Chapter 3: Order-Disorder investigation of hard magnetic FePt nanostructured alloy

In this chapter, an attempt is made to understand the structural ordering in FePt system as a function of annealing temperature. This chapter deals with the synthesis of FePt nanoparticles using the polyol process and co-reduction process. Polyol process shows the formation of monodispersed FePt cluster with no evidence of a hard magnetic phase even on annealing. The synthesis using the autoclave assisted co-reduction method show well dispersed FePt nanoparticles. A systematic temperature dependent structural and magnetic transformation is investigated in detail on well dispersed FePt nanoparticles. The effect of the phase transformation on the electronic state of Fe and Pt in FePt nanoparticles is analysed using XPS. The degradation of the capping as a function of thermal annealing is also presented. The correlation between magnetic phase transformation and structural transformation is discussed in detail.
3.1 Introduction

Synthesis of chemically ordered FePt nanostructures with high magnetocrystalline anisotropy (MCA) \( \sim 10^7 \text{Jm}^{-3} \) with a small particle size \( \sim 4 \text{ nm} \) is an important goal for material scientists. These FePt alloy nanoparticles are the best candidates for technological applications in the areas such as ultra – high density magnetic recording media (Sun et al. 2000; Liu et al. 2005; Leslie et al. 1999), exchange – coupled nano-composite magnets (Zeng et al. 2002), bio medicines and biomedical applications (Chiang et al. 2007), as a catalyst (Schaffel et al. 2002), etc. Such small nanoparticles of <10 nm are single domain and exhibit superparamagnetic behavior due to thermal fluctuations of the spins even at room temperature. To overcome this, there is a need to enhance the magnetocrystalline anisotropy (MCA), which can be achieved by chemical ordering. A high degree of control on size and shape of nanoparticles are achieved invariably by chemical methods. There is plethora of physical and chemical techniques to prepare the FePt nanoparticles. The synthesis of well dispersed FePt nanoparticles demonstrated by Sun and co-workers (Sun et al. 2000) created a lot of interest in self assembled nanoparticles for high density data storage applications. Wet chemical synthesis gives a magnetically soft, disordered phase with face centred cubic (FCC) structure that transforms to a magnetically hard, ordered face centred tetragonal (FCT) structure when subjected to annealing (Yamashita et al. 2008; Sham et al. 1990; Tobita et al. 2007). The temperature at which FCC phase completely transforms to an ordered FCT phase known as the ordering temperature, depends upon the rate of annealing, time span of annealing, atomic composition of Fe and Pt in the system etc. Over the past few years various iron precursors such as, iron pentacarbonyl, iron acetylacetonate and ferric chloride etc. and platinum precursors such as platinum acetylacetonate, and platinum chloride (Sun et al. 2003; Chen et al. 2006) have been used to prepare FePt alloys. Chen et al successfully synthesized FePt nanocubes and observed an enhancement in the crystallographic orientation along (001) using the co-reduction method (Chen et al. 2006). Core/shell a structure of FePt/Fe3O4 was synthesized by Cherevko by using the same method is also helpful to achieve high density data storage media (Cherevko et al. 2009).
Very small particles of size ~4nm have a tendency to oxidize quickly and this poses a major challenge for device application. The use of surfactants 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. Moreover, such layers also enhance the biocompatibility of magnetic nanoparticles. Presa et al. has reported the exchange of the organic capping with mercaptoundecanoic acid (MUA) and proposed the use in the hyperthermia application (Presa et al. 2008). Magnetic capsules containing FePt nanoparticles for guided drug delivery has been reported (Fuchigami et al. 2011). The use of FePt nanoparticles in the dual modal computerized tomography (CT) and molecular MRI imaging have been successfully demonstrated (Chou et al. 2006). High magnetic moment in the presence of applied magnetic field helps these nanoparticles to be used as a contrasting agent in molecular imaging.

