Chapter 6: Effect of off-stoichiometric and additives on the ordering temperature of FePt nanoparticles

This chapter deals with the methodology employed to lower down the ordering temperature in FePt alloy system. Two different techniques have been used to lower down the ordering temperature and discussed in Section A and Section B.

In Section A, an attempt to synthesize the off stoichiometric composition of FePt nanoparticles was made using the chemical co-reduction methods. Structural and magnetic phase transition as a function of annealing temperature has been investigated in detail. Enhancement and stabilization in the structural and magnetic phase transformation is observed by means of Pt diffusion into off stoichiometric FePt from Pt under layer. The effect of different additives like Ag, Cu, and Ba on the structural and magnetic phase transformation of FePt nanoparticles is elaborated in Section B.
6.1 Introduction

The primary challenge for research in the field of magnetic recording devices is the synthesis of nanoparticles with high coercivity but low ordering temperatures. FePt nanoparticles in the L1\_0 phase with chemically stable and very high magneto-crystalline anisotropy of the order of $7 \times 10^7$ erg/cm\(^3\), are good candidates for magnetic recording devices with data storage densities of about 1 Tbit/in\(^2\) (Sun et al. 2000; 2003; 2006 Chokprasombat 2011; Medwal et al. 2012). The L1\_0 phase which is the thermodynamically favoured structure for the FePt nanoparticles in the near-equiatomic composition, is achieved only at high annealing temperature (> 600\(^0\)C) (Sun et al. 2000; Gutfleish et al. 2005; Chen et al. 2004, Medwal et al 2012). However, the high annealing temperatures required for phase transformation can lead to particle sintering growth and agglomeration (Medwal et al. 2012; Yano et al. 2008; Sehdev et al. 2011, Thomson et al. 2005). However, an important pre-requisite for applications in ultra-high density storage media is the presence of monodispersed particles with a controlled size.

Most of the research effort in this direction is focused on prevention of sintering by using salt-annealed matrices as well as core-shell systems with SiO\_2, MgO etc as the oxide-shell (Yan et al. 2009; Kohda et al. 2008, Ishio et al. 2012). However, such assemblies give limited coercivities and exhibit presence of a soft magnetic phase.

Alternatively, by varying the relative composition of Fe and Pt in the FePt alloy system ordering temperature can be reduced (Seki et al. 2003; Dong et al. 2009; Andrew et al. 2004). This can be achieved either by synthesizing the FePt nanoparticles with off-stoichiometric composition or introducing the Pt under layer (Chen et al. 2003; Seki et al 2003). In “Section A” of this chapter, an attempt to lower down the ordering temperature by synthesizing off-stoichiometric FePt nanoparticles has been made. The effect of Pt under layer on the prepared FePt nanoparticles as a function of annealing temperature has also been investigated to further lowering down the ordering temperature. The correlation between the magnetic and structural studies with phase transformation from A1 to L1\_0 to A1 has also been investigated in detail.
Metal additives and in particular non magnetic are also used to tailor the magnetic and structural properties of FePt alloy nanoparticles (Lui et al. 2009; Harrell et al. 2005; Feng et al. 2006; Lai et al. 2005; Mei et al. 2007; Ikempto et al. 2008; Yu et al. 2010). The choice of metal should be in such a way that the element added does not form a solid solution with FePt nanoparticles but induce high mobility of Fe and Pt in the FePt unit cell. This results in the enhanced structural and magnetic phase transformation even at very low temperature. In Section B an attempt to achieve a chemical ordering with high to moderate coercivity at low temperature, to avoid the coalescing and agglomeration process is made. Metals such as Ag, Cu were chosen (Xu et al. 2004; Aimuta et al. 2004; Wang et al. 2010’ Sun et al. 2003; Kura et al. 2004; Brombacher et al. 2012). Addition of Ba during chemical synthesis of FePt alloy nanoparticles is also been investigated.

Section A

Off stoichiometry driven chemical ordering

6.2 Experimental

The metal precursors iron (III) acetylacetonate (Fe(acac)_3, 97% pure) and platinum(II) acetylacetonate (Pt(acac)_2, 97% pure), solvent phenyl ether, reducing agent 1,2 hexadecanediol and surfactants oleic acid and oleylamine purchased from Sigma Aldrich were used as obtained for the preparation of the FePt nanoparticles.

