Order–disorder investigation of hard magnetic nanostructured FePt alloy

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Abstract
Well dispersed FePt nanoparticles are synthesized by the reduction of platinum (II) acetylacetonate and iron (III) acetylacetonate in the presence of oleic acid and oleylamine as a surfactant. Detailed investigations on the correlation between the magnetic and structural properties of these nanoparticles are presented as a function of annealing temperature. Transmission electron microscopy shows well dispersed nanoparticles with an average size of 4 nm. The phase of FePt nanoparticles has been studied using selected area electron diffraction which shows the clear transition from disordered face centre cubic (DFCC) to ordered face centre tetragonal (OFCT) at 750 °C. The x-ray diffraction as well as the magnetic measurements confirms the complete transformation from DFCC to OFCT phase at 750 °C with initiation of ordering at 500 °C. The magnetic measurements at room temperature show a single phase hysteresis loop at 750 °C with a coercivity of $H_c \approx 11.8$ kOe.

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic alloy nanoparticles based on transition metals such as Co and Fe have attracted considerable attention in recent years because of their technological applications in areas such as ultra-high density magnetic recording media [1–3], exchange-coupled nano-composite magnets [4], bio medicines and biomedical applications [5] and as a catalyst [6]. FePt alloy nanoparticles are among the best candidates for these applications due to the chemical stability and high magnetocrystalline anisotropy (MCA) $\sim 10^7$ J m$^{-3}$ of its ordered L$_1^0$ phase. Thermal fluctuations resulting in superparamagnetism in such small nanoparticles of $<10$ nm are overcome by the presence of high MCA material. The FePt nanostructures can be synthesized via vacuum deposition techniques such as sputtering [7, 8], chemical vapour deposition [9], pulse laser depositions [10] and molecular beam epitaxy [11, 12]. On the other hand, various chemical methods have also been used to synthesize FePt nanoparticles such as electrochemical method [13, 14], co-reduction method [1, 15–17] and solvothermal synthesis [18]. A high degree of control on size and shape of nanoparticles is achieved invariably by chemical methods. The synthesis of well dispersed FePt nanoparticles demonstrated by Sun et al [1] created a lot of interest in self assembled nanoparticles for high-density data storage applications. Over the past few years various iron precursors such as iron pentacarbonyl, iron acetylacetonate and ferric chloride and platinum precursors such as platinum acetylacetonate and platinum chloride [19, 20] have been used to prepare FePt alloys. Depending on the preparation methods, different shapes and structures can be formed such as nanocubes [20] and core/shell structure of FePt/Fe$_3$O$_4$ [14].

The magnetic properties of FePt nanoparticles strongly depend on the size of the particles and the relative composition of Fe and Pt in the alloy [21, 22]. As-synthesized FePt nanoparticles are reported to have a chemically disordered face centre cubic (DFCC) phase that can be transformed to an ordered face centre tetragonal (OFCT) phase by annealing at different temperatures for different span of time. Annealing at higher temperatures may lead to undesirable sintering of nanoparticles. Recent reports show that the sintering growth can be reduced by adding a third nonmagnetic element such as Ag, Au and Cu. This leads to the reduction in ordering temperature and hence controls the grain growth [23, 24].

In this paper, an attempt has been made to understand the structural ordering in the FePt system as a function of annealing temperature. A detailed analysis of the structural
parameters obtained from the x-ray diffraction (XRD) and using the Rietveld fitting has been presented. The investigation of this ordering process is further correlated with the magnetic phase transformation.

2. Experimental

FePt nanoparticles were synthesized by the chemical co-reduction of platinum (II) acetylacetonate (Pt(acac)2) and iron(III) acetylacetonate (Fe(acac)3) with 1,2 hexadecanediol (1,2 HDD) as a reducing agent. Metal precursors Fe(acac)3 [97% pure], Pt(acac)2 [97% pure], oleic acid (OA), oleylamine (OAm), 1,2 HDD and diphenyl ether as obtained from Sigma Aldrich was used for the preparation of these nanoparticles. The entire synthesis process was carried out under the blanket of argon atmosphere so as to avoid the oxidation of iron. In this procedure 0.5 mmol Pt(acac)2, 0.5 mmol Fe(acac)3, 4 mmol 1,2 HDD were mixed in 70 ml of diphenyl ether as a solvent. 0.5 mmol oleic acid and 0.5 mmol oleylamine was used as a surfactant in order to obtain well dispersed nanoparticles. After stirring for an hour, the solution was kept at 180 °C for 3 days in Teflon lined autoclave which was further cooled to room temperature. A black colour solution is obtained indicating the complete reduction and hence formation of FePt nanoparticles. Ethanol was added to the solution to precipitate the FePt nanoparticles which was separated by centrifugation at 12000 rpm for 15 min and finally dispersed in hexane.

The as-prepared hexane-dispersed FePt nanoparticles were drop casted on polished silicon to form a thick film. The FePt coated silicon substrates were subjected to heat treatments at 400, 500, 600, 700 and 750 °C for 120 min using a microprocessor controlled furnace. The annealing process was performed under the presence of high purity forming gas (Ar+5% H2), to avoid oxidation and assist further reduction. These films were used for structural and magnetic investigations.

Table 1. Variation in lattice parameters and degree of ordering as a function of annealing temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>3c/a</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>3.840</td>
<td>3.840</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>3.840</td>
<td>3.840</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>3.851</td>
<td>3.792</td>
<td>0.9838</td>
<td>0.7092</td>
</tr>
<tr>
<td>600</td>
<td>3.854</td>
<td>3.771</td>
<td>0.9784</td>
<td>0.8190</td>
</tr>
<tr>
<td>700</td>
<td>3.860</td>
<td>3.749</td>
<td>0.9712</td>
<td>0.9457</td>
</tr>
<tr>
<td>750</td>
<td>3.860</td>
<td>3.742</td>
<td>0.9694</td>
<td>0.9748</td>
</tr>
</tbody>
</table>

Table 2. Ordering parameter S* of FePt as a function of annealing temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>S*001</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0.5397</td>
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<tr>
<td>600</td>
<td>0.6708</td>
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<tr>
<td>700</td>
<td>0.9626</td>
</tr>
<tr>
<td>750</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

X-ray diffractrogram (XRD) analysis in the 2θ range 20°–75° was performed using a Bruker (D8) diffractometer and the TOPAS software has been used for rietveld refinement purchased with Bruker (D8) diffractogram. A Tecnai T30 Transmission Electron Micrograph (TEM) was used to estimate the size and shape of the nanoparticles dispersed on the copper grid. Selected area electron diffraction (SAED) was carried out for phase investigation. Vibrating sample magnetometer (VSM) Micro Sense EV9 with maximum field of 2.2 T was used for recording the hysteresis loop at room temperature. All the magnetic measurements have been performed in the ‘in plane geometry’ with the field parallel to the film.

