification of size and shape of the NPs, the distances between them, and their size distribution were examined by TEM analysis using a Philips EM 208 TEM (100 kV) with a resolution of 200 kX. The samples were each annealed in a 90% Ar + 10% H₂ atmosphere at 600 °C for 4 h. X-ray diffraction measurements were conducted to determine the NPs' structure, using a Seifert system with Cu-K_α radiation ($\lambda = 1.54 \text{ \AA}$). The magnetization of the FePt samples in a variable magnetic field was measured using a vibrating sample magnetometer (VSM).

Results and Discussion

Figure 1 shows a characteristic spectrum collected by EDS analysis. By comparing the area under each peak to a set of standards with known element concentrations, the concentration of the elements could be quantified,

and the chemical formula gave an Fe:Pt stoichiometry of 68:32.

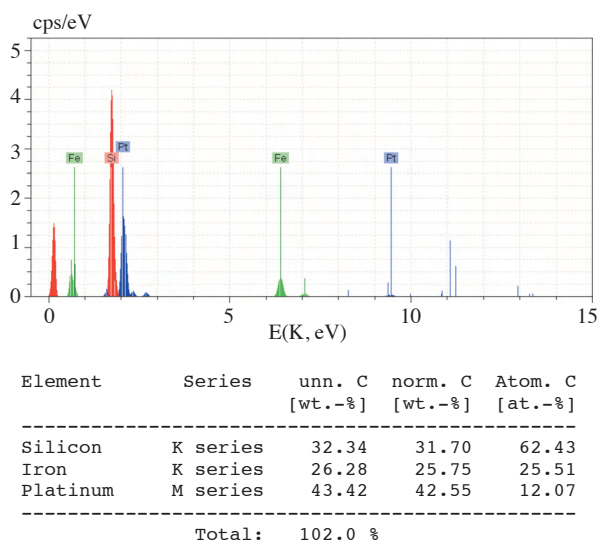


Figure 1. Energy dispersive spectroscopy (EDS) pattern of nanoparticles.

Figure 2 shows the XRD patterns for the FePt nanoparticles before and after annealing. Before annealing, the structure of the NPs was fcc. The large width of the peaks (Figure 2a) indicated that the particles were in nanometer scale. After annealing under a flow of 90% Ar + 10% H₂, extra peaks appeared. These peaks provide evidence of a chemical ordering phase (L1₀) transition. The results of magnetic measurements before and after heat treatment indicated that the as-made FePt was first superparamagnetic at room temperature, and after annealing at 600 °C for 4 h, the coercivity was raised to 6 kOe. These results confirm the suitable magnetic property of the nanoparticles.

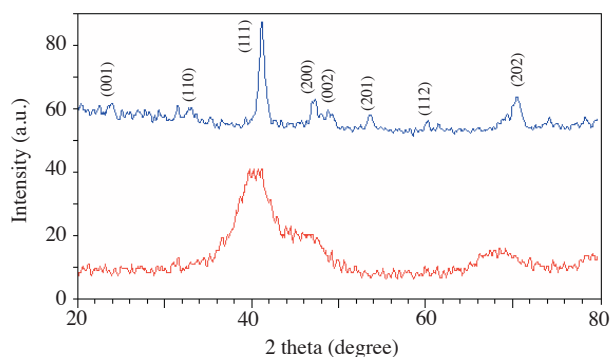


Figure 2. X-ray diffraction ($\lambda = 1.54 \text{ \AA}$, Cu-K α radiation) pattern of a) as-prepared and b) annealed FePt.

Figure 3 show the TEM images of the as-synthesized fcc FePt particles. Figures 3a and 3b reveal 2 different stability conditions. In Figure 3a, the sample was prepared without oleic acid surfactant in the centrifugation stage. It can be seen that some FePt grains were connected to each other and formed chains as a result of interactions. On the contrary, in Figure 3b, the dispersity of particles is proportionally uniform. In fact, oleic acid and oleylamine molecules were attached to the NPs and established a layer around each particle to prevent the NPs from approaching each other, assisting the monodisperse formation of particles.