It is to be mentioned here that the FePt nanoparticles prepared using 0.5mM Pt (acac)_2 and 0.5 mM of Fe(acac)_3 yielded a composition of Fe_{46}Pt_{54}, which is nearly equiatomic. This is discussed in Chapter 3 and Chapter 4. In this chapter the aim is to prepare off-stoichiometric composition. Keeping in view the phase diagram (chapter 1), for obtaining a lower ordering temperature, excess of Fe is preferred. Hence the Pt and Fe salts composition were so chosen to obtain as nearly Fe_{3}Pt composition.
FePt alloy nanoparticles were synthesized by the chemical co-reduction method. The metal precursors iron(III) acetylacetonate (Fe(acac)) and platinum(II) acetylacetonate (Pt(acac)) are co-reduced in the presence of 1,2 hexadecanediol as a reducing reagent and oleic acid and oleylamine as a surfactant. An off-stoichiometric amount of Pt(acac) (0.35 mmol) and Fe(acac) (0.65 mmol) were mixed in 40ml phenyl ether in the presence of 0.5 mmol of oleic acid and oleylamine with 4mmol of 1,2 hexadecanediol. This mixture was stirred for half hour at room temperature under inert atmosphere. The metallic ions from the metal precursors are converted to the metal nanoparticles by refluxing the solution at 250°C for 30 min with continuous stirring. The solution was cooled down to room temperature under argon atmosphere. 40ml ethanol was added to solution to precipitate the solution and separated by centrifugation at 12000 rpm for 15 minutes and washed with ethanol twice or thrice. The final precipitate obtained was dispersed in hexane. The elemental composition of the prepared off-stoichiometric FePt is estimated using the Rutherford back scattering and found to be Fe60Pt40. Table 6.1 summarizes the amount of Pt and Fe salts used along with the elemental composition obtained.

<table>
<thead>
<tr>
<th>Pt (acac)</th>
<th>Fe(acac)</th>
<th>FeₓPt₁₀₀₋ₓ (Expected)</th>
<th>FeₓPt₁₀₀₋ₓ (Experimental)</th>
<th>Chapter 3 and 4 (equiatomic), Chapter 6 (Fe rich FePt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>Fe₅₀Pt₅₀</td>
<td>Fe₆₆Pt₅₄</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>0.65</td>
<td>Fe₆₅Pt₃₅</td>
<td>Fe₆₀Pt₄₀</td>
<td></td>
</tr>
</tbody>
</table>

The as-prepared off-stoichiometric FePt nanoparticles is here afterwards denoted as Fe₆₀Pt₄₀ or Fe rich FePt. They were drop-casted on polished Si wafer and Pt-coated Si wafers. Pt was deposited using DC sputtering. In order to determine the ordering temperature at which the phase transformation from FCC to FCT phase occurs annealing was carried out at different temperatures. The annealed samples were investigated for the structural and magnetic properties.
Chapter 6

Effect of off-stoichiometric and additives on the ordering temperature...

6.3 Results and discussions

6.3.1 Transmission electron microscopy (TEM) studies

Figure 6.1 shows the TEM image of as prepared nanoparticles dispersed on TEM grids with an average particle size of 3 nm. A hexagonal closed packed array is observed. The periodic hexagonal arrangement of the particles is represented by Fast Fourier Transformation (FFT) and shown as an inset. The observed hexagonal packing is due to the use of oleic acid and oleylamine during the synthesis of FePt nanoparticles. These particles are subjected to heat treatment for structural and magnetic phase transformation studies.

![Figure 6.1: TEM image of as prepared Fe\textsubscript{60}Pt\textsubscript{40} alloy nanoparticles. FFT pattern is given as an inset.]

6.3.2 Structural studies

Figure 6.2(a-f) shows the XRD pattern for the as prepared sample and samples annealed at different temperatures on the polished silicon substrate. The as prepared sample shows humps centred at 40.17\(^0\) corresponding to (111) plane as shown in
Figure 6.2(a). On annealing at 400 °C, a shift in 2θ corresponding to (111) is observed. The observed (111) plane corresponds to FCC phase shown in Figure 6.2(b). This may be attributing to the disturbance and rearrangement of the Fe and Pt atoms in FePt alloy unit cell. On further annealing at 500 °C, an appearance of an additional hump at 47.43° (200) was observed (Figure 6.2(c)) but still corresponding to the disordered FCC phase.

