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Low-temperature FCC to L₁₀ phase transformation in CoPt(Bi) nanoparticles

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This work is focused on the effects of Bi substitution on the synthesis of CoPt nanoparticles with the L₁₀ structure using a modified organometallic approach. The structural and magnetic properties of the nanoparticles have been studied and compared directly with those of CoPt nanoparticles synthesized by the same technique but in the absence of Bi substitution. The as-synthesized particles at 330 °C have an average size of 11.7 nm and a partially ordered L₁₀ phase with a coercivity of 1 kOe. The coercivity is increased to 9.3 kOe and 12.4 kOe after annealing for 1 hour at 600 and 700 °C. The structural and magnetic properties suggest that Bi promotes the formation of ordered L₁₀ phase at low temperatures leading to the development of high coercivities. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4943932>]

INTRODUCTION

Research in the area of ultrahigh-density magnetic-recording media has led to dramatic increase in the areal density over the past several years which, however, is limited by the fundamental properties of the ultra-small particles. The main issue for achieving a density of 10 Tb/in² is the size of magnetic particles; when their size is below 10 nm, most ferromagnetic materials usually exhibit a superparamagnetic behavior.¹ However, materials such as CoPt, FePt, and FePd with the L₁₀-type crystal structure overcome the size-limiting factor due to their high magnetocrystalline anisotropy ($K_u = 50 \text{ Merg/cm}^3$ in the case of CoPt), making them ideal for the application in ultra-high density magnetic-recording media.² Such high anisotropy allows for preparation of nanoparticles with size as small as 3 nm, which are still ferromagnetic and stable against demagnetization and thermal effects. CoPt is ideal for this application not only for its magnetic properties, but also because of its high resistance to oxidation and corrosion. Previously, CoPt nanoparticles prepared chemically they were in the A1 (fcc) phase, which is magnetically soft and requires annealing above 650 °C to obtain a fully ordered L₁₀ structure, causing particle growth and sintering.³

A commonly used technique in FePt/CoPt thin films to lower the ordering temperature is to add a small amount of another element such as Ag, Bi, B, Cu, C, Sn, Sb, SiO₂, or Pb.⁴⁻⁹ Another attempt was made to use B as an additive in chemically synthesized CoPt particles which was successful in reducing the ordering temperature to 600 °C, but not in the as-synthesized particles.¹⁰ Work in FePt has shown that addition of noble metals such as Au can produce partial ordering in the as-synthesized materials with an onset ordering temperature as low as 325 °C; however, similar attempts in CoPt have been unsuccessful until now.¹¹ Bi was chosen due to its low surface energy as compared to both Co and Pt atoms; surface segregation of the Bi atoms would promote interdiffusion of Co and Pt atoms in annealed particles, increasing atomic ordering at lower temperatures as indicated by research done in thin films.⁴

In this study, we report the effects of Bi substitution on the development of L₁₀ structure in CoPt nanoparticles synthesized by an organometallic method. We also investigate the effects of annealing to obtain a fully ordered L₁₀ phase with high coercivity.

EXPERIMENTAL METHOD

The procedure used is a modification of the commonly used organometallic synthesis method without the use of harsh reducing agents such as super hydrides, or the metal carbonyls of $\text{Fe}(\text{CO})_5$ or $\text{Co}(\text{CO})_8$. The synthesis technique is based on the reduction of anhydrous cobalt(II) chloride and platinum(II) acetylacetonate in the presence of a small amount of bismuth (III) acetylacetonate by the use of 1-2 hexadecanediol at elevated temperatures (300 to 360 °C) under argon/hydrogen atmosphere.

The synthesis was carried out by dissolving CoCl_2 (1 mmol), $\text{Pt}(\text{acac})_2$ (0.5 mmol) and a small percentage of $\text{Bi}(\text{acac})_3$ (0 to 10% atomic weight of precursors) into 20 mL of oleylamine in a 3-stopper flask, with the addition of 5 mmol of 1-2 hexadecanediol and 35 mg of palmitic acid, at room temperature. The flask was continuously purged with forming gas (5% H_2 – 95% Ar) for 2 hours before the solution was heated to the refluxing temperature to avoid oxygen contamination. At the refluxing temperature, the reaction would begin to take place with the red-brown solution slowly turning completely black during the course of the refluxing time. The refluxing temperature was varied between 300 to 360 °C and held constant for 2 hours before being allowed to cool to room temperature. The optimal refluxing temperature for both the right particle size and crystal structure was found to be about 330 °C. Once the solution was cooled to room temperature, the particles were separated from the solution magnetically. The black magnetic material was washed with ethanol and hexane, and again was separated from the solution magnetically. The last stage of the washing procedure involved ultra-high sonication in both ethanol and hexane, to remove as much as possible of the oleylamine and palmitic acid. The black powder was then dried in air at room temperature.