3. Results

3.1. Structure and morphology: XRD and TEM

Figures 1(a)–(f) show the XRD spectra for the as-prepared sample and samples annealed at different temperatures. The as-obtained sample shows broad humps at 40.205° corresponding to the (111) plane with a trace of (200) plane at 47.100° as seen in figure 1(a). Appearance of an additional hump at 69.324° corresponding to (220) was observed upon annealing at 400 °C (figure 1(b)). These humps correspond to the DFCC phase. The above broad humps evolve as relatively sharper peaks upon annealing at 500 °C marked with the appearance of a superlattice peak at 32.874° corresponding to the (h k l) plane (1 1 0), and an additional shoulder at 47.100°. At 600 °C, a second superlattice peak is observed at 2θ = 23.921° corresponding to (0 0 1). On further annealing at 700° this shoulder appears as a distinct peak at 48.969° corresponds to the (0 0 1) plane. The splitting of the peak at 47.100° into two distinguishable peaks corresponding to the (2 0 0) and (0 0 2) planes is a clear indication of its transformation from DFCC to OFCT phase. It is also observed that intensity of both the superlattice peaks increases upon annealing and reach to 30% intensity relative to 100% intensity peak (1 1 1) at 750 °C. The

Figure 1. XRD pattern of FePt nanoparticles. (a) As-prepared sample and samples annealed at (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C and (f) 750 °C.
Figure 2. Phase investigation from Rietveld refined XRD pattern (in red) of FePt nanoparticles annealed at 750 °C using TOPAS.

Table 3. Atomic position and occupancy of Fe and Pt in FePt unit cell.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Wyckoff site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For the FCC phase</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Pt</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt</td>
<td>1c</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1c</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>For the FCT phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Pt</td>
<td>1c</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>2e</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

peaks are indexed to their \((h k l)\) values using the ICDD data (00-026-1139). The lattice constants were also estimated for all the annealed samples and given in table 1.

To determine the degree of ordering, the \(c/a\) value was calculated from the ratio of the interplanar distances \(d_{200}\) and \(d_{002}\) corresponding to the (200) and (002) planes, respectively.

The degree of ordering \(S\) was estimated using the following relation [25] and is presented in table 1:

\[
S^2 = (1 - c/a)_{\text{exp}}/(1 - c/a)_{\text{ad}}.
\]

(1)

From the table it is observed that as the annealing temperature increases, the cubic symmetry of unit cell is disturbed with an increment in the ‘\(a\)’ value and decrement in ‘\(c\)’ value which causes tetragonality in the structure. The degree of ordering also enhances with annealing temperature attaining a maximum of 0.9748 at 750 °C. However, this is not sufficient to confirm the atomic ordering, as \(S\) given in equation (1) indicates only the percentage of the tetragonal phase. In order to determine the atomic ordering, ordering parameter \(S^*\) was estimated using the superlattice peak, namely (0 0 1) indicated in figure 1. The transformation from disordered to ordered atomic arrangement of Fe and Pt in unit cell has been calculated using the following formula [26, 27]:

\[
S^2_{hk1} = \left( \frac{I_{hk1}}{I_{111}} \right)_{\text{exp}} \left( \frac{I_{hk1}}{I_{111}} \right)_{\text{ad}}
\]

(2)

where \(I_{hk1}\) is the intensity of the superlattice peak.

The ordering parameter estimated for superlattice peaks \(S^*_{001}\) is given in table 2.

The ordering parameter increases with annealing temperature reaching a value of 99.98% at 750 °C, indicating an almost perfect atomic ordering.

Figure 3. (a) TEM image of as-prepared FePt nanoparticles, (b) magnified image of (a) and (c) corresponding SAED pattern.

In order to further confirm the atomic ordering in the system a slow scan of XRD was performed on the sample annealed at 750 °C as shown in figure 2, which shows the maximum ordering parameter from the above analysis. The degree of long range chemical ordering in a unit cell depends
The long range ordering \( L \) is quantified using the following formula:

\[
L = r_{Pt} + r_{Fe} - 1
\]  

(3)

where \( r_{Pt} \) (or \( r_{Fe} \)) is the fractional site occupied by Pt (or Fe) atom \([28]\). The peak profile parameter and phase parameters are refined separately with space group \( Fm\text{-}3m \) and \( P4/\text{mmm} \) for the FCC and FCT phases as shown in figure 2 \([29]\). In order to determine the percentage of the DFCC and OFCT phases, the double-phase model is used for Rietveld analysis with the atomic positions of Fe and Pt in the unit cell for both FCC and FCT phase as given in table 3. The pattern at bottom is the difference between the experimental and calculated data. The pattern represented by arrow shows the presence of the OFCT phase in the system with their respective estimated percentage of 99.92% showing complete ordering.

The lattice parameters were estimated for the OFCT phase using the refined pattern and found to be \( a = 3.858 \) Å and \( c = 3.736 \) with goodness of fitting (chi\(^2\)) value 1.37.

Transmission electron microscope was used to investigate the size and phase of as-prepared nanoparticles and nanoparticles annealed at 400\( ^\circ \)C and 750\( ^\circ \)C. Figures 3(a) and (b) show the bright field images of as-prepared FePt nanoparticles dispersed on a copper grid. Well assembled FePt nanoparticles were observed. The size distribution is given as an inset in figure 3(a) shows particles with a mean size of 4 nm. Such well assembled nanoparticles are due to the use of oleic acid and oleylamine as a surfactant. Figure 3(b) shows the magnified image of figure 3(a). The analysis of the SAED shown in figure 3(c) gives a DFCC phase with the presence of the \((1 1 1)\) and \((2 0 0)\) planes as also observed from XRD. The diffuse rings

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{TEM image of sample (a) annealed at 400 \(^\circ\)C (b) corresponding SAED pattern (c) annealed at 750 \(^\circ\)C (d) corresponding SAED pattern (e) corresponding particle size distribution.}
\end{figure}
observed are due to the low degree of crystallinity in sample. Upon annealing at 400 °C, particles start agglomerating due to degradation of surfactant as seen in figure 4(a). The SAED shown in figure 4(b) shows that the DFCC phase of particles are retained with the enhancement in the crystallinity. On further annealing at 750 °C the particles grow in size as observed in figure 4(c). The corresponding indexed SAED pattern in figure 4(d) shows all the rings corresponding to the OFCT phase with the superlattice structure becoming very prominent which matches well with the XRD results. The average particle size is estimated using Gaussian distribution function for the sample annealed at 750 °C is 29 nm as shown in figure 4(e).