![Figure 6.2: XRD patterns of Si/Fe<sub>60</sub>Pt<sub>40</sub> nanoparticles (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C (f) 750°C](image)

At 600°C, superlattice peaks corresponding to (001) and (110) with sharp intensity is observed at 2θ, 24.13° and 33.04° respectively. The thermal energy induced superlattice peaks are characteristic peak of the onset of chemical ordering in the system. This chemical ordering is attributed to the stacking of Fe and Pt atomic plane alternatively. In addition, a spilt in (200) peak corresponding to (200) and (002) at 2θ, 47.36° and 49.23° respectively is also observed (Figure 6.2(d)). The observed splitting reveals the induced tetragonality in the unit cell as a result of chemical ordering. On further annealing at 700°C a fall in the intensity with an additional shoulder start appearing at the base of (111) observed from the asymmetry of the peak. This is also followed by a reduction in the peak of the preferred orientation along (001) (Figure 6.2(e)). At 750°C, shoulder
become distinct and clear with enhanced intensity indicating the additional phase identified as Fe$_3$Pt phase (shown by *) as shown in Figure 6.2(f). The lattice constants were also estimated for all annealed samples and were used to determine the c/a value and are given in Table 6.2. The estimate of c/a indicate the degree of asymmetry of the unit cell which in turn denote the phase transformation from cubic to tetragonal phase.

**Table 6.2: Variation in c/a values as a function of annealing temperature for Si/Fe$_{60}$Pt$_{40}$.**

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>c/a</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>1</td>
<td>FCC</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>FCC</td>
</tr>
<tr>
<td>500</td>
<td>0.974</td>
<td>FCT</td>
</tr>
<tr>
<td>600</td>
<td>0.964</td>
<td>FCT</td>
</tr>
<tr>
<td>700</td>
<td>0.930</td>
<td>FCT</td>
</tr>
<tr>
<td>750</td>
<td>0.940</td>
<td>FCT</td>
</tr>
</tbody>
</table>

From the table it is can be concluded 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 the tetragonality in the structure.

XRD measurement has also been performed on the Si/Pt/Fe$_{60}$Pt$_{40}$ as a function of annealing temperature. The off-stoichiometric Fe$_{60}$Pt$_{40}$ prepared as mentioned above is dispersed on Pt coated silicon. Figure 6.3(a-f) shows the XRD spectra for the as prepared sample and samples annealed at different temperatures on the polished silicon substrate. The as prepared sample shows humps centred at 40.08$^\circ$ corresponding to (111) plane as shown in Figure 6.3(a). On annealing at 400 $^\circ$C, no variation is observed (Figure 6.3(b).) On further annealing at 500 $^\circ$C, a shift in 2θ corresponding to (111) is observed along with broadening of hump. This broadening corresponds to the presence of two peaks corresponding to two different phases. This broad (111) plane may correspond to FCC phase of Fe$_3$Pt and partial transformation into FCC FePt as indicated in Figure 6.3(c). This is due to the onset of the disturbance and rearrangement of the Fe and Pt atoms in FePt alloy unit cell. An
appearance of an additional hump at 47.43° corresponding to (200) was also observed (Figure 6.3(c)).

At 600°C, superlattice peaks corresponding to (001) and (110) with sharp intensity is observed at 2θ, 23.95° and 33.08° respectively as shown in Figure 6.3(d). The observed asymmetric shape of the (111) reflection is also attributed to the presence of additional peak which seem to be merged with (111) peak. The thermal energy induced superlattice peaks are characteristic peak of chemical ordering in the system. The ordering process is a thermally activated process which requires heat treatment to impart energy so to stimulate the atom mobility from one layer to another layer. This energy also allows the atoms to move from one lattice site to another lattice site result in a chemically ordered FePt unit cell. This chemically ordering in the unit cell is attributed to the stacking of Fe and Pt atomic plane alternatively.