The as-made particles were further annealed at different times and temperatures. The samples were sealed in quartz tubes using a rough pump and diffusion pump, filled with forming gas (5% H_2 – 95% Ar), and then subjected to heat treatment for 1 hour; this process was repeated twice to ensure minimal oxidation. The crystal structure of the as-made and annealed samples was analyzed by X-ray diffraction (XRD), and selective area diffraction (SAD) in a Jeol 3010 TEM. The magnetic properties were measured with a vibrating sample magnetometer (VSM), and the particle size and distribution were obtained from TEM images.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction data in both the CoPt and CoPt(Bi) s as-synthesized and annealed nanoparticles at 600 °C and 700 °C. The as-synthesized CoPt nanoparticles are indexed to

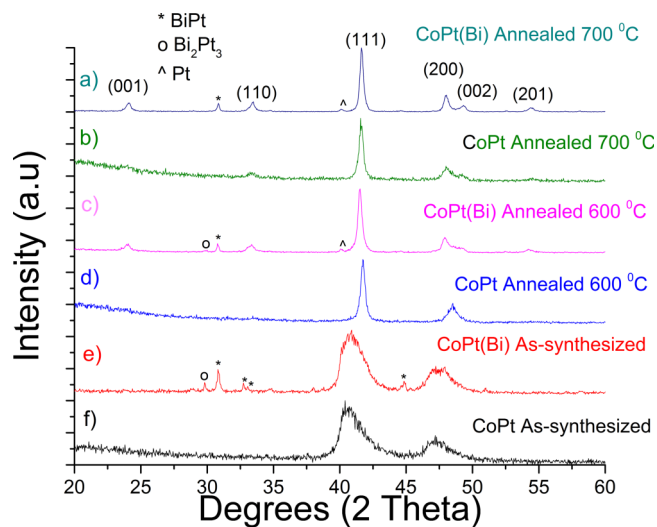


FIG. 1. XRD patterns of as-synthesized CoPt(Bi) and CoPt nanoparticles shown in e) and f) which were annealed at 700 °C shown in a) and b), and 600 °C shown in c) and d).

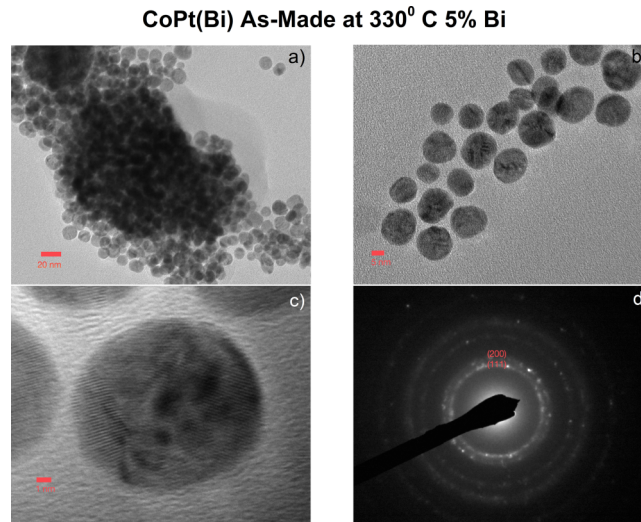


FIG. 2. a), b), CoPt(Bi) as-synthesized at different magnifications c) high resolution TEM showing lattice fringes d) selective area diffraction which is indexed to A1 phase with a slight broadening of the (111) peak.

the fcc A1 structure with lattice constant of $a_0 = 0.3862$ nm. The asymmetrical shape of (111) also indicates the beginning of $L1_0$ ordering in these particles which can't be clearly seen because of the broadness of the peaks (Fig. 1(f)). The onset of ordering is more obvious in as-synthesized CoPt(Bi) nanoparticles as can be seen from the splitting of (200) peak in addition to the asymmetry of (111) peak (Fig. 1(e)).

