

General Strategy for Direct Synthesis of L1₀ Nanoparticle Alloys from Layered Precursor: The Case of FePt

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The chemically ordered L1₀ FePt alloy has gained a lot of interest in ultrahigh density magnetic recording¹ and permanent-magnet nanocomposite² because of its large uniaxial magnetocrystalline anisotropy ($K_u \approx 7 \times 10^6 \text{ J/m}^3$).³ Films of FePt nanoparticles were obtained using vacuum deposition techniques⁴ or chemical routes.⁵ Recently FePt nanoparticles were synthesized by reduction of mixed metal salts (i.e., Fe(CO)₅ and Pt(acac)₂), in the presence of a long chain carboxylic acid and primary amines in organic solvent.⁶ Generally, FePt nanoparticles are obtained in the chemically disordered face-centered cubic (fcc) phase, and a postgrowth annealing treatment at about 600 °C is necessary to induce the transition to the chemically ordered face-centered tetragonal (fct) phase (L1₀). The high annealing temperature causes coalescence phenomena with the consequent increase of the particle size, size dispersion, and reduction of the magnetic anisotropy. To avoid these effects, many attempts have been made to decrease the annealing temperature. The use of metal additives (such as Au, Cu, etc.) to catalyze the fcc–fct phase transition at lower temperatures is also

reported.⁷ New chemical routes for a direct synthesis of the FePt L1₀ structure have been proposed,⁸ but the fraction of nanoparticles in the ordered phase is usually low, unless the reaction temperature is increased up to 600 °C.⁹ Teranishi et al.¹⁰ showed that the use of pure H₂ during the annealing treatment leads to a reduction of the temperature (300 °C) at which the transition takes place. The authors ascribe this result to the increase of Fe and Pt atom mobility due to hydrogen interstitial diffusion. A more remarkable temperature reduction (down to 275 °C) has been observed in sputtered FePt films obtained by the alternate growth of Fe and Pt atomic layers.^{11,12} This last result suggests that the structural organization of Pt and Fe atoms in the starting material plays a key role in obtaining the fct phase at low temperature. With this in mind, we report a new chemical strategy for the direct synthesis of FePt alloy nanoparticles starting from a polycrystalline molecular compound, the iron(II)chloroplatinate hexahydrate (FePtCl₆·6H₂O), in which Fe and Pt atoms are arranged on alternating planes like in the fct FePt structure. The reduction of such compound by 5% H₂ and 95% Ar at 400 °C leads directly to a highly ordered L1₀ phase. Thermal analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), and superconducting quantum interference device (SQUID) magnetometry were used to characterize starting and final products.

Single crystals of FePtCl₆·6H₂O, characterized by a perfect hexagonal shape, were obtained by recrystallization of the crude product (see experimental section for the synthesis in the Supporting Information). The crystal structure has been solved,¹³ and the cif file is supplied in the Supporting Information. A view of the crystal packing is shown in Figure 1a, with octahedrals representing [PtCl₆]²⁻ and [Fe(H₂O)₆]²⁺ ions, linked together through a network of hydrogen bonds. Two different sets of alternating Fe and Pt atomic planes can be distinguished along the [001] and [011] directions, respectively. This atomic arrangement is similar, but much more ordered, than that one obtained growing alternate Fe/Pt multilayers.^{11,12} Since we used as starting material for the synthesis the polycrystalline FePtCl₆·6H₂O powder, obtained by manual milling from the single crystal, we first checked if crystalline structure was retained in the powder by