Figure 6.3: XRD patterns of Si/Pt/Fe_{60}Pt_{40} nanoparticles (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C (f) 750°C

A spilt in the (200) peak into (200) and (002) corresponding to 2θ value 47.36° and 49.23° respectively is also observed (Figure 6.3(d)). This confirms the induced tetragonality in the unit cell due to chemical ordering. On further annealing at 700°C, an asymmetry at the base of (111) become more prominent with enhanced preferred orientation along (001) (Figure 6.3(e)). At 750°C, asymmetric peak split into two
distinct peak at 2θ value 40.41° and 41.03° corresponding to (111) of Fe₃Pt and FCT FePt respectively as shown in Figure 6.3(f). A shift in 2θ value is observed. For the sake of clarity, an expanded view of the region between 2θ 38° to 43° is given in Figure 6.4 to indicate the three different phases viz. FCC FePt, FCC Fe₃Pt and FCT FePt. An estimate of c/a with annealing temperature is given in the Table 6.3.

Figure 6.4: Expanded XRD of Figure 6.2 showing (111) of three different phases corresponding to Fe₆₀Pt₄₀ FCC, Fe₆₀Pt₄₀ FCT and Fe₃Pt FCC at (a) as prepared (b) 400°C (c) 500°C (d) 600°C (e) 700°C (f) 750°C.

Table 6.3: Variation in c/a values as a function of annealing temperature for Si/Pt/Fe₆₀Pt₄₀.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>c/a</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>1</td>
<td>FCC</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>FCC</td>
</tr>
<tr>
<td>500</td>
<td>0.969</td>
<td>FCT</td>
</tr>
<tr>
<td>600</td>
<td>0.960</td>
<td>FCT</td>
</tr>
<tr>
<td>700</td>
<td>0.935</td>
<td>FCT</td>
</tr>
<tr>
<td>750</td>
<td>0.930</td>
<td>FCT</td>
</tr>
</tbody>
</table>
From the Table 6.3 it is can be concluded 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.

6.3.3 Magnetic Measurements

The magnetic behaviour of off-stoichiometric Fe$_{60}$Pt$_{40}$ nanoparticles were investigated as a function of annealing temperature. Figure 6.5(a-f) shows the M-H behaviour at room temperature of the as prepared Fe rich Fe$_{60}$Pt$_{40}$ nanoparticles and nanoparticles annealed at 400$^0$C, 500$^0$C, 600$^0$C, 700$^0$C and 750$^0$C. The as prepared sample does not exhibit a hysteresis loop with no tendency to saturate as shown in Figure 6.5(a). Sample annealed at 400$^0$C exhibits a small coercive field of 300 Oe but saturates at the available field (Figure 6.5(b)). The hysteresis loop obtained on the sample annealed at 500$^0$C shows enhanced coercivity, Hc~ 2.3 kOe as shown in Figure 6.5(c). On further annealing the sample at 600$^0$C marked increase in coercivity ~ 11.7 kOe is observed (Figure 6.5(d)).

However in the case of equiatomic FePt, coercivity ~5.8 kOe was observed at 600$^0$C. This marked increase in coercivity indicates the formation of the hard magnetic phase as a result of high magnetocrystalline anisotropy. Figure 6.5(d) also shows the presence of small shoulder near the low magnetic field indicating the presence of the soft magnetic phase. The presence of above shoulder is attributed to the partial transformation of FCC phase to the FCT phase. When the sample is subjected to 700$^0$C shows a coercivity of 13.3 kOe. Moreover, the hysteresis loop do not show presence of any shoulder even at low magnetic field indicating the absence of any soft magnetic phase (Figure 6.5(e)). The hysteresis at 750$^0$C in Figure 6.5(f) shows the decrease in the coercivity ~ 6.0 kOe with a pinch loop indicating the transformation from ordered L1$_0$ phase to A$_1$ phase. The XRD also shows the presence of Fe$_3$Pt.

Hence, the hysteresis studies clearly reveal that with heat treatment there is a gradual transformation from soft magnetic phase (A1) to hard magnetic phase (L1$_0$) to soft magnetic phase (A$_1$) with an intermediate mixed phase.
Figure 6.5: MH loop of off-stoichiometric Si/Fe\textsubscript{60}Pt\textsubscript{40} nanoparticles (a) as prepared and annealed at (b) 400\(^\circ\)C (c) 500\(^\circ\)C (d) 600\(^\circ\)C (e) 700\(^\circ\)C (f) 750\(^\circ\)C.