The Bi addition leads also to the formation of minor non-magnetic phases which are identified as BiPt, Bi_2Pt_3 , and Pt. When the as-made samples are annealed at 600 °C, a significant shift in the (111) peaks is observed indicating a much greater degree of ordering, with the effect being much stronger in the CoPt(Bi) as compared to the CoPt, (Fig. 1(c), 1(d)). The obvious difference between the two samples annealed at 600 °C is the appearance of superlattice peaks and the splitting of (200) peaks in the CoPt(Bi) sample. The XRD patterns of samples annealed at 700 °C (Fig. 1(a), 1(b)) are different primarily in the intensity of the $L1_0$ superlattice peaks, with the CoPt(Bi) nanoparticles showing a much clearer differentiation in (200) and (002) peaks, and increased intensity of the (001) and (110) peaks when compared to the CoPt sample. All of these observations in the structural data strongly suggest that the addition of Bi seems to promote an increase in the $L1_0$ ordering which leads to an increase in coercivity at all annealing temperatures (as discussed below). Figure 2 shows the TEM micrographs of as-synthesized CoPt(Bi) nanoparticles. The particle size distribution obtained from Fig. 2(a) shows an average size of 11.7 nm with $\sigma = 2.37$ nm (Figure 3). The SAD (Fig. 2(d)) is in agreement with the XRD showing a broadening of the (111) ring with a small evidence of two rings very close together indicative of the onset of the $L1_0$ phase in this sample.

Fig. 4 shows the hysteresis loops for the as-synthesized and annealed at 600 °C CoPt and CoPt(Bi) nanoparticles. The as-synthesized CoPt nanoparticles show soft ferromagnetic properties, while the CoPt(Bi) nanoparticles exhibit a slightly hard ferromagnetic behavior with a coercivity of 1 kOe, (Fig 4(a)). The decrease in magnetization in the CoPt(Bi) nanoparticles can be attributed to the minor non-magnetic phases of BiPt, Bi_2Pt_3 , and Pt that form with the addition of bismuth.

The effects of Bi addition on the coercivity of CoPt nanoparticles can be seen in Figure 5 which shows the dependence of coercivity (H_c) on the annealing temperature. The data show that for both nanoparticles the H_c initially increases slightly with temperature, but in the CoPt(Bi) the coercivity increases more drastically between 500 °C and 600 °C as compared to the CoPt nanoparticles without Bi. At higher annealing temperatures the coercivities tend to converge to similar values. The large increase in H_c is an indication of a more ordered $L1_0$ phase in the particles with Bi. The CoPt nanoparticles show a similarly large increase in H_c between 600 °C and 700 °C suggesting again a more ordered $L1_0$ phase which however occurs at higher temperatures in the samples without Bi. In

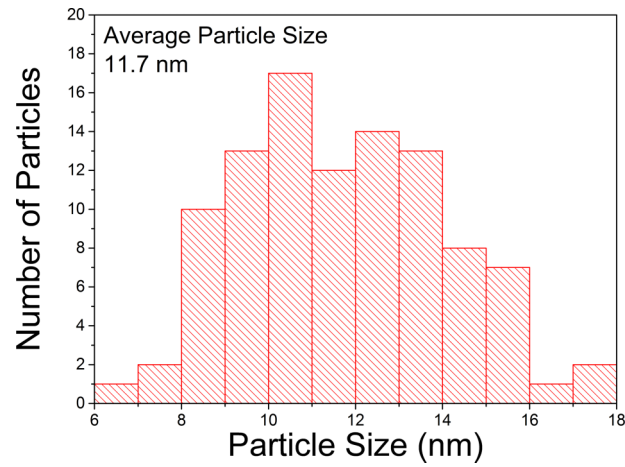


FIG. 3. Particle size distribution from Fig. 2(a) is shown with an average particle size of 11.7 nm and $\sigma = 2.37$ nm.

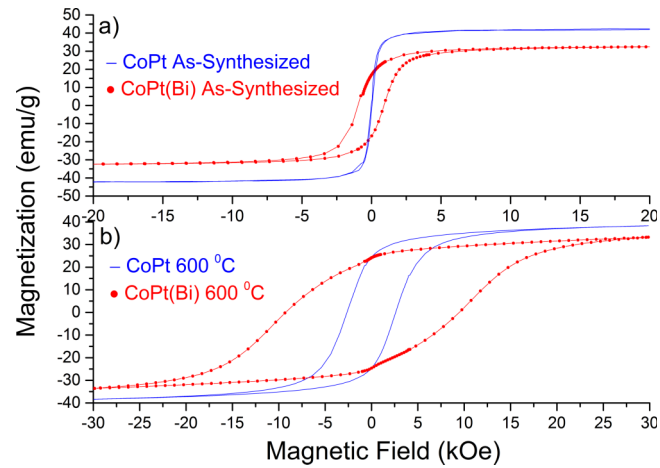


FIG. 4. $M(H)$ loops of the as-synthesized a) and annealed at 600 °C CoPt and CoPt(Bi) samples b).