The approach to control the composition of elements Fe and Pt in FePt alloy nanoparticles is of crucial importance for metallurgical process. Andrew et al. has demonstrated the effect of the atomic composition on the ordering temperature in the solution phase (Andrew et al. 2004). The control on the atomic composition of Fe$_x$Pt$_{1-x}$ in the range of 40<x<60 is needed to achieve a phase transformation from A1 to L1$_0$. However, the size of nanoparticles also plays a prominent role in the ordering temperature. Takahashi et al. has reported that the critical particle size of the nanoparticles to transform to ordered structure is 4 nm. However, the phase transformation length (temperature range) from disorder to order depends on the interfacial energy, critical size, and type of matrix used during the synthesis etc. (Takahashi et al. 2004). The presence of oxygen on the surface of nanoparticles and processing temperature changes the behaviour of these materials drastically. The diffusion of the oxygen at high processing temperatures may result in oxides formation of Fe e.g. Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO. Moreover, a higher processing or annealing temperature to obtain the ordered alloy phase may also lead to the formation of magnetically soft Fe$_3$Pt or FePt$_3$ (Liu et al. 2003).

Range of interaction among the atomic arrangements of Fe and Pt in the FePt unit also affects the electronic states of the materials. Acker et al. in 1991 was the first to report the electronic states of bulk FePt. Different covalent interaction between the
metallic states and the relative distribution of the Fe and Pt minority and majority spin has also been understood (Acker et al. 1991). The material existing in different oxidation states have different ranges of interaction, leading to a change in the binding energy (BE) (Yamashita et al. 2008; Dablemont et al. 2008; Murugesan et al. 2008). Sham et al. demonstrated the change in the binding energy attributed to phase transformation from disordered phase to ordered phase in the AuCu system (Sham et al. 1990). Similar exercise has been performed for FePt system with particle size ~4nm and the evolution of the valance states in these nanoparticles has also been understood with the presence of valance band states in the system (Stahl et al. 2003).

A detailed investigation of the disordered – ordered transformation in terms of structural studies, magnetic studies and binding energy has been presented. The effect of the ageing on the structural and magnetic stability as a result of carbonaceous coating over the L1₀ nanoparticles has also been discussed. An attempt was made to estimate the anisotropy energy density of the material by comparing the results of the simulation (collaborative work) with the magnetic measurements performed.

### 3.2 Polyol process

#### 3.2.1 Synthesis

The metal precursors iron(III) acetylacetonate (Fe(acac)₃) and platinum(II) acetylacetonate (Pt(acac)₂) are dissolved in ethylene glycol which serves as not only a solvent but also as a reducing reagent. Polyvinylpyrrolidone (PVP), which is known to act as a capping agent was also used. Fe (acac)₃ [97% pure], Pt(acac)₂ [97% pure] and PVP [molecular weight 40,000] from Sigma Aldrich was used as obtained for the preparation of the FePt nanoparticles.

Fe(acac)₃ is a ferric salt which can be 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 (1mmol) and Fe(acac)₃ (1mmol) were mixed in ethylene glycol (100ml) in the presence of PVP (0.9 mmol). This mixture was stirred for 48 hours at
room temperature under argon atmosphere. The reduction of metallic precursors into metal nanoparticles occurs by refluxing the solution at 200 °C for four hours with continuous stirring. During refluxing the colour of the solution changes from yellowish pink to black indicating the probable formation of FePt nanoparticles. The solution was allowed to settle down at room temperature. The settled black precipitate was separated by centrifugation at 12000 rpm and washed with ethanol. Finally it was dried to obtain the powder. The obtained powder was annealed at 700°C in the presence of argon atmosphere for one hour. Figure 3.1 summarizes the above mentioned process.

**Figure 3.1:** Flow diagram of synthesis procedure with experimental setup

### 3.2.2 Structural studies

**Figure 3.2 (a)** shows the diffraction pattern of the as obtained FePt nanoparticles with broad peaks and satellite humps. The XRD pattern is fitted using the Gaussian multipeak fitting method in order to separate the two merged peaks at 40.27° and 46.64°. The observed peak positions at 40.27°, 46.64° and 67.98° correspond to the \( hkl \) planes (111), (200) and (220) respectively. Analysis of these peaks using JCPDS data indicates the presence of a disordered FCC phase of FePt.
Figure 3.2: XRD pattern of FePt nanoparticles (a) as obtained (b) annealed at 700\(^\circ\)C in argon atmosphere for one hour.