Figure 6.6(a-f) shows the M-H behaviour at room temperature of the as prepared Si/Pt/Fe\textsubscript{60}Pt\textsubscript{40} nanostructures and annealed samples at 400\(^\circ\)C, 500\(^\circ\)C, 600\(^\circ\)C, 700\(^\circ\)C and 750\(^\circ\)C. The as prepared nanoparticles show the soft magnetic behaviour with an added paramagnetic contribution as shown in Figure 6.6(a). On annealing at 400\(^\circ\)C, Si/Pt/Fe\textsubscript{60}Pt\textsubscript{40} nanostructures shows a loop with coercivity \(\sim 1.2\) kOe as compared to Si/FePt (Figure 6.5(b)) which is further increased on annealing at 500\(^\circ\)C (Figure 6.6(b,c)). At 600\(^\circ\)C a sudden jump in the coercivity from 2.3 kOe to 12.4 kOe is observed confirming the formation of hard magnetic FePt L\textsubscript{10} phase (Figure 6.6(d)).
The presence of shoulder near the low magnetic field is also minimised in comparison to Si/Fe$_{60}$Pt$_{40}$.

![MH loop of Si/Pt/Fe$_{60}$Pt$_{40}$ nanoparticles (a) as prepared and annealed at (b) 400$^\circ$C (c) 500$^\circ$C (d) 600$^\circ$C (e) 700$^\circ$C (f) 750$^\circ$C](image)

Figure 6.6: MH loop of Si/Pt/Fe$_{60}$Pt$_{40}$ nanoparticles (a) as prepared and annealed at (b) 400$^\circ$C (c) 500$^\circ$C (d) 600$^\circ$C (e) 700$^\circ$C (f) 750$^\circ$C

When the sample is treated at 700$^\circ$C, a reduction in the coercivity is observed due to onset of the transformation from chemically ordered (L1$_0$) to chemically disordered (A$_1$ phase). However at 750$^\circ$C MH loop shown in Figure 6.6(f) retains the hard magnetic behaviour. This may be attributed to the diffusion of Pt atoms to the Fe rich FePt and facilitates to maintain the near equiatomic composition of FePt alloy, helping to retain the hard phase.
In order to compare the change in coercivity as a function of annealing temperature for Si/Fe$_{60}$Pt$_{40}$ and Si/Pt/Fe$_{60}$Pt$_{40}$, a plot of coercivity is given as Figure 6.7. The variation of coercivity for Fe$_{46}$Pt$_{54}$ (chapter 3) on annealing is plotted here for comparison. The off-stoichiometric samples show a higher coercivity at lower temperatures. This shows that the introduction of Pt layer beneath Fe rich FePt nanoparticles (i) promotes the phase transformation at low temperature and (ii) helps in retaining a high coercivity over a long range of temperature.

![Figure 6.7: Plot of coercivity as a function of temperature.](image)

**Section B**

**The role of Metal additives on the ordering temperature of FePt alloy**

Addition of nonmagnetic metals during the synthesis of bimetallic FePt nanoparticles has been demonstrated to lower the ordering temperature. Hence, the effect of different metals viz. Ag, Ba and Cu, on the magnetic and structural phase transformation, is investigated and discussed below.
6.4 Synthesis of FePt-M (M: Ag, Cu, Ba)

The synthesis of FePt-M (M: Ag, Cu, Ba) involves reduction of platinum (II) acetylacetonate (Pt (acac)$_2$) and iron(III) acetylacetonate (Fe(acac)$_3$) with a corresponding third additive silver nitrate (AgNO$_3$), copper (II) acetylacetonate (Cu(acac)$_2$) or barium (II) acetylacetonate (Ba(acac)$_2$). In order to achieve reduction, 1,2 hexadecanediol (1,2 HDD) which acts as a reducing agent is used. Oleic acid (OA), oleylamine (OAm) was used as surfactants which helps in controlling the shape and size of nanoparticles. The reaction was performed in diphenyl ether which serves as a solvent. All the chemicals were obtained from Sigma Aldrich and used as procured. The entire process was carried under argon atmosphere to avoid oxidation of iron.