3.2. Magnetic measurements

The magnetic behaviour of FePt nanoparticles were investigated as a function of annealing temperature. Figures 5(a) and (b) show the M–H behaviour at room temperature of the as-prepared FePt nanoparticles and nanoparticles annealed at 400 °C. The as-prepared sample does not exhibit a hysteresis loop indicating the super paramagnetic nature, in accordance with the ∼4 nm size obtained by TEM analysis. The sample annealed at 400 °C exhibits a small coercive field of 290 Oe. The relatively low value of the magnetization for the as-prepared FePt particles is due to the presence of oleic acid and oleylamine that acts as capping agents. Both oleic acid and oleylamine boils off at about 350 °C thereby resulting in an increase in the magnetization of FePt annealed at 400 °C. The hysteresis loop obtained on the sample annealed at 500 °C shows a marked increase in coercivity, \( H_c \sim 4.67 \text{ kOe} \) as shown in figure 6(a) which further increases to 5.8 kOe at 600 °C (figure 6(b)). This marked variation in the coercivity indicates the set in of the hard magnetic phase. It is seen from figures 7(a) and (b) that the sample annealed at 700 °C shows a coercivity of 8.70 kOe. However, the hysteresis loop also shows a small shoulder indicating the co-existence of both the soft and hard phase as a result of an incomplete phase transition. The hysteresis at 750 °C in figure 7(b) shows a perfect loop with \( H_c \sim 11.8 \text{ kOe} \) suggesting the complete conversion from DFCC to OFCT. The hysteresis studies clearly reveal that with heat treatment there is a gradual transformation from the soft phase to hard phase with an intermediate mixed phase.

In order to correlate the magnetic and structural phase change occurring in the system upon annealing, a plot of coercivity along with ordering parameter as a function of annealing temperature is given in figure 8. It is observed that both ordering parameter and coercivity increase with annealing temperature following the same trend. For a perfectly ordered system both magnetic and structural parameters play an equally important role. As observed from figure 8, irrespective of the high coercivity achieved at 700 °C the ordering parameter is not sufficiently high which is also indicated as a shoulder in the hysteresis loop. However, a perfect hysteresis is observed at 750 °C with an increased coercivity and enhanced ordering parameter of 99.94% confirming the complete conversion to the OFCT phase. A plot of magnetization, \( M \) at 2.2 T as a function of annealing temperature is shown as the inset in figure 8. The value of \( M \) increases with annealing temperature up to 600 °C then decreases on further annealing. As the
conversion from the DFCC to OFCT is accompanied by the asymmetry in the crystal structure, the hard phase is marked with the reduction in the value of magnetization.

4. Conclusion

Well dispersed and well assembled FePt nanoparticles were successfully synthesized by the chemical co-reduction method using autoclave with an average size \( \sim 4 \) nm. The ordering parameter and the degree of ordering estimated from the structural analysis are in conformity with the phase transition observed from the magnetic measurement. The coercivity of 11.8 kOe was observed for the perfectly OFCT phase with the ordering parameter 99.94%. In spite of higher ordering observed in the present investigation, the control of particle size has not been achieved which is also essential for high density media recording application. The monodispersity can be obtained by incorporating the FePt particles into a nonmagnetic matrix. Such a process will avoid the sintered growth. This can also be achieved by using ion beams. Hence achieving monodispersed FCT nanoparticles are under process.

Acknowledgments

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References

Electronic states of self stabilized L1₀ FePt alloy nanoparticles

Rohit Medwal · Neeru Sehdev · Govind · S. Annapoorni

Abstract The ligand capped bimetallic FePt alloys were prepared by using the chemical coreduction method in the presence of oleic acid and oleylamine. An X-ray photoelectron spectroscopy (XPS) study on the as prepared and annealed samples reveals the degradation of hydrocarbon capping with annealing temperature along with a phase transformation to a L1₀ phase. This degradation of organic capping results in formation of capping layer over FePt which has been observed using High Resolution Transmission electron microscopy (HRTEM). This capping layer over the FePt nanoparticles was further investigated with Raman studies confirming the presence of the graphitic carbon. The presence of the graphitic layer enhances the stability of FePt nanoparticles by protecting the surface against oxidation. This was confirmed by the magnetic measurements which show a high coercivity of 11.8 kOe, retained over a period of one year.

1 Introduction

Study of the structural phase transition from disordered A1 phase (space group Fm3m) to ordered phase L1₀ (space group P4/mmm) observed in FePt, CoPt, AuCu, etc., is one of the most frontier areas of research due to the interesting phase transition that is observed on annealing [1–5]. The FePt alloys in ordered L1₀ phase are very useful for ultra high density magnetic media recording device. It is well known that particles of a size smaller than a certain critical dimension exhibit superparamagnetic behavior along with reduction in magnetization which limits the application of these nanoparticles for the magnetic recording device. This can be circumvented by high chemical stability and high magnetocrystalline anisotropy (K) that allows the reduction in particle size of FePt nanoparticles with stability in magnetization against the thermal fluctuation. However, the properties such as high magnetization and high coercivity depends not only on the particle size, but also strongly on the atomic composition of Fe and Pt in FePt alloy viz. Fe₃₃Pt₆₇, Fe₅₀Pt₅₀, and Fe₆₇Pt₃₃ [6]. Hence, it is important to control the size as well as the composition in such type of alloys for potential applications. Modification in the properties was also observed by incorporation of a third element like Au, Ag, etc. of appropriate composition resulting in lowering of the ordering temperature and enhancement in coercivity by inducing a strain [7–10].