The lattice constant is estimated to be, \(a=3.879\pm 0.001\ \text{Å}\). The broad XRD peaks indicates the small size of particles, about 2.5 nm as calculated using Scherrer’s formula. Figure 3.2 (b) shows the diffraction pattern of the FePt nanoparticles.
annealed at 700 °C in the presence of argon atmosphere. This pattern is marked with narrow and well resolved peaks with increase in intensity showing more crystalline nature. The hkl planes corresponding to the peak positions at 33.15°, 35.65°, 40.12°, 46.43°, 49.39°, 54.08° and 67.89° (as indexed in the Figure 3.2 (b)), shows the formation of FCT phase. Observation of the superlattice peaks at 33° confirms the transformation of FCC phase to the chemically ordered L10 (FCT) phase. The estimated lattice constant for FCT phase are, a=3.880±0.0001 Å and c=3.697±0.001 Å. Apart from the FCC and FCT phase of FePt, iron oxide phase is also present. All the present phases are indicated in the Figure 3.2(b).

3.2.3 Transmission electron microscopy (TEM) studies

Transmission electron microscopy (TEM) has been done using a carbon coated copper grid. The grid is prepared by drop casting the FePt nanoparticles dispersed in ethanol. Figure 3.3(a) shows the bright field image of as prepared FePt cluster with an average size of 130 nm. Figure 3.3 (b) shows the magnified image of the Figure 3.3(a) showing a homogeneous shape and size distribution. The average particle size is estimated to be 2.7±0.3 nm as shown in Figure 3.3(c). Furthermore, the selected area electron diffraction (SAED) is investigated for as prepared FePt nanoparticles confirming the presence of FCC phase as given in Figure 3.3(d). The (hkl) planes indentified is shown in Figure 3.3(d)

![Figure 3.3: TEM image of (a) unannealed FePt nanoparticles (b) magnified image of (a) and corresponding (c) particle size distribution and (d) SAED pattern.](image)
Figure 3.4 shows the bright field image of 700°C annealed FePt nanoparticles. This shows formation of particles of 150 nm after annealing. The SAED image shows the presence of mixed phase as shown in inset. It is not possible to identify the (hkl) planes due to the presence of several phases, as clearly indicated in XRD pattern of Figure 3.2(b).

Figure 3.4: TEM image of annealed FePt nanoparticles and corresponding SAED as an inset

3.2.4 Magnetic measurements

The magnetic properties of the FePt nanoparticles for both as prepared and post annealed samples were investigated by their hysteresis curve obtained at room temperature as shown in Figure 3.5(a) and 3.5(b) respectively. The as prepared nanoparticles have a zero coercivity i.e. behave superparamagnetically at room temperature. However a complete magnetic saturation is not observed even at a magnetic field of 7 Tesla. The unsaturated magnetic moment observed may be due to high magnetocrystalline anisotropy of magnetic materials and the presence of a paramagnetic phase in the sample. On annealing the FePt nanoparticles, a small loop starts appearing with a coercivity of 700 Oe. The shape of the hysteresis loop does not indicate the hard magnetic behaviour which is generally observed in FCT FePt system. The coercivity observed may possibly be due to the grain growth and several phases that coexist in the system.
This process does not yield a single phase with hard magnetic behaviour. Hence, a controlled chemical process was attempted and the results obtained are discussed below.

![MH curve of FePt nanoparticles](image)

**Figure 3.5:** MH curve of FePt nanoparticles (a) annealed (b) annealed at 700°C

### 3.3 Autoclave assisted co-reduction process

#### 3.3.1 Synthesis

FePt nanoparticles of equiatomic composition of Fe and Pt 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 in the presence of oleic acid (OA) and oleylamine (OAm).
Table 3.1: Structure of the chemical used in the reaction

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure</th>
<th>Melting point/Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron(III) acetylacetonate</td>
<td><img src="image" alt="Structure" /> Fe^{3+}</td>
<td>182°C/---</td>
</tr>
<tr>
<td>Platinum(II) acetylacetonate</td>
<td><img src="image" alt="Structure" /> Pt^{0+}</td>
<td>249°C/---</td>
</tr>
<tr>
<td>Oleic acid</td>
<td><img src="image" alt="Structure" /></td>
<td>---/360°C</td>
</tr>
<tr>
<td>Oleylamine</td>
<td><img src="image" alt="Structure" /></td>
<td>---/350°C</td>
</tr>
<tr>
<td>1,2 Hexadecanediol</td>
<td><img src="image" alt="Structure" /></td>
<td>70°C / 356°C</td>
</tr>
<tr>
<td>Diphenyl ether</td>
<td><img src="image" alt="Structure" /></td>
<td>17°C / 268°C</td>
</tr>
</tbody>
</table>