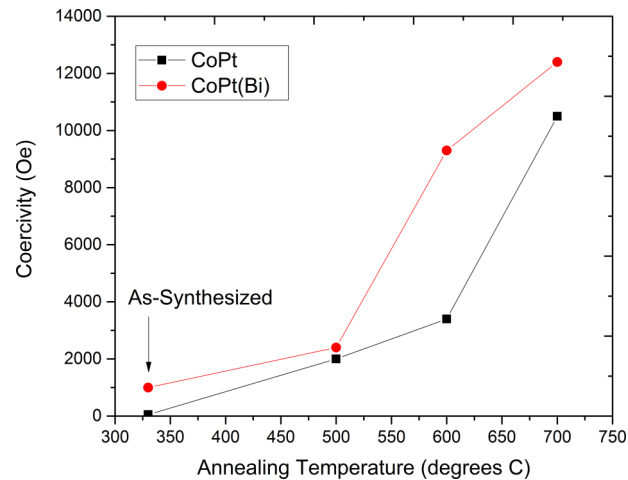


FIG. 5. H_c versus annealing temperature of the CoPt and CoPt(Bi) nanoparticles.

summary, a comparison of the structural and magnetic data indicates that the transformation to $L1_0$ in the CoPt(Bi) nanoparticles occurs at a lower temperature by about 100 °C. The CoPt nanoparticles reach a maximum coercivity of 10.5 kOe at 700 °C, while the CoPt(Bi) nanoparticles reach a similar value of 9.3 kOe at 600 °C. From the data in Fig. 4(b) of CoPt(Bi) sample we approximate the anisotropy constant to be $K_u = 37.5$ Merg/cm³. Additionally, when the CoPt(Bi) nanoparticles are annealed at 700 °C a maximum coercivity of 12.4 kOe is achieved with an anisotropy constant of 38 Merg/cm³.

The results shown in Fig. 5 represent the primary interest of this research, which is the enhancement of coercivity at lower temperatures due to Bi addition. The high H_c of 9.3 kOe in the CoPt(Bi) nanoparticles compared to the 3.4 kOe in CoPt, means that the majority of particles have transformed to the $L1_0$ phase due to Bi addition, as previously mentioned; however, we note that there is a minor shoulder in the CoPt(Bi) sample annealed at 600 °C. The shoulder is an indication that a small percentage of A1 phase still remains in the sample, and the hysteresis loop is a combination of a majority $L1_0$ phase with a minority A1 phase. The characteristic of a shoulder occurring in the CoPt(Bi) nanoparticles has also been observed in thin films with similarly doped element CoPt(Ag) and CoPt(Sb).^{12,13}

CONCLUSIONS

The effect of Bi substitution on the fabrication and ordering of $L1_0$ CoPt nanoparticles prepared by chemical synthesis is reported. We have shown by direct comparison of CoPt nanoparticles prepared without Bi, that Bi addition promotes $L1_0$ ordering in as-synthesized nanoparticles at temperatures as low as 330 °C, as well as, a lowering of the annealing temperature to obtain a more ordered $L1_0$ phase by about 100 °C, which is significantly lower than previously published work in CoPt. After annealing at 700 °C for 1 hour, a coercivity of 12.4 kOe was obtained which is higher than previously published values in CoPt nanoparticles.^{5,10} Annealing at 600 °C produces coercivity of 9.3 kOe comparable to the value of CoPt of 10.5 kOe when annealed at 700 °C. A possible explanation for the effects of Bi is that Bi is distributed on the surface of as-made nanoparticles because of its reduced surface energy and then is released after annealing, increasing the interdiffusion of Co and Pt atoms causing the $L1_0$ phase to form more easily at lower temperatures. The reduction in ordering temperature found in this study allows for CoPt nanoparticles to be more easily produced for the application of magnetic recording media.

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