There is plethora of physical and chemical techniques to prepare the FePt nanoparticles. The chemical method is preferred over the physical methods due to better control on shape and size of nanoparticles. The wet chemical synthesis method gives face centered cubic (fcc) disordered FePt nanoparticles which transform to ordered face centered tetragonal (fct) nanoparticles with annealing temperature [11–13]. The temperature at which the fcc phase completely transforms to an ordered fct phase known as the ordering temperature, depends upon the rate of annealing, time of annealing, atomic composition of Fe and Pt in the system, etc. The heat treatment is also accompanied by formation of bigger particles [6, 14–16]. To avoid the growth of smaller nanoparticles to bigger size, salt matrix annealing has been developed [17]. Attempts of synthesizing direct fct...
FePt nanoparticles have also been reported using the solution method, however, a low degree of ordering and very low coercivity has been obtained which is attributed to a partial transformation from the disordered to ordered phase [18, 19].

The nanoparticles with small particle size of the order of 4 nm have a tendency to oxidize quickly and this poses a major challenge for device application. The structural relaxation at the surface of the FePt icosahedral nanoparticles has been investigated using the TEM and electronic density of states [20, 21]. The use of surfactant during the preparation process helps in not only controlling the size of the nanoparticles formed, but also act as a protective layer thereby avoiding oxidation. These surfactants on annealing tend to form a carbonaceous layer which prevents oxidation of the core alloy particles. Moreover, such layers also enhance the biocompatibility of magnetic nanoparticles [22, 23]. Biocompatible FeCo coated with graphitic shell for MRI imaging and infrared agents have been reported by Seo et al. [23]. In FePt catalyzed carbon nanotubes, the graphene layer is found to grow preferentially along (111) [24].

The approach to the control of composition of elements in the existing phase of materials is of crucial importance for metallurgical process. The chemical behavior of the system like bulk composition and presence of oxygen, temperature, etc. changes the behavior of the materials drastically [6, 16, 25, 26]. Range of interaction among the atomic arrangements also affects the electronic states of the materials. The material existing in different oxidation states have different ranges of interaction, leading to a change in the binding energy (BE) [27–30]. This change in the binding energy may also be attributed to phase transformation from disordered phase to ordered phase with the presence of valence band states in the system [31, 32].

In the present report, the electronic states of Fe and Pt in FePt nanoparticles have been investigated as a function of annealing temperature. The L10 phase formation of alloy nanoparticles is supported by valence band spectra. The direct and indirect evidence of graphitic layer has been presented using HRTEM and Raman spectra, respectively. The benefit of the formation of this carbonaceous layer over FePt nanoparticles with annealing temperature that acts as a protective layer has been thoroughly investigated. This protective layer prevents the oxidation of FePt, hence providing a long term stability which has been demonstrated with the magnetic measurement.

2 Experimental

FePt nanoparticles were synthesized using an autoclave by a modified chemical route proposed by Sun et al. [1, 2]. As prepared ligand coated fcc FePt nanoparticles were treated at 500 °C. The choice of the temperature of 500 °C is taken to decompose the organic capping on the FePt nanoparticles. Further annealing at 750 °C is done for the transformation of FePt (A1) disordered fcc phase to FePt (L10) ordered fct phase. X-ray diffractogram (XRD) was recorded at the glancing angle of 0.5° in the 2θ range 20°–75° with a Bruker (D8) diffractometer using a Cu Kα (λ = 1.5405 Å). High resolution transmission electron microscopy (HRTEM) was performed using Tecnai T30, Vibrating Sample Magnetometer (VSM) EV9 with maximum field of ±2.2 Tesla was used for magnetic measurements at room temperature. The Raman Spectra were recorded using a Renishaw in Via Raman microscope. Laser beam of wavelength 514 nm (Ar-gon Laser) was focused on the surface of the FePt film deposited on silicon. The X-ray photoelectron spectroscopy (XPS) studies were performed using a Perkin–Elmer system (model No. PHI-1257). The XPS chamber is equipped with dual anode Mg Kα/Al Kα where Al Kα (1486.6 eV) source has been used as an X-ray source and a high resolution hemispherical energy analyzer for energy resolved electron detection.

3 Results and discussion

Figure 1 shows the XRD pattern of as prepared FePt nanoparticles and nanoparticles annealed at 750 °C for 2 h. The recorded pattern confirms the transformation from fcc phase (A1) to fct phase (L10) on annealing. Diffraction peaks corresponding to 2θ at 40.20°, 47.10°, and 69.32° with (hkI) reflections (111), (200), and (220) are shown in Fig. 1(a) corresponding to fcc phase of as prepared nanoparticles. Figure 1(b) shows the XRD pattern for sample annealed at 750 °C. A transformation to fct phase with a simultaneous enhancement in the particle size, as suggested
from the decrease in full width at half maxima (FWHM) was observed. The ordering has been confirmed from the origination of superstructure peaks corresponding to (110) and (001) due to atomic arrangements of Fe and Pt atom in the unit cell upon annealing. This atomic arrangements lead to the distortion in the cubic symmetry in a unit cell resulting in a shift (δ) in 2θ corresponding to (111). The induced tetragonality due to the distortion in the system was further observed by the splitting of peaks corresponding to (200) into (200) and (002). In an earlier report, the effect of temperature on the degree of ordering along with the ordering parameter as a function of annealing temperature have been presented. A systematic analysis using Rietveld refinement shows a complete ordering from A1 phase to L1₀ for the FePt alloy nanoparticles annealed at 750 °C [2].

The X-ray photoelectron spectroscopy (XPS) technique was used for the identification of elemental composition and different oxidation states available in the system. The variations in binding energy with respect to structural transformation from the disordered to ordered phase has been studied. The core level spectra of C (1s), O (1s), Fe (2p), and Pt (4f) and valance band spectra were recorded to investigate the electronic states of order–disorder system. All the experimentally observed core level spectra were calibrated with the binding energy of C1s (284.6 eV). The presence of small amount of oxygen was observed from the core level scan of O (1s) for as prepared capped FePt nanoparticles. The observed contribution of oxygen is due to the presence of oleic acid and oleylamine. Core level scan of O (1s) for the sample annealed at high temperature did not show the presence of oxygen. Hence, the formation of oxides of iron is not taken into account while fitting XPS spectra.