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 were used as a surfactant in order to obtain well dispersed nanoparticles. Table 3.1 describes the structure of the chemicals used in the reaction. 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 indicating the formation of FePt nanoparticles. Ethanol was added to the solution to precipitate the nanoparticles obtained which was separated by centrifugation at 12000 rpm for 15 minutes and
finally dispersed in hexane. Figure 3.6 summarizes the preparation process of FePt nanoparticles using the co-reduction process assisted by autoclave.

The as prepared hexane dispersed FePt nanoparticles were drop casted on polished precleaned silicon to form a thick film. The FePt coated silicon substrates were subjected to heat treatments at 400 °C, 500 °C, 600 °C, 700 °C and 750 °C for 2 hrs 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 and are presented in the following sections.

3.3.2 Structural studies (XRD)

Figure 3.7(a-f) shows the XRD pattern for the as prepared sample and samples annealed at different temperatures. The as obtained sample shows broad humps at 40.21° indicated by arrows corresponding to (111) plane with a trace of (200) plane at 47.10° as seen in Figure 3.7(a). Appearance of an additional hump at 69.32° corresponding to (220) was observed upon annealing at 400°C (Figure 3.7(b)). These humps correspond to the disordered FCC phase. The above broad humps evolve as
relatively sharper peaks upon annealing at 500°C marked with the appearance of a superlattice peak at 32.87° corresponding to (hkl) plane (110), and an additional shoulder at 47.10°. At 600°C, a second superlattice peak is observed at 20, 23.92° corresponding to (001).

On further annealing at 700°C this shoulder appears as a distinct peak at 48.97° corresponds to (002) plane. The splitting of the peak at 47.10° into two distinguishable peaks corresponding to (200) and (002) planes is a clear indication of its transformation from disordered FCC to ordered FCT phase. It is also observed that intensity of both the superlattice peaks increases upon annealing and reaches to 30% intensity relative to highest intensity peak (111) at 750°C. The peaks are indexed to their (hkl) values using the ICDD data (00-026-1139).

The lattice constants were also estimated for all the annealed samples and are given in Table 3.2. From the table it is evident that the ‘a’ values increases with annealing temperature from 3.84 to 3.86 Å while ‘c’ values decreases from 3.84 to 3.74 Å. This also indicates the deviation from cubic symmetry, which is also seen from (c/a) estimates given in the table, the (c/a) decreases from 1 to 0.9694.

![Figure 3.7: 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](image_url)
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 (200) and (002) planes respectively. The degree of ordering, $S$ was estimated using the equation 3.1 (Chen et al. 2006) and is presented in Table 3.2.

$$S^2 = \frac{(1 - c/a)_{exp}}{(1 - c/a)_{std}}$$  \hspace{1cm} (3.1)

From the Table 3.2 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 indicating 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 (3.1) indicates only the percentage of tetragonal phase. It is more appropriate to determine the atomic ordering, using the ordering parameter ($S^*$), estimated using the superlattice peak viz. (001) indicated in Figure 3.7.

Table 3.2: Variation of 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>c/a</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>3.84</td>
<td>3.84</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>3.84</td>
<td>3.84</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>3.85</td>
<td>3.79</td>
<td>0.9838</td>
<td>0.7092</td>
</tr>
<tr>
<td>600</td>
<td>3.85</td>
<td>3.77</td>
<td>0.9784</td>
<td>0.8190</td>
</tr>
<tr>
<td>700</td>
<td>3.86</td>
<td>3.75</td>
<td>0.9712</td>
<td>0.9457</td>
</tr>
<tr>
<td>750</td>
<td>3.86</td>
<td>3.74</td>
<td>0.9694</td>
<td>0.9748</td>
</tr>
</tbody>
</table>

The transformation from disordered to ordered atomic arrangement of Fe and Pt in unit cell has been calculated using the following formula (Sakuma et al. 2006; Kalyan et al. 2010).

$$S^*_{hkl} = \frac{(I_{hkl}/I_{111})_{exp}}{(I_{hkl}/I_{111})_{std}}$$  \hspace{1cm} (3.2)
\[ I_{hkl} \] is the intensity of the superlattice peak, which corresponds to \( I_{001} \) in the present case.