In the synthesis procedure, metal precursors, 0.5 mmol Pt (acac)$_2$, 0.5 mmol Fe(acac)$_3$, 0.5 mmol of an additive reagent (AgNO$_3$ for FePtAg, Cu(acac)$_2$ for FePtCu and Ba(acac)$_2$ for FePtBa) are mixed in 40 ml diphenyl ether in the three neck round bottom flask. 0.5 mmol of OA and 0.5 mmol of OAm along with 0.5 mmol of 1,2, HDD were injected to the flask. The solution was stirred using a magnetic stirrer in a heating mantle for 30 min. Then the mixture was refluxed at a temperature of 250 °C for 1 hour under the argon atmosphere. The colour of the solution turned to black, indicating the formation of FePtX(X= Ag, Ba, Cu) nanoparticles. The reaction vessel and the solution was allowed to cool down to room temperature. Once the solution achieves room temperature, 40 ml ethanol with 0.5 mmol of OA and 0.5 mmol of OAm was added to the solution. Ethanol was added to precipitate the solution and OA and OAm were used to ensure a better dispersion of the nanoparticles and stability of the colloid. In order to separate out the nanoparticles, the obtained solution was centrifuged at 12000 rpm for 15 min.

The hexane-dispersed FePt-M nanoparticles were drop casted on polished silicon for the structural and magnetic studies. Nanoparticles coated silicon substrates were subjected to heat treatments at 400 °C, 500 °C, 600 °C, 700 °C for one hour using a microprocessor controlled furnace. The annealing process was performed under the presence of high purity forming gas (Ar+5% H$_2$), to avoid oxidation and assist further reduction in case of any oxide coating present on surface.
6.5 Results and discussions

6.5.1 Transmission electron Microscopy

Figure 6.8: Bright field TEM image of as-prepared (a) FePt-Ag (b) FePt-Cu and (c) FePt-Ba nanoparticles. The magnified image is shown as an inset.

Figures 6.8(a,b,c) show the bright field image of as-prepared FePt-M (M=Ag, Cu, Ba) nanoparticles dispersed on a copper grid. The copper grid was prepared using the hexane dispersed colloidal sol. A drop of sol was dispersed on the copper grid and
kept in desiccators for drying purpose. An investigation, under TEM, on the prepared grid shows the monodispersed nanoparticles with hexagonal closed pack organization for all the three case FePt-Ag, FePt-Cu and FePt-Ba.

Well dispersed nanoparticles, with no agglomeration were seen for all the three system. Such well assembled nanoparticles are due to the use of oleic acid and oleylamine as a surfactant during the synthesis of FePt-M alloy systems. However, it is very clear from the TEM, that the packing of FePt-Ag nanoparticles over a longer range is very high as compared to FePt-Cu and FePt-Ba. The particle size of as prepared nanoparticles for all the three systems is almost 3nm.

6.5.2 Structural analysis

Figure 6.9 shows the XRD patterns of as prepared sample and sample annealed at different temperature for FePt-Ag. The as prepared sample shows broad humps centered at 2θ values 38.14° and 40.39° corresponding to (111) of Ag and chemically disordered FePt respectively given in Figure 6.9(a).

![XRD patterns](image)

*Figure 6.9: XRD patterns of FePt-Ag (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C*
In order to obtain the chemically ordered FePt alloy nanoparticles, samples are subjected to heat treatment at 400 °C, 500 °C, 600 °C, 700 °C for one hour. At 400 °C, the peaks at 23.80° and 32.78° corresponding to (001) and (110) of FePt are clearly visible. These peaks evolve due to the chemical ordering of Fe and Pt in the FePt unit cell and known as superlattice peaks. This results in a shift in the 2θ value from 40.39° to 41.10° confirming a lattice distortion and given in Figure 6.9(b). The hump at 47.17° and 48.90° which is a trace of (200) and (002) respectively are also visible. The presence of these planes clearly indicating the transformation of FCC phase to FCT phase as a result of induced asymmetry in the unit cell.