Figure 2 shows the Fe 2p core level scan for iron with \(2p_3/2\) peaks for as prepared sample and the sample annealed at different temperatures. The core level spectra of Fe (2p3/2) for as prepared FePt nanoparticles shows the peaks at 707.2 eV, 708.3 eV, and 711.2 eV as shown in Fig. 2a. The peak at 707.2 eV indicates the presence of pure iron while peak at 708.3 eV and 711.2 eV is due to the presence of surface lattice distortion and hydrocarbon interaction on the surface caused by the surfactant used for capping the nanoparticles. The binding energy corresponding to pure iron is 706.7 eV and the shift of 0.5 eV observed presently is due to the bimetallic bonding between iron and platinum [30, 31]. For the samples annealed at 500 °C, the hydrocarbon outgas and the peak intensity at 707.2 eV shows an enhancement while the intensity of peaks at 708.3 eV and 711.2 eV suppress relatively with a slight shift in the binding energy as shown in Fig. 2b. The enhancement in intensity and shift in binding energy reveals the removal of the organic capping of the nanoparticles. The variation in the binding energy observed for the alloy annealed at 750 °C as seen from Fig. 2c is attributed to the phase transformation from fcc to fct phase.

Figure 3 shows the core level Pt (4f) spectra of as prepared FePt alloy and annealed at different temperatures. The spectra for as prepared nanoparticles clearly show the presence of two distinct but broad peaks at Pt 4f5/2 (72.4 eV) and Pt 4f7/2 (75.6 eV), respectively. The peaks corresponding to Pt 4f5/2 were deconvoluted giving rise to peaks at 72.1 eV and 73.6 eV. The peak at 72.2 eV is due to the presence of pure metallic Pt while the peak at 73.6 eV indicates Pt due to the presence of organic capping. A similar exercise on the Pt 4f7/2 results in peaks at 75.6 eV for pure Pt and 76.9 eV for capped Pt. The origin of the Pt peaks at higher binding energy may be due to the interaction of the surfactant (amine and hydrocarbons) with the surface of nanoparticles. Figure 3b shows the XPS spectra of sample annealed at 500 °C.
It is observed that the peaks corresponding to higher binding energy is suppressed and the intensity of peaks corresponding to pure Pt is enhanced with a shift in the binding energy revealing a reduction in organic capping. The samples were further subjected to annealing at 750°C, where the variation in binding energy is due to the phase transformation from disorder to ordered phase. The binding energy corresponding to pure Pt is 70.9 eV which is 0.5 eV lesser than the observed binding energy of Pt. This shift in the binding energy is due to the bimetallic bonding between the Fe and Pt, resulting in the formation of ordered L1₀ alloy [30, 31]. Elemental composition of Fe and Pt estimated using the core level spectra of Fe (2p) and Pt (4f) is Fe$_{46}$Pt$_{54}$.

Figure 4 presents the valence band spectra of as prepared FePt nanoparticles capped with oleic acid and oleylamine as well as nanoparticles annealed at 500 °C and 750 °C. The spectrum of as prepared nanoparticles show hump without any emerging peaks or features corresponding to any particular binding energy of FePt. Broad spectra with distinguished shoulders appear for both 500 °C and 750 °C annealed samples. On deconvolution of broad spectra, the presence of peaks at 0.3 eV, 2.0 eV, 4.0 eV, and 6.0 eV is very clear from Figs. 4b and 4c, respectively. The valance band spectra shows the states near the Fermi level (E$_f$), i.e., 0.3 eV for pure Fe and Pt. The peaks at 2 eV and 4.0 eV are the characteristic feature of FePt alloy which also resembles the pure Pt [33, 34]. The peak at 6.0 eV is the prominent characteristic peak of FePt which shows the presence of ordered L1₀ phase [34].

Figures 5 and 6 shows the bright field TEM image of as synthesized nanoparticles and nanoparticles annealed at 750 °C along with their respective selected area electron diffraction (SAED) pattern, respectively. The size of FePt nanoparticles estimated is 4 nm for as prepared FePt nanoparticles as shown in Fig. 5a. To investigate the phase of as prepared nanoparticles SAED has been performed. The rings observed as shown in Fig. 5b are indexed with their respective (hkl) planes and confirms the fcc phase. The rings are diffused due to the small particle size and short range ordering in the system. Figure 6a shows TEM of 750 °C annealed FePt nanoparticles and HRTEM of carbon encapsulated FePt nanoparticles as an inset. The estimated interplaner distance from the lattice fringes is 3.5 Å, giving the direct evidence of carbon capping on the FePt nanoparticles. This layer may be a carbonaceous covering formed due to the outgas of hydrogen and oxygen from organic capping. Moreover, the presence of superstructure ring seen in Fig. 6b corresponding to (001) and (110) planes confirms the structural ordering of Fe and Pt in the crystal structure of FePt.

Further, the nature of capping over the FePt nanoparticles is investigated in detail as a function of annealing temperature. Figure 7 shows the Raman spectra of as prepared FePt nanoparticles capped with organic molecules oleic acid and oleylamine as ligands and the nanoparticles annealed at 400 °C, 500 °C, 600 °C, 700 °C, and 750 °C. No Raman signal for the as prepared FePt nanoparticles is observed. When the nanoparticles are subjected to heat treatment, the capped ligands transform to the pure carbon leading to the
formation of graphitic carbon encapsulated FePt nanoparticles as observed by the two bands centered at 1335 cm\(^{-1}\) and 1600 cm\(^{-1}\) for all the annealed samples. These bands have been identified as the D band and G band, respectively, which occur for graphitic carbon. The graphitic band (G band) has been observed for the graphitic nature of the carbon materials whereas disordered band (D band) has been attributed to the presence of the unorganized carbon atom in the sample \([35–37]\). This phenomenon of formation of carbon on the FePt nanoparticles with forming gas makes the system pure and avoids the formation of graphitic oxide.

The ratio of the intensities of G band and D band viz. \(I_G\) and \(I_D\), respectively, is indicative of the degree of disordering of graphitic carbon atom. The ratio of \(I_D/I_G\) as a function of annealing temperature is shown in Table 1. The increasing value of \(I_D/I_G\) with annealing represents the dominance of ordered graphitic carbon on the surface of FePt nanoparticles.