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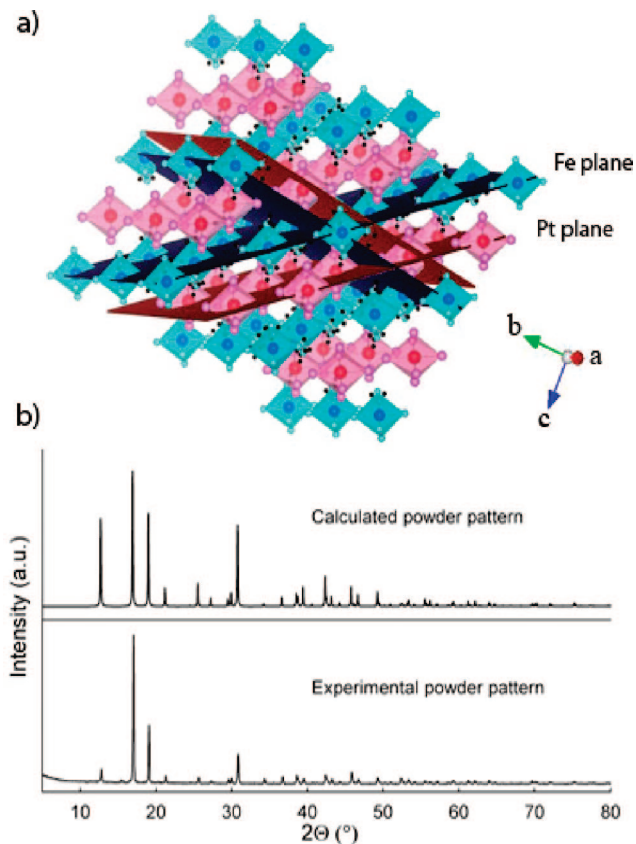


Figure 1. (a) FePtCl₆·6H₂O crystal packing showing the alternating Fe and Pt atomic planes; (b) the calculated (up) and experimental (bottom) XRD patterns of FePtCl₆·6H₂O powder.

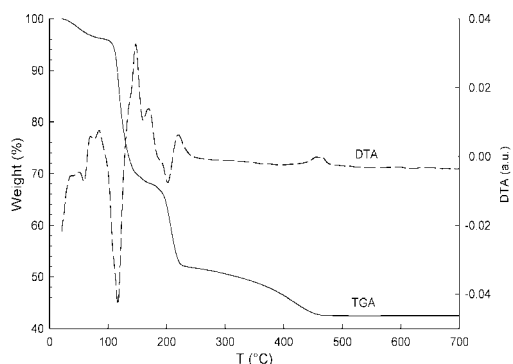


Figure 2. TGA-DTA of FePtCl₆·6H₂O under flux of 95% Ar and 5% H₂.

comparing its diffraction pattern with the theoretical one calculated from single crystal data. This comparison is reported in Figure 1b, confirming the good agreement between the two sets of data. The heating process of the FePtCl₆·6H₂O powder under reductive atmosphere, was monitored by a thermogravimetric and differential thermal analysis (TGA-DTA) performed up to 700 °C under 0.1 L/min flux of 95% Ar and 5% H₂, with a heating rate of 5 °C/min. The typical results are reported in Figure 2. In the TGA curve, four well distinct losses are observed, corresponding to a total loss of 56% in weight, related to the expected elimination of six H₂O molecules and six Cl atoms. Although it was not possible to isolate and characterize each single step, the processes being partially overlapped (see DTA curve), we propose a reasonable sequence of steps that

can occur under the thermogravimetric experimental conditions. The first broad loss ($\approx 4\%$) below 100 °C, likely due to water desorption, is followed by three losses starting at (a) 120 °C ($\approx 28\%$), (b) 200 °C ($\approx 16\%$), and (c) 230 °C ($\approx 10\%$) rather broadened. The dropping at 120 °C is probably related to the elimination of six H₂O molecules linked to Fe atoms and two Cl atoms, according to the following reduction reaction:



The elimination of the remaining four Cl atoms occurs in a wide range of temperatures above 200 °C. The small DTA bump at 450 °C could be attributed to a structural rearrangement occurring when the Cl loss is completed. For temperatures higher than 450 °C up to 700 °C no further weight losses are observed and the DTA curve does not show any indication of a crystal phase transition. This indicates that the fct FePt alloy is achieved after the elimination of Cl atoms. To verify this result a sample of FePtCl₆·6H₂O crystalline powder was treated at lower temperature for a longer time (400 °C for 1 h with heating rate of 5 °C/min). XRD measurements show the typical pattern of the L1₀ FePt phase (Figure 1 of Supporting Information). According to the TEM image (Figure 2a of Supporting Information) the sample is an aggregation of linked FePt nanoparticles (nanowire-like) with an average transverse size of approximately 10 nm. High resolution TEM analysis (Figure 2b of Supporting Information) shows the fct structure of the FePt nanoparticles with an interplanar distance of 0.378 ± 0.004 nm along $\langle 001 \rangle$ direction. The low temperature requested to obtain this phase without any evidence of fcc–fct phase transition can be related to the ordered arrangement of the metal ions on the alternating atomic planes present in the FePtCl₆·6H₂O crystals. Indeed, in a work presented by Lyubina et al. on the Fe₅₀Pt₅₀ alloy¹⁴ it is demonstrated that the activation energy requested for the phase transition from the chemically disordered fcc to the chemically ordered fct phase is higher than the energy needed for a gradient-assisted diffusion in a system of Fe and Pt microlamellae obtained by ball milling. From a thermodynamic point of view, the peculiar Fe–Pt atomic arrangement on alternating planes, as in the crystalline structure of FePtCl₆·6H₂O, represents the driving force for the direct formation of the fct FePt alloy when the last chlorine atoms are eliminated from the crystal; thus, the crystalline structure of FePtCl₆·6H₂O used for the synthesis acts as a template to obtain the chemically ordered L1₀ FePt phase. To prove our assumption and to obtain separated monodisperse nanoparticles, we performed two experiments using silica gel, SiO₂ (with dimensions from 35 to 70 μm), as a binder to avoid the particle agglomeration. In the first one we solubilized 100 mg of crystalline FePtCl₆·6H₂O in 5 mL of distilled water, and then we added 5 g of amorphous SiO₂ to the solution until its complete absorption on the SiO₂ particles surface. In this way we obtained a 2% solid mixture of FePtCl₆·6H₂O in an amorphous form. The mixture was

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then heated at 400 °C with a rate of 5 °C/min, under H₂/Ar reductive atmosphere, and then treated with HF to eliminate the SiO₂ (see experimental details in Supporting Information). The FePt nanoparticles washed in water and dried under vacuum show fcc structure, as revealed by XRD and magnetic measurements (see Figure 3a,b of Supporting Information). For these nanoparticles, a significant fct phase transition can be obtained at temperatures higher than 650 °C, as reported for many typical chemical syntheses.⁶ In the second experiment, 100 mg of crystalline FePtCl₆·6H₂O were mixed again with 5 g of SiO₂ and ground in a ball milling for 2 h. In this case we obtained a solid mixture where FePtCl₆·6H₂O keeps its crystalline form, as shown by the XRD pattern reported in Figure 3a (the arrows indicate the peaks of pure FePtCl₆·6H₂O). The mixture was heated at 400 °C and then treated with HF to eliminate the SiO₂, like in the first experiment. The XRD pattern reported in Figure 3b shows the presence of the peaks characterizing the L1₀ FePt phase. The lattice parameters *a* and *c* were determined from Rietveld refinement of XRD data and are 3.8489(3) and 3.7307(5) Å, respectively. From the axial *cla* ratio we determined the ordering parameter *S*, according to¹⁵

$$S^2 = 1 - (c/a)/1 - (c/a)_{Sf}$$

where *cla* is the axial ratio for the partially ordered phase and (*cla*)_{Sf} is for the fully ordered phase. Our value *S* = 0.93 indicates the high chemical order present in this sample (*S* = 1 means the fully ordered phase). The presence of the L1₀ phase has been also confirmed by the high value of the coercive field (*H*_c = 15 kOe) at room temperature (Figure 3c).¹⁶ In Figure 3d we report a typical TEM image of the fct sample. With this synthesis procedure the FePt particles are now well separated with an average size of about 5 ± 2 nm. Energy dispersive spectroscopy (EDS) (Figure 4 of Supporting Information) confirms the Fe/Pt molar ratio of 1.