At 500 °C, the intensity of the peak at 2θ values of 38.14° corresponding to (111) of Ag enhances. This enhancement in intensity indicates the growth in particle size. At 600 °C, the superlattice peaks and splitting of (200) and (002) into two distinct peaks become sharper, hence confirming a chemically order FCT structure as shown in Figure 6.9(d). Simultaneously, the Ag peaks (111) and (200) centered at 38.14° and 44.01° also shows an enhancement in crystallinity. However, upon annealing at higher temperature i.e. 700 °C, the intensity of superlattice peaks, (001) and (110), is suppressed and the peak corresponding to (111) broadens. Moreover a shift in the (111) from 41.10° to 40.25° is also observed as given in Figure 6.9(e).

This indicates the transformation of the chemically ordered FePt alloy to chemically disordered alloy. A complete disappearance of Ag peak is clear from XRD. This coupled with the observed shift in the 20 probably indicates the formation of FePt-Ag ternary alloy. The structural studies clearly reveal presence of L10 phase of FePt with Ag as separate clusters, which however transform to a ternary alloy at higher annealing temperature (700°C).

Figure 6.10 shows the XRD patterns of as prepared sample and sample annealed at different temperatures for FePt-Cu. Figure 6.10(a) shows the presence of FCC phase with broad hump centred at 40.3° corresponding to (111). No separate Cu peaks were visible. However, annealing at 400°C result in the sharpness of hump, indicating the enhancement in crystallinity as shown in Figure 6.10(b).
Figure 6.10: XRD pattern of FePt-Cu (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C.

Figure 6.11: XRD pattern of FePt-Ba nanoparticles (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C.
Further annealing at $500^\circ\text{C}$ give rise to chemical ordering in the system as indicated by the evolution of superlattice peaks at $24.02^0$ and $32.83^0$ corresponding to (001) and (110) respectively as given in Figure 6.10(c). Asymmetry in the peak shown as an arrow corresponding to (111) at $41.27^0$ indicates an addition phase with FCT FePt phase. It is to be noted from the Figure 6.10(d) that the FWHM of the peaks increases with annealing temperature at $600^0\text{C}$. The observed asymmetry and increased FWHM is probably due to the mixing of Cu with FePt. At $700^0\text{C}$, three distinct peaks are observed at $40.38^0$, $41.27^0$ and $42.21^0$ along with suppressed superlattice peaks. The peak at $40.38^0$ shows the FCC FePt phase due to order to disorder phase transformation while a peak at $41.27^0$ corresponds to FCT phase. A new peak at $42.21$ might be due to presence of Cu$_3$Pt alloy or ternary alloy formation as shown in Figure 6.10(e).

Cu has high affinity as compared to Fe to form alloy with Pt at high temperature. The suppressed superlattice peaks is due to high domination of Cu$_3$Pt alloy system over the FePt alloy system at high temperature (Brombacher C et al. 2012).

Figure 6.11 shows the XRD pattern of as prepared and annealed nanoparticles for FePt-Ba. The as prepared sample shows a broad hump at the $40.24^0$ as seen from Figure 6.11(a). As prepared nanoparticles do not show the evidence of either the superlattice peak of FePt or presence of Ba and its other form. Figure 6.11(b) shows sample annealed at $400\text{ }^0\text{C}$, the evolution of superlattice peaks at $23.92^0$ and $32.78^0$ corresponding to (001) and (110) shows the onset of chemical ordering in the system. However at $500\text{ }^0\text{C}$, the peaks corresponding to superlattice and (111) show a significant increase in intensity as shown in Figure 6.11(c). Higher temperature annealing at $600\text{ }^0\text{C}$ and $700\text{ }^0\text{C}$ shows disintegration in (111) peaks along with suppression in superlattice peak intensity as observed from Figure 6.11(d,e). It is not very clear from the XRD analysis, if there is any formation of a ternary alloy of FePt with Barium.