Our earlier work on the structural and magnetic properties of these nanoparticles shows a complete structural ordering with simultaneous transformation to hard magnetic phase wherein a maximum \(H_c \sim 11.8\) kOe has been reported \([2]\). It is interesting to observe that the presence of such graphitic carbon acts as a protective layer. This was observed by recording the \(M–H\) loop, shown in Fig. 8, over a period of one year which shows no significant change in the coercivity, and thus retains a stable FePt phase.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(I_D/I_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.682</td>
</tr>
<tr>
<td>500</td>
<td>0.721</td>
</tr>
<tr>
<td>600</td>
<td>0.752</td>
</tr>
<tr>
<td>700</td>
<td>0.842</td>
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<tr>
<td>750</td>
<td>0.841</td>
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</table>
4 Conclusion

The XPS shows a shift in the binding energy of as prepared and 500 °C annealed samples giving a clear evidence of interaction between the nanoparticles and organic capping. The chemical shift with respect to pure Fe and Pt confirms the formation of alloy. The observed valence band spectra shows the origination of observed metallic states with annealing confirming the complete phase transformation at 750 °C from A1 to L10. The HRTEM image shows the presence of a carbon layer coated over FePt nanoparticles. The Raman spectra reveals the enhancement in the intensity of G band which is indicative of the graphitic shell over the FePt nanoparticles. Graphitic layer over FePt nanoparticles induced by annealing does not show any effect on the electronic states. The graphitic capping avoids oxidation and helps in retaining the hard magnetic phase.

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References

Temperature-dependent magnetic and structural ordering of self-assembled magnetic array of FePt nanoparticles

Rohit Medwal · Neeru Sehdev · S. Annapoorni

Abstract Hexagonal close-packed 2D assembly of monodispersed FePt nanoparticles by the co-reduction method have been synthesised with particles size ~ 3 nm. The X-ray diffraction (XRD) studies reveal a structural transformation from a chemically disordered faced-centred cubic (FCC) phase to a chemically ordered face-centred tetragonal (FCT) phase with heat treatment. The percentage of phase transformation from FCC to FCT has also been investigated by the XRD profile fitting. Annealing at 750 °C gives 95 ± 1 % FCT phase. The structural transformation was further confirmed by the presence of two superlattice rings corresponding to (001) and (110) by the selected area electron diffraction. Transmission electron microscopy (TEM) shows the grain growth with annealing temperature. High resolution TEM shows the presence of the carbonaceous layer over FePt after annealing. This carbonaceous layer has been investigated by the Raman spectroscopy. Magnetic measurement shows the presence of magnetic hard phase with coercivity of 1 Tesla. The soft/hard compositions have also been investigated by the hysteresis measurements.

Keywords FePt alloy · Array · Nanoparticles · Hexagonal close-packed

Introduction

The alloy Iron-Platinum (FePt) (tetragonal, L1₀-type structure and space group P4/mmm) with near equiatomic composition is found to be very useful in applications like magnetic recording media and permanent magnet due to its high magneto crystalline anisotropy (\(7 \times 10^7 \text{ J/m}^3\)) and chemical stability (Sun et al. 2000; Kim et al. 2007; Nguyen et al. 2006; Yao and Coffey 2008; Zeng et al. 2003; Sasaki et al. 2004). This high value of K is due to the spin orbit interaction between Fe and Pt and hybridization between the 3d state of Fe and 5d state of Pt elements (Gutfleish et al. 2005). As-prepared FCC phase FePt nanoparticles have a magnetically soft behaviour which transform to FCT phase with high magnetcrtalline anisotropy (MCA) on annealing. The change in the MCA is a result of distortion from a highly symmetric cubic phase (space group Fm3m) to asymmetric tetragonal phase (space group p4/mmm) (Medwal et al. 2012a, b; Laughlin et al. 2005; Skomski 2003). FePt nanostructures can be prepared by both chemical and physical method. The FePt films prepared by physical techniques are found to be highly crystalline, but with an inhomogeneous size distribution. However, chemically synthesized FePt nanoparticles capped with a surfactant not only results in a very
homogeneous distribution of size and shape but also provide chemical stability to the system. Chemical processes, e.g. reduction, co-reduction and seed-mediated growth, etc., have been used to synthesize FePt nanoparticles (Sun et al. 2000; Elkins et al. 2003; Sasaki et al. 2005; Sun et al. 2003). Depending on the preparation methods, different shapes and structures can be formed like nanocubes, nanorod and nanosphere and also core/shell structure with oxide layer as the shell and FePt as a core (Chen et al. 2006; Chen et al. 2004; Hou et al. 2006).

Annealing at higher temperatures results in the process of coalescence to form bigger particles followed by the conversion of the superparamagnetic FCC phase to ferromagnetic FCT phase. Achieving the ordering temperature at which the FCC phase transform to FCT (L1₀) phase before coalescence process starts is of current research interest. Hence, lowering down the ordering temperature, while retaining the smaller particle size, is an important aspect of L1₀ system. The decrement in the ordering temperature by adding a third element, viz. silver or gold, during the synthesis of FePt nanoparticles has been reported by several groups (Jeyadevan et al. 2003; Sehdev et al. 2011; Sehdev et al. 2012). An alternative method of controlling the sintering growth of nanoparticles is by annealing the FePt nanoparticles in the nonmagnetic matrix which can sustain high degree of temperature (Rong et al. 2008).

The magnetic properties of FePt nanoparticles strongly depend on the size of the particles and also on the composition of Fe and Pt in FePt alloy, i.e. the value of \( x \) in Fe₇Pt₁₋₅ (Andrew et al. 2004). The most common precursors used in the synthesis of FePt alloy are iron pentacarbonyl (Fe(CO)₅) and Pt(acac)₂. The disadvantages associated with Fe(CO)₅ are its highly toxic nature and highly flammable nature even at room temperature. The boiling point of Fe(CO)₅ is low (103 °C) as compared to the melting point of Pt(acac)₂ (249 °C) thereby making it difficult to maintain the composition of the alloy Fe₇Pt₁₋₅ (Nguyen et al. 2006). The Fe(acac)₂ is also used in the synthesis of FePt alloy as an alternative precursor to form monodispersed 2D array.