The ordering parameter estimated for superlattice peaks \( S^*_{001} \) is given in Table 3.3.

**Table 3.3: 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>
</tr>
<tr>
<td>600</td>
<td>0.6708</td>
</tr>
<tr>
<td>700</td>
<td>0.9626</td>
</tr>
<tr>
<td>750</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

The ordering parameter increases with annealing temperature reaching a value of 0.9998 at 750°C, indicating an almost perfect atomic ordering. 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 3.8, which shows the maximum ordering parameter from the above analysis. The degree of long range chemical ordering in a unit cell depends upon the atomic position. The long range ordering (L) is quantified using the following formula:

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

(3.3)

where \( r_{Pt} \) (or \( r_{Fe} \)) is the fractional site occupied by Pt (or Fe) atom (Warren B.E).

The peak profile parameter and phase parameters are refined separately with space group Fm-3m and P4/mmm (International table of crystallography) for FCC and FCT phases respectively. In order to determine the percentage of disordered FCC and ordered FCT phase, 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 the Table 3.4. The pattern shown in Figure 3.8 is difference between the experimental and calculated data. The pattern represented by arrow shows the
presence of ordered FCT phase in the system with their respective estimated percentage of 99.92% showing a complete ordering. This is conformity with the ordering parameter $S^* \sim 99.98\%$. The lattice parameters were estimated for ordered FCT phase using the refined pattern and found to be $a=3.858$ Å and $c=3.736$ Å with goodness of fitting ($\chi^2$) value 1.37.

Table 3.4: Atomic position and occupancy of Fe and Pt in FePt unit cell.

For FCC Phase

<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>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>
</tbody>
</table>

For FCT Phase

<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>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>

Figure 3.8: Rietveld refined X-ray diffraction pattern (in red) of FePt nanoparticles annealed at 750°C using TOPAS.
Using the profile fitted Rietveld data, an attempt was made to reconstruct the unit cell corresponding to Fm-3m and P4/mmm space group and is represented in Figure 3.9(a,b) respectively.

![Figure 3.9: FePt unit cell corresponding to (a) Fm-3m and (b) P4/mmm space group](image)

### 3.3.3 Transmission electron microscope (TEM) Studies

Transmission electron microscope was used to investigate the size and phase of as prepared nanoparticles and nanoparticles annealed at 400\(^{0}\)C and 750\(^{0}\)C. Figure 3.10(a) and 3.10(b) shows the bright field images of as prepared FePt nanoparticles dispersed on a copper grid. Assembled FePt nanoparticles were observed. The size distribution is given as an inset in Figure 3.10(a) showing particles with a mean size of 4 nm but with non spherical shape. Such well assembled nanoparticles are due to the use of oleic acid and oleylamine that act as a surfactant. Figure 3.10(b) shows the magnified image of Figure 3.10(a). The analysis of the SAED shown in Figure 3.10(c) gives a disordered FCC phase with the presence of (111) and (200) planes as also observed from XRD. The diffuse rings observed are due to the low degree of crystallinity in the sample. Upon annealing at 400\(^{0}\)C, particles start agglomerating due to degradation of surfactant with no monodispersity as seen in Figure 3.11(a). The SAED shown in Figure 3.11(b) shows that the disordered FCC phase of particles is retained but with an enhancement in the crystallinity. On further annealing at 750\(^{0}\)C the particles grow in size as observed in Figure 3.11(c). The corresponding indexed SAED pattern in Figure 3.11(d) shows all rings corresponding to ordered FCT phase with superlattice structure becoming very prominent which matches well with XRD results. Annealing results in the growth of nanoparticles with a broad distribution.
Figure 3.10: TEM image of (a) as prepared FePt nanoparticles, (b) Magnified image of (a) and (c) corresponding SAED pattern

Figure 3.11: TEM image of FePt nanoparticles (a) annealed at 400°C (b) corresponding SAED pattern (c) annealed at 750°C (d) corresponding SAED pattern
The average particle size is estimated using Gaussian distribution function for sample annealed at 750°C is 29 ± 1.8 nm. Some particles look elongated and some clustered. This can be due to the growth of the nanoparticles.