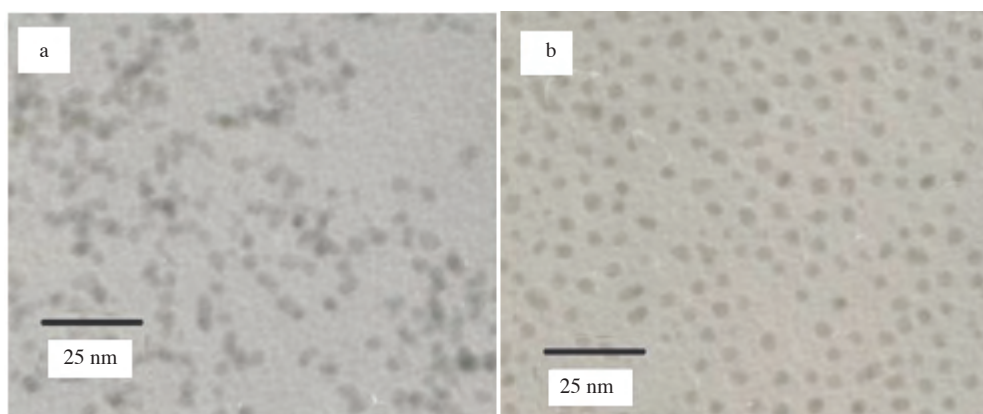


Figure 3. TEM images of the FePt nanoparticles after evaporation of hexane a) without and b) with oleic acid, respectively.

Figure 4 shows the size measurement of 100 randomly selected particles. TEM images show a narrow size distribution (Figure 3b). Fitting it with a log normal curve leads to a measured mean diameter of 3.5 nm, with standard deviation of about 10%.

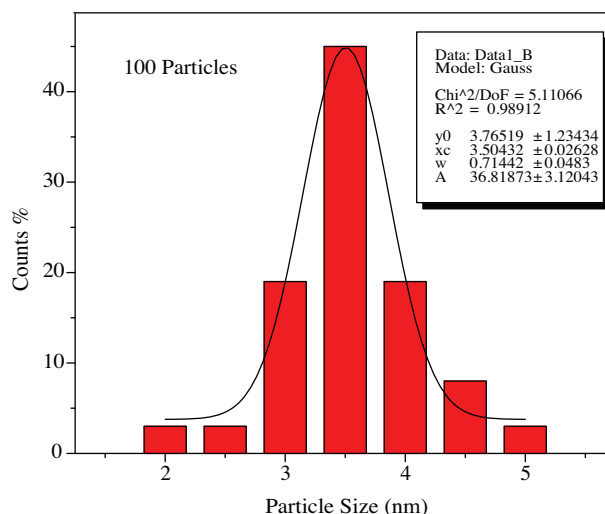


Figure 4. Particle diameter histogram of fcc FePt NPs; the line plotted corresponds to fit using a log normal distribution.

Spectrophotometric analysis showed that another effect of surfactants for colloidal samples is to prevent the metal NPs from precipitation by the transmittance spectra for different colloidal solutions of NPs. In the Table, using spectrophotometric analysis, the surfactant concentration and the transmittance percentage for wavelength 1572 nm of the 4 colloidal solutions are compared. T is the transmission of solution samples based on the surfactant ratio, ΔT is the transmission difference between hexane and solution, and $\Delta T/T$ is proportional to the FePt NPs' concentration of colloidal solution. The FePt nanoparticles used in each of these solutions consisted of the same relative amount of particles in hexane solution, realizing that solutions b_1 and b_2 were relatively transparent and metal particles were precipitated in them due to the absence of surfactants on their surface. On the other hand, solutions b_3 and b_4 had more adsorption ability and their colloidal solutions were

stable thanks to sufficient surfactant pairs. The TEM image of solution b_4 (Figure 3b) also indicates a suitable dispersity of these NPs.

Table. The data obtained using spectrophotometric analysis for different surfactant concentrations of FePt nanoparticles solutions.

Solution samples	Oleic Acid (μL)	Oleylamine (μL)	T	ΔT	$(\Delta T/T)$ %
Hexane	2	1	82.615	0	0
b_1	0	0	73.834	8.781	10.9
b_2	0	4	66.264	16.351	19.8
b_3	6	4	27.532	55.083	66.7
b_4	10	5	25.463	57.152	69.2

The results of magnetic measurements before and after heat treatment (Figure 5) indicate that the as-made FePt sample was first superparamagnetic at room temperature (Figure 5a); after annealing under an Ar atmosphere at 600 °C for 4 h, the saturation magnetization increased to 50 emu/g and coercivity to 6 kOe (Figure 5b). This high coercivity is a consequence of the magnetocrystalline anisotropy in the $L1_0$ phase for annealed FePt nanoparticles.