In this paper, an attempt has been made to synthesis monodispersed array of FePt nanoparticles by the co-reduction chemical method in the presence of different concentration of surfactant. The systematic studies of the structural and magnetic transformation by means of the Rietveld and deconvolution of hysteresis, respectively, have been investigated as a function of annealing temperature. The effect of the surfactant on the 2D array has also been investigated.

**Experiment**

FePt nanoparticles were synthesized by the chemical co-reduction method (Sun et al. 2000; Medwal et al. 2012a). The metal precursors iron(III) acetylacetonate (Fe(acac)₃, 97 % pure) and platinum(II) acetylacetonate (Pt(acac)₂, 97 % pure) were co-reduced using 1,2 hexadecanediol which serves as a reducing reagent. Phenyl ether was used as a solvent in the presence of oleic acid and oleylamine which act as surfactants. All the above-mentioned chemicals were procured from Sigma Aldrich and used as obtained for the preparation of the FePt nanoparticles. Fe(acac)₃ is a ferric salt which gets easily oxidized in oxygen atmosphere. Hence, an oxygen-free environment is created throughout the experiment. The iron salt is not easily reducible; however, the platinum salt readily reduces to Pt ions and also helps in the reduction of iron salt, thus accelerating the reduction process. A stoichiometric amount of Pt(acac)₂ (0.5 mmol) and Fe(acac)₃ (0.5 mmol) were mixed in 40 ml phenyl ether in the presence of 0.5 mmol of oleic acid and oleylamine with 4 mmol of 1,2 hexadecanediol. This mixture was stirred for one hour at room temperature under argon atmosphere. The chemical co-reduction of metallic precursors into metal nanoparticles occurs by refluxing the solution at 250 °C for one hour with continuous stirring in the presence of high purity argon gas. During refluxing, the colour of the solution changes from yellowish pink to black indicating the formation of FePt nanoparticles. The solution was allowed to settle down at room temperature under inert atmosphere. The chemical composition of the alloy Fe₇Pt₁₋₅ was separated by centrifugation at 12,000 rpm for 15 min and washed with ethanol twice. Finally, the powder obtained was dispersed in hexane and used for further characterization.

X-ray diffractogram (XRD) in the 2θ range 20°–75° was performed using a Bruker (D8) diffractometer. The software TOPAS was used for Rietveld refinement to study the formation of the different phases of the alloy provided with Bruker (D8) diffractometer. A Tecnai
T30 Transmission Electron Microscope (TEM) was used to estimate the size and shape of the nanoparticles dispersed on the copper grid. Selected area electron diffraction (SAED) was also carried out for phase investigation. Vibrating Sample Magnetometer (VSM) Micro Sense EV9 with maximum field of ±2.2 Tesla was used for recording the hysteresis loop at room temperature.

Results and discussion

Transmission electron microscopy

Figure 1a, b, c, d shows the as-prepared FePt nanoparticles synthesized using the different ratios of oleic acid to oleylamine, viz. 0.5:0.5, 0.5:1, 1:0.5 and 1:1, respectively. All the TEM images reveal a very well-organized monodispersed FePt array with the particle size ~3 nm. The interparticle distance can be controlled with oleic acid and oleylamine used as a surfactant during the synthesis. The hexagonal close-packed FePt array shown in Fig 1a is observed for the 0.5:0.5 mmol concentration of oleic acid and oleylamine, respectively. The hexagonal close-packed structure can be tuned to honey comb packed array with increasing the surfactant ratio as shown in Fig 1b. On further increasing the concentration of surfactant, the interparticle distance can be increased as shown in Fig 1c, d followed by the disturbance of array. The surfactant not only acts as stabilizing ligands for the
FePt nanoparticles but also helps in the formation of array of larger area which is essential for recording media. Typical selected area electron diffraction is shown in Fig 1e obtained for the above array and confirms the formation of FCC phase. It is important to mention that the largest area of the array was observed for the hexagonal close-pack system with 0.5 mmol: 0.5 mmol oleic acid and oleylamine for which further investigations were performed on the system.

The dispersed arrays were subjected to different annealing temperature and HRTEM and SAED were recorded. At high temperature, the surfactant starts degrading and the particles coalesce. The sintering growth effect dominates, leading to the formation of particles with bigger size. Figure 2 shows the TEM of sample annealed at 600 °C along with HRTEM showing the lattice fringes with interplaner distance of 2.22 Å corresponding to (111). The presence of the superlattice ring in the SAED in inset (Fig 2) reveals the formation of chemically ordered FCT phase. The evolution of superlattice rings is due to the chemically arranged Fe and Pt stacking in the FePt unit cell with annealing. The size of nanoparticles has been estimated with log normal distribution function with average particle size of 5 nm as shown in Fig 2c. On further annealing at 750 °C, the particles are found to attain irregular shape of bigger size as shown in Fig 3a. The indexed SAED pattern shown in Fig 3b. The presence of superlattice ring corresponding to (001) and (110) confirming the formation of ordered L10 phase. The sharpness of the ring indicates the enhanced crystallinity. HRTEM shown in Fig 3c shows the interplaner distance of 2.20 Å which is indentified as the 111 plane. A capping over the FePt nanoparticles has also been observed in High Resolution TEM. It is well known that, with annealing, the organic surfactant-capped nanoparticles convert into the carbonaceous coating on the surface of FePt nanoparticles. This carbonaceous capping was investigated by Raman spectra. The Raman spectra showed the presence of D band and G band peak as shown in Fig 3d due to the presence of graphitic carbon layer over the FePt nanoparticles (Medwal et al. 2012a, b). Figure 4 shows the TEM image for the particles annealed at 750 °C, demonstrating coalesce and sintering growth of the nanoparticles. The area under the marked circle shows the inter particle diffusion bridge between two coalesced nanoparticles. The random interparticle diffusion and fast growth rate leads to the formation of the irregular and elongated shapes of the annealed nanoparticles. Further temperature-dependent XRD measurements were performed to confirm the phase transformation and given in detail below.
X-ray diffraction