### 3.3.4 Magnetic Measurements

The magnetic behaviour of FePt nanoparticles were investigated as a function of annealing temperature by recording the hysteresis loop at RT. Figure 3.12(a and b) shows 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 with almost zero coercivity indicating the super paramagnetic nature, as expected for FePt nanoparticles of ~4 nm size. Sample annealed at 400°C exhibits a small coercive field of 290 Oe. The relatively low value of the magnetization and no tendency to saturate even at 20 kOe field 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 shown in Figure 3.12(b). The hysteresis loop obtained on the sample annealed at 500°C shows a marked increase in coercivity, $H_c \approx 4.67$ kOe and also a saturating behaviour as shown in Figure 3.13(a) which further increases to 5.8 kOe at 600°C (Figure 3.13(b)).

This marked variation in the coercivity indicates the set in of the hard magnetic phase. It is seen from Figure 3.14(a) 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 3.14(b) shows a perfect loop with $H_c \approx 11.8$ kOe suggesting the complete conversion from disordered FCC to ordered FCT. The hysteresis studies clearly reveal that with heat treatment there is a gradual transformation from soft phase to hard phase with an intermediate mixed phase.

The transformation to the hard phase with the high value of coercivity is due to the high magnetic anisotropy associated with the FCT phase, as a result of spin orbit coupling (Sun et al. 2000). Hysteresis measurements are not sufficient to determine anisotropy, but experiment like ferromagnetic resonance needs to be performed.
However an alternative way to obtain anisotropy is by means of model simulations. This includes information on the size, interaction and temperature.

![MH loop of (a) as prepared sample and (b) sample annealed at 400°C](image1)

**Figure 3.12:** MH loop of (a) as prepared sample and (b) sample annealed at 400°C

![MH loop of sample annealed at (a) 500°C and (b) 600°C](image2)

**Figure 3.13:** MH loop of sample annealed at (a) 500°C and (b) 600°C
An estimate of the anisotropy energy density of the material by comparing the results of the simulation with the magnetic measurements were performed on the chemically prepared FePt. Magnetic nanoparticle arrays are modelled as clusters of polydispered single domain magnetic particles with randomly oriented easy axes placed in a cubical cell. The magnetizations of the arrays are simulated using the Monte Carlo method using the standard Metropolis algorithm. The simulation system consists of 64 magnetic nanoparticles of varying sizes, distributed according to a lognormal distribution, dispersed randomly in a cubic volume. The behaviour of the system is decided by the physical attributes of the nanoparticles, which are the size and the anisotropy energy density and the interparticle interactions in the system, viz. the dipolar and exchange interactions.

The Hamiltonian for a system of interacting single domain magnetic nanoparticles with an uniaxial anisotropy energy density $K$ in a magnetic field $H$ (Lamba 2004) is written as:

$$
\mathcal{H} = -K \sum_i v_i \left( \frac{\tilde{\mu}_i \cdot \tilde{\mu}_i}{|\tilde{\mu}_i|^2} \right) - \sum_{i<j} \mu_0 \sum_{i<j} \frac{3(\tilde{\mu}_i \cdot \tilde{g}_{ij})(\tilde{g}_{ij} \tilde{\mu}_j) - \tilde{\mu}_i \cdot \tilde{g}_{ij}}{r_{ij}^3} - \mu_0 \sum_i \tilde{H} \cdot \tilde{\mu}_i
$$

(3.4)
where \( \hat{n}_i \) is the unit vector along the easy (anisotropy) axis of each particle and \( \hat{r}_{ij} \) is the unit vector along the separation between a pair of particles \( i \) and \( j \), which is \( \vec{r}_{ij} \).

The value of \( K \) is a parameter in the simulation and later we shall estimate a value for \( K \) which would give a best fit to the experimental data. \( \mu_i \) is the magnetic moment of the \( i \)th nanoparticle and is given by \( M_S V_i \), where \( M_S \) is the saturation magnetization of bulk FePt (1.43 T) (Skomski et al. 2003) and the volume \( V_i \) is the volume of a sphere with a diameter equivalent to the particle size \( D_i \) (20 x_i nm).