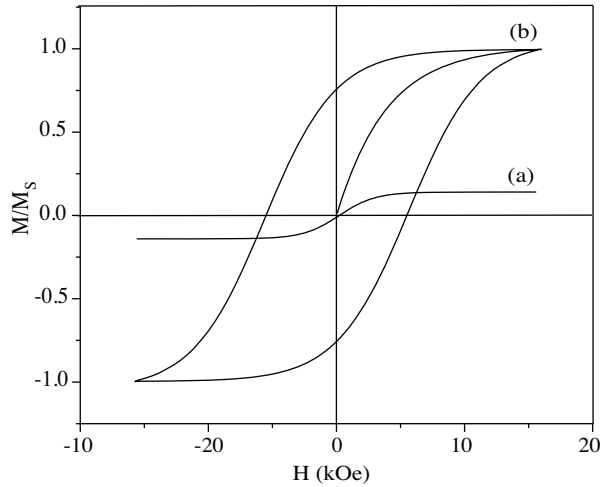


Figure 5. Magnetic hysteresis loops of sample b_3 , a) as-synthesized and b) annealed FePt nanoparticle.

Conclusion

The magnetic results before and after heat treatment for FePt nanoparticles indicate that the as-made FePt nanoparticles were first superparamagnetic at room temperature, and after annealing under an Ar atmosphere at 600 °C for 4 h, the saturation magnetization increased to 50 emu/g. These results confirm the suitable magnetic property of the particles, with a coercivity of 6 kOe.

Acknowledgments

This work was supported in part by the Physics Research Center, Science and Research Campus at Islamic Azad University, and the Center of Excellence in Complex Systems and Condensed Matter (CSCM) at Sharif University of Technology.

References

- Acet, M., Mayer, C., Muth, O., Terheiden, A. and Dyker, G., "Formation of Extended Ordered Monolayers of FePt Nanoparticles", *J. Cryst. Growth*, 285, 365-370, 2005.
- Christodoulides, A.J., "Intrinsic and Hysteresis Properties of FePt Nanoparticles", *Phy. Rev. B*, 68, 054428-054433, 2003.
- Elkins, K., Li, D., Poudyal, N., Nandwana, V., Jin, Z., Chen, K. and Li, P.J., "Monodisperse Face-Center Tetragonal FePt Nanoparticles with Giant Coercivity", *J. Phys. D: Appl. Phys.*, 38, 2306-2311, 2005.
- Liu, P.J., Elkins, J., Li, D., Nadwana, V. and Poudyal, N., "Phase Transformation of FePt Nanoparticles", *IEEE Trans. Magn.*, 42, 3036-3041, 2006.
- Nguyen, N.H., Howard, M.E.L., Giblin, R.S., Tanner, K.B. and Terry, I., "Synthesis of Monodispersed fcc and fct FePt/FePd Nanoparticles by Microwave Irradiation", *J. Mater. Chem.*, 15, 5136-5142, 2005.
- Scherer, C. and Neto, F.A., "Ferrofluids: Properties and Applications", *Braz. J. Phys.*, 35, 718-723, 2005.
- Sellmyre, D. and Skomski, R., "Advanced Magnetic Nanostructures", Springer, 2006.
- Shukla, N., Ahner, J. and Weller, D., "Dip-Coating of FePt Nanoparticle Films: Surfactant Effects", *J. Magn. Magn. Mater.*, e1349, 272-277, 2004.
- Shukla, N. and Svedberg, B.E., "Surfactant Isomerization and Dehydrogenation on FePt Nanoparticles", *Colloids. Surf. A*, 301, 113-117, 2007.
- Sun, S., "Recent Advances in Chemical Synthesis, Self-Assembly, and Applications of FePt Nanoparticles", *Adv. Mater.*, 18, 393-403, 2006.
- Sun, S., Anders, S., Thomas, T., Baglin, J.E.E., Hamann, F.H., Murray, C.B. and Terris, B.D., "Controlled Synthesis and Assembly of FePt Nanoparticles", *J. Phys. Chem. B*, 107, 5419-5426, 2003.
- Vazquez, M., Luna, C., Morales, P.M., Sanz, R., Serna, J.C. and Mijangos, C., "Magnetic Nanoparticles: Synthesis, Ordering and Properties", *Physica B*, 354, 71-77, 2004.
- Wang, X.S. and Taratorin, M.A., "Magnetic Information Storage Technology", Academic Press, New York, 1999.