On the basis of XRD analysis, the chemical ordering of FePtAg nanoparticles is observed at $400\text{ }^0\text{C}$ which is required to avoid the grain growth and coalescing of nanoparticles. A lowering in the ordering temperature is not being observed in the case of FePt-Cu. This may be attributed to a mixing of Cu with FePt alloys resulting in a mixed alloy viz. FePt-Cu and Cu$_3$Pt at high annealing temperature. No systematic conclusions were drawn for FePt-Ba system.
6.5.3 Magnetic measurements

Figure 6.12, 6.13 and 6.14 shows the room temperature MH loop for the as prepared and annealed nanoparticles at different temperatures for FePt-Ag, FePt-Cu and FePt-Ba respectively. MH loop of as prepared samples for all the three system shows a superparamagnetic behaviour with zero coercivity as shown in Figure 6.12(a), 6.13(a) and 6.14(a) respectively. This is due to very small particle size as revealed by TEM which does not result in the magnetic stability of the nanoparticles. However, on annealing, the samples show a hard magnetic behaviour. At 400°C, the coercivity of ~ 7 kOe is observed in the case of FePt-Ag nanoparticles while FePt-Cu and FePt-Ba do not result in a hard magnetic phase as given in Figure 6.12(b), 6.13(b) and 6.14(b). The high value of coercivity is due to chemical ordering of FePt nanoparticles.

![MH loop of FePt-Ag nanoparticles (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C.](image)

Figure 6.12: MH loop of FePt-Ag nanoparticles (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C.
Figure 6.13: MH loop of FePt-Cu nanoparticles (a) as prepared and annealed at (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C.

In the case of FePt-Ag, annealing at 500 °C result in increase in the coercivity of ~ 8 kOe which further increase to 14 kOe at 600 °C as given in Figure 6.12(c,d) while at 700 °C, a decrease in coercivity to 9 kOe is observed indicating the transformation from the ordered state to disordered state shown in Figure 6.12(e). However, the FePt-Cu does not result in a hard magnetic phase even at higher temperature annealing while FePt-Ba results in a coercivity ~ 4.5 kOe at 500 °C as seen from Figure 6.14(c). On further annealing the FePt-Ba at 600 °C, a decrease in coercivity to 2kOe is observed. However, at 700 °C, further reduction in coercivity value to 1 kOe is also seen as shown in Figure 6.14(d,e).
Among the three additives with FePt, Ag as an additive is more advantageous. The surfactant used in the preparation viz oleic acid and oleylamine are stable up to 350 °C to 400 °C hence the coalescing and sintering growth of the nanoparticles do not take place. A high value of coercivity ~7 kOe is observed for FePt-Ag even at 400 °C making the nanoparticle suitable for the memory application. The observed pinched hysteresis is perfect indication of mixed phase. It is clear that the coercivity improvement is not there for the addition of Cu. Though, a respectable coercivity of 4.5 kOe was observed for the FePt-Ba system at 500 °C. The structural aspect is not yet clear. Figure 6.15 shows a plot of coercivity vs. annealing temperature for all the three additives with FePt.

Figures 6.14: MH loop of FePt-Ba nanoparticles (a) as prepared and annealed at (b) 400°C (c) 500°C (d) 600°C (e) 700°C
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Figure 6.15: Plot of coercivity vs. annealing temperature for all the three additives with FePt

6.6 Conclusion

The synthesis of off-stoichiometric FePt nanoparticles has been done using the chemical method. Atomic percentage of Fe and Pt in the FePt system in L1$_0$ phase in Fe rich system is Fe$_{60}$Pt$_{40}$. High value of coercivity $\sim$ 13 kOe is observed at 600 $^\circ$C for Si/ Fe$_{60}$Pt$_{40}$. Si/Pt/ Fe$_{60}$Pt$_{40}$ does show only a marginal enhancement in maximum coercivity but helps in retaining the hard phase (FCT) over a broader temperature region.

The synthesis of well dispersed and well assembled FePtAg, FePtBa, and FePtCu nanoparticles were successfully carried out using chemical co-reduction method with an average particle size of 3 nm for as prepared case. The influence of Ag, Cu and Ba in FePt system on magnetic and structural phase transformation from FCC structure to FCT structure is discussed as follows:

1. Addition of Ag with FePt lower down the ordering temperature with maximum Hc $\sim$ 14 kOe.

2. Ternary alloy formation with no improvement in the magnetic properties was observed in FePt-Cu.

3. A complicated behaviour was seen in FePt-Ba system and needs more analysis.
6.7 References


Kura H, Sato T Physica Status Solidi (C) 1 (2004) 3499

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Walailaki KC J. Sci. Tech. 8 (2011) 87