Figure 3.15 (a) Variation of coercivity for three different values of anisotropy energy density at 10 K and 300 K for strong dipolar interactions (\( a = 10 \)) and varying exchange interactions compared with the experimental values of coercivity (b) hysteresis at 300 K and 10 K
Figure 3.15 (a) below shows the plot of strength of the exchange and coercivity obtained using simulation for the L10 phase at temperature 300 K and 10 K. The experimental coercivity data obtained from the present work is shown as dotted line for both 300 K and 10 K. The hysteresis recorded at RT and 10 K is shown in Figure 3.15(b).

It is seen from the Figure 3.15 that the high value of the room temperature coercivity is due to the presence of strong exchange interactions along with a high value of anisotropy energy density, estimated to lie between 2.25 – 2.5 MJ m\(^{-3}\) for FePt particle of size ~30 nm. The magnetic behaviour of the alloy nanoparticles are not decided by only the size. The phase transformation depends very much on the percentage composition of Fe and Pt in the FePt alloy which was determined using XPS.

3.3.5 X-ray photoelectron spectroscopy (XPS) studies

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 FePt nanoparticles and used to estimate the elemental composition. All the experimentally observed core level spectra were calibrated with the binding energy of C (1s) which is (284.6 eV). The C (1s) spectra recorded for the FePt system as prepared and annealed is given in Figure 3.16. The binding energy is estimated to be 284.8 eV, hence giving a chemical shift of \(\Delta E = -0.2\) eV.

The presence of a small amount of oxygen was observed from the core level scan of O (1s) for as prepared capped FePt nanoparticles and is given in Figure 3.17(a). 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 as clearly indicated in Figure 3.17(b) and 3.17(c) respectively. Hence the formation of any oxides of iron is ruled out. Hence the fitting was performed for the pure alloy formation.
Figure 3.16: C (1s) spectra recorded for the FePt system (a) as prepared (b) 500°C (c) 750°C

Figure 3.17: Core level scan of O (1s) for (a) as prepared (b) 500°C (c) 750°C

Figure 3.18 shows the Fe 2p core level scan for iron with 2p\(3/2\) peaks for as prepared sample and sample annealed at different temperatures. The core level spectra of Fe (2p\(3/2\)) for as prepared FePt nanoparticles yields after deconvolution three peaks at 707.2 eV, 708.3 eV and 711.2 eV as shown in Figure 3.18(a). The peak at 707.2 eV indicates the presence of pure iron while peak at 708.3 eV and 711.2 eV is a result 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 (Murugesan et al. 2008; Yamashita et al. 2008). 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 gets suppressed with a slight shift in the binding energy as shown in Figure 3.18(b).

The enhancement in intensity and shift in binding energy reveals the removal of the organic capping on the nanoparticles. On annealing the sample further at 750 °C (Figure 3.18(c)), no change in the binding energy corresponding to pure Fe was observed. However a chemical shift is observed from 709.3 to 708.9 eV and from 711.4 eV to 710.9 eV. This may be attributed to the phase transformation of FePt alloy from disordered to an ordered state.

Figure 3.18: Fe 2p\(_{3/2}\) core level XP Spectra of Fe (a) as prepared (b) annealed at 500°C and (c) 750°C

Figure 3.19(a,b,c) shows the core level Pt (4f) spectra of as prepared FePt alloy and annealed at 500 and 750 °C respectively. The spectra for as prepared nanoparticles clearly show the presence of two distinct but broad peaks at Pt 4f\(_{5/2}\) (72.4 eV) and Pt 4f\(_{7/2}\) (75.6 eV) respectively. The peaks corresponding to Pt 4f\(_{5/2}\) 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 4f\(_{7/2}\) 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 3.19(b) 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 disordered to ordered phase. The binding energy corresponding to pure Pt is 70.9 eV which is 0.5 eV is 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 (Murugesan et al. 2008; Yamashita et al. 2008; Sham et al. 1990). The elemental composition of Fe and Pt estimated using the area under the loop of the core level spectra of Fe (2p) and Pt (4f) is Fe 46% and Pt 54% which is nearly in the range of ordering composition according to the phase diagram of Figure 1.10. However, the formation of the alloy is confirmed by studying the valence band spectra.