In conclusion, we report the direct synthesis of magnetic nanoparticles of FePt alloy in the chemically ordered fct phase by heating FePtCl₆·6H₂O crystalline powder at 400 °C. The method allows nanoparticles with an average diameter of 5 nm to be obtained. The starting compound showed a crystal packing with iron and platinum ions distributed in an ordered way on alternating atomic planes. This peculiar arrangement gives rise to the direct formation of the L1₀ phase, after a thermal treatment at a temperature lower than the one usually requested for the fcc–fct phase transition. In this case, in fact, the heating process produces only the reduction of the metals, with the corresponding formation of the high ordered L1₀ FePt alloy. Our synthesis method is proposed as an easy and general chemical route to prepare, starting from layered MePtCl₆·6H₂O (Me = Co, Ni, etc.) L1₀ alloys at lower temperatures. Further work is in progress to optimize the synthesis conditions, such as the

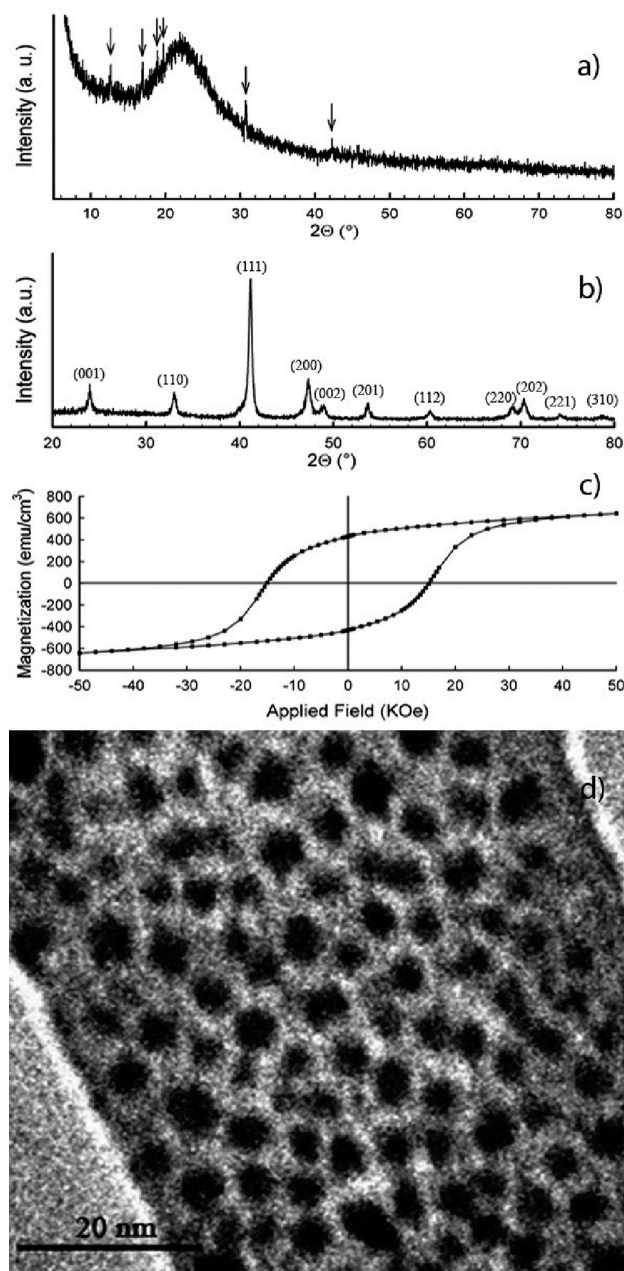


Figure 3. (a) XRD pattern of FePtCl₆·6H₂O milled with silica gel. The broad peak is due to silica, while the arrows indicate the peaks of crystalline FePtCl₆·6H₂O powder. L1₀ FePt nanoparticles: (b) XRD pattern, (c) RT hysteresis loop, and (d) TEM image.

heating rate, and to achieve L1₀ FePt alloy as thin films and ordered nanoparticles arrays for technological applications.

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Supporting Information Available: Detailed procedures for the synthesis of the samples and characterization are included (PDF) as well as crystallographic information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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