XRD measurements have been performed on the as-prepared samples and samples annealed at different temperatures. The annealed samples exhibit both FCC and FCT phase. The percentage of FCC and FCT in the annealed samples depends upon the annealing time and temperature. Investigation on the phase composition of FCC and FCT in the system the Rietveld analysis has been performed on the as prepared and annealed samples. The fitting of experimental XRD patterns has been performed using double phase model for Fm3 m and P4/mmm space group. The details of the Wyckoff position of both Fe and Pt in the unit cell used for the analysis are reported elsewhere (Medwal et al. 2012a, b; Hahn 2005). Figure 5 shows the XRD pattern of as prepared nanoparticles with plane corresponding to (111) indicating the presence of disordered face-centred cubic phase (A1). The samples were subjected to heat treatments at 600, 700 and 750 °C for the structural transformation. The samples annealed at 600 °C shows the evolution of FCT with superlattice peaks of L1₀ phase confirming the onset of FCT phase (L1₀ Type) shown in Fig 6a, b. Further, annealing at higher temperature (700 and 750 °C) also enhance the intensity of superlattice peaks at 2 theta 24° and 33° corresponding to (001) and (110), respectively. The splitting observed for (200) reveals the transformation from cubic (A1, Fm3m) to tetragonal (L1₀, P4/mmm) as shown in Figs 7 and 8. The estimated percentage for FCC and FCT phase using the profile fitting at different annealing temperature are tabulated in Table 1. This evolution of super lattice peaks is due to the rearrangement of the Fe and Pt position in the unit cell of FePt alloy giving rise to chemical ordering. The rearrangement of Fe and Pt position depends upon the degree of annealing
temperature and time for which sample is exposed. The distortion in the unit cell resulting in the contraction of lattice in c direction is due to the difference in the atomic radii of Fe and Pt. This is also accompanied with shift in 2 theta value for (111) and splitting of (200) peaks. Lattice parameter has been estimated for both FCC and FCT phase. The estimated c/a ratio for FCC and FCT phase were used for the analysis of degree of ordering while intensity of superlattice peaks are taken into account to investigate the ordering parameter. These are tabulated in Table 2. The performed structural refinement shows the 95 ± 1% chemical ordering of the Fe and Pt in the FePt alloy unit cell at 750 °C. One of our earlier reports showed the 99% chemical ordering at 750 °C annealing temperature, but with poor particle size distribution (Medwal et al. 2012a, b).

Magnetic studies

In order to study the effect of annealing on magnetic properties of FePt nanoparticles, M(H) loop of all the sample annealed at different temperature were recorded at room temperature. It is well understood that the as-prepared nanoparticles with FCC phase are soft magnetic and L10 phase nanoparticles with FCT phase are hard magnetic. However, the magnetic transition is not very sharp with annealing temperature.
In the intermediate state, the soft and hard phases coexist. Hence, to determine the percentage of the soft and hard composition the obtained M-H loop is deconvoluted. The as-prepared nanoparticles exhibit super paramagnetic behaviour with zero coercivity as shown in Fig 9. The normalized M-H loops corresponding to the annealed samples were deconvoluted by Eq. 1 (Kang et al. 2005).
\[
M(H) = \sum_n \frac{2M_s}{11} \arctan \left( \frac{H + H_c}{H_c} \tan \left( \frac{S}{2} \right) \right) \tag{1}
\]

Where \( M_s \) is the saturation magnetization, \( H_c \) is the coercivity, \( S \) is the squareness (ratio of \( M_r \) to \( M_s \)) and \( n \) is the ferromagnetic component in the system.

The deconvoluted loop along with the curve fitting for sample annealed at 600, 700 and 750 °C are shown in Figs 10, 11 and 12 respectively. The fitting has been performed with two ferromagnetic components, the hard magnetic FCT (L1_0) and soft magnetic FCC (A1) phases. The contribution of hard magnetic

| Table 1 Estimated percentage of FCC and FCT phase of FePt alloy by Rietveld analysis |
|---|---|---|
| (°C) | FCC (%) | FCT (%) |
| As prepared | 100 | 0 |
| 600 | 38 | 62 |
| 700 | 10 | 90 |
| 750 | 5 | 95 |

| Table 2 Degree of ordering and ordering parameter as a function of annealing temperature |
|---|---|---|---|
| (°C) | c/a | Degree of ordering | \( I_{001}/I_{111} \) (%) | Ordering parameter (\( S_{001} \)) (%) |
| As prepared | 1 | 0.00 | 0.00 |
| 600 | 0.9848 | 0.6881 | 8.51 |
| 700 | 0.9801 | 0.7873 | 19.79 |
| 750 | 0.9692 | 0.9795 | 26.93 |

Fig. 9 M–H loop for as prepared hexagonal close-packed FePt array

Fig. 10 M–H loop of hexagonal close-packed FePt array annealed at 600 °C

Fig. 11 M–H loop of hexagonal close-packed FePt array annealed at 700 °C

Fig. 12 M–H loop of hexagonal close-packed FePt array annealed at 750 °C
and soft magnetic part from the total has been determined from the deconvolution of experimental data and tabulated in Table 3.

From the Table 3, for the sample annealed at 600 °C, the net coercivity of the FePt nanoparticles is low due to the presence of high percentage of soft magnetic phase confirming the partial ordering of phase. The increase in coercivity is observed with increase in the annealing temperature with low degree of soft phase which is in conformity with the XRD analysis. The onset of the hard phase is observed at 600 °C with low value of $H_c \approx 0.27T$. This transforms to a hard magnetic phase with large value of $H_c \sim 1$ Tesla at 750 °C, along with small amount of soft phase, which is in agreement with the XRD measurement.

**Conclusion**

The formation of monodispersed FePt nanoparticles in the form of 2D array in the presence of oleic acid and oleylamine as a spacer has been demonstrated. It was observed that the interparticle distance in the FePt array can be manipulated by varying the ratio of oleic acid and oleylamine. The 0.5 mM oleic acid and 0.5 mM oleylamine give the completely close-packed hexagonal array which can be tuned to honey comb closed packing with 1 mM oleylamine. The long range positional ordering up to 100 nm has been observed with the as-prepared nanoparticles due to the presence of spacer with superparamagnetic behaviour. The structural transformation in the case of the hexagonal close-packed assembly is found to be $95 \pm 1\%$ by means of XRD profile fitting at 750 °C. At higher temperatures, disorder in the 2D FePt array along with the increase in the particle size is observed which is attributed to coalesce and sintered growth of the nanoparticles. The deconvolution of room temperature hysteresis loop recorded for different annealing temperature was used to estimate the fraction of composition of hard and soft magnetic phase. The theoretical investigation for the various fraction of soft and hard phase is essential to understand the above behaviour and this work is in progress.

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