![Figure 3.19: 4f core level XP Spectra of Pt (a) as prepared (b) annealed at 500°C and (c) 750°C](image_url)
Figure 3.20 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 the broad spectra the presence of peaks at 0.3 eV, 2.0 eV, 4.0 eV and 6.0 eV is very clear from Figure 3.20(b) and 3.20(c) respectively. The valence 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 (Tobita et al. 2007; Boven et al. 2005). The peak at 6.0 eV is the prominent characteristic peak of FePt which shows the presence of ordered L1₀ phase (Boven et al. 2005).

3.3.6 Carbon encapsulated FePt nanoparticles

It was observed from the TEM of Figure 3.21(a) that the samples annealed at 750°C, exhibits agglomeration with a large distribution of particle size. HRTEM was performed on the sample and shown as an inset of Figure 3.21(a). The estimated interplaner distance from the lattice fringes is 3.5Å. Also, the figure gives the direct
evidence of a capping on the FePt nanoparticles. This layer may be carbonaceous covering formed due to outgas of hydrogen and oxygen from organic capping as represented pictorially in Figure 3.21(b).

Figure 3.21: (a) HRTEM image of FePt nanoparticles annealed at 750°C and HRTEM as an inset (b) Pictorial representation of the carbonaceous layer over the FePt nanoparticles
Further the nature of capping over the FePt nanoparticles is investigated in detail as a function of annealing temperature. **Figure 3.22** shows the Raman spectroscopy recorded using $\lambda = 514$ nm of as prepared FePt nanoparticles capped with organic molecules oleic acid and oleylamine as ligand 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 centred at 1335 cm$^{-1}$ and 1600 cm$^{-1}$ for all the annealed samples. These bands have been identified as D band and G band respectively, which occur for graphitic carbon. The graphitic carbon band (G band) has been observed for the graphitic nature of the carbon materials whereas disordered carbon band (D band) has been observed for the unorganized carbon atom in the sample and explained in several ways (Iqbal et al. 1981; Ferrari et al. 2007; Tuinstra et al. 1970). This phenomenon of formation of carbon on the FePt nanoparticles with forming gas makes the system pure and avoids the formation of oxide on the alloy nanoparticle.

![Figure 3.22: Raman spectra of as prepared and samples annealed at different temperatures.](image)

**Figure 3.22:** Raman spectra of as prepared and samples annealed at different temperatures.
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 the Table 3.5. The increasing value of $I_D / I_G$ with annealing represents the dominance of graphitic carbon on the surface of FePt nanoparticles.

**Table 3.5: Ratio of $I_D / I_G$ as a function of annealing temperature**

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

![MH loop of L1₀ FePt nanoparticles kept for a year under normal atmosphere.](image)

It is interesting to observe that the presence of such graphitic carbon acts as a protective layer. This was observed by recording the MH loop over a period of one
year which shows no significant change in the coercivity and hence retaining a stable FePt phase shown in Figure 3.23.

3.4 Conclusion

The as synthesized nanoparticles using polyol process are superparamagnetic at room temperature with a disordered fcc phase. TEM studies reveal uniform spherical particles of about 2.5 nm size within the cluster size of ~130 nm. On annealing, a mixed phase of FCT FePt, FCC FePt and Fe-O is obtained. MH curve do not saturate for pre and post annealed particles suggesting the presence of either magnetocrystalline anisotropy along the easy axis or the presence of some percentage of paramagnetic phase. The shape of the hysteresis loop strongly indicates the existence of multiple magnetic phases such as FePt, FePt₃ or Fe₃Pt in the system.

![Figure 3.24: Coercivity and ordering parameter as a function of annealing temperature](image)

Well dispersed and well assembled FePt nanoparticles were successfully synthesized by chemical co-reduction method using autoclave with an average size~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 ordered FCT 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.

For a perfectly ordered system both magnetic and structural parameters play an equally important role. This is evident from the plot of coercivity and order parameter as a function of temperature (Figure 3.24).

The XPS results show a formation of Fe$_{46}$Pt$_{54}$ with no oxide formation and confirming phase transformation from A1 to L1$_0$. The HRTEM image shows the presence of a carbon layer coated over FePt nanoparticles which was attributed to the presence of graphitic/carbonaceous layer which was also confirmed from Raman spectroscopy. The graphitic layered capping avoids oxidation and helps in retaining the hard magnetic phase for long duration.
3.5 References


Chapter 3  
Order- Disorder investigation of hard magnetic FePt nanostructured alloy


