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Evolution of FePt Nanoparticle Shape and $L1_0$ Order during In-situ Annealing

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In the $L1_0$ (CuAuI) ordered state, equiatomic FePt exhibits exceptional magnetic properties with uniaxial-magnetocrystalline anisotropy (K_u) greater than 10^7 ergs/cm^3. However, monodispersed FePt nanoparticles produced by chemical synthesis methods [1] are face-centered cubic (FCC) and require annealing to chemically order into the tetragonal $L1_0$ structure. $L1_0$-ordered FePt nanoparticles display outstanding magnetic properties with coercivity that can exceed 22 kOe [2]. Therefore, understanding the $L1_0$-ordering phase transformation is critical for incorporating these FePt nanoparticles into magnetic nanostructures [3]. The current study employs in-situ heating using Protochips Aduro™ heater chips and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), also known as atomic-number contrast or Z-STEM, to investigate the development of $L1_0$ order and particle-shape changes during annealing of FePt nanoparticles.

The FePt nanoparticles were synthesized using a standard method that is described elsewhere [1]. A surfactant of oleic acid and oleyl amine stabilizes the FePt particle-size distribution with a standard deviation of less than 5%. One drop of the FePt nanoparticles suspended in hexane was deposited onto a Protochips device (a prototype of the Aduro™ heating holder [4]). Heating the sample to 500°C for 60 sec in the vacuum of the microscope removed the surfactant layer and allowed for contamination-free imaging. The FePt nanoparticles were annealed at temperatures from 500 to 650°C both in vacuum and in the airlock of the microscope, which was backfilled with Ar-H_2 (9:1). STEM images were recorded at 200 kV with a sub-0.1-nm probe in a probe-corrected JEOL 2200FS-AC. However, the in-situ annealing treatments were conducted without exposure to the electron beam because of potential beam-induced artifacts [5]. After the annealing treatments, the composition of individual FePt nanoparticles studied on the Protochips device was measured by energy-dispersive spectroscopy (EDS) using a Philips CM200-FEG with a defocused probe to minimize composition change from beam damage.

Consistent with previous investigations concerning composition variation in chemically synthesized FePt nanoparticles [6], the nanoparticles studied in this experiment ranged in composition from 37 to 56at.% Fe with an average composition of 47at.%Fe - 53at.%Pt. Figure 1 shows an example of a 6.4-nm diameter particle with a composition of 48at.%Fe – 52at.%Pt after annealing at 500°C. The large difference in atomic number between Fe (26) and Pt (78) allows for high-contrast Z-STEM images where the bright Pt atoms reveal the d_{001} interplanar spacing (0.379 nm) of the $L1_0$ ordered structure. After 1 min at 500°C to remove the surfactant, there is already some evidence for $L1_0$ order at the surfaces, especially at the top-right of the nanoparticle in Fig. 1 (a). The HAADF image in Fig. 1 (b) reveals that 5 min at 500°C produced low-index facets with the c-axis of the tetragonal unit cell forming at two orthogonal orientations on the left side and the top of the particle. Anti-site defects (brightly imaging Pt on the "Fe planes") are present as well as local regions such as at the bottom of the particle that are indicative of $L1_2$ order [5] expected for Pt_3Fe. Fig. 1 (c) shows that annealing for 15 min at 500°C results in the formation of the tetragonal phase on all four sides of the particle with an anti-phase boundary (APB) where the Pt planes are out of registry on the right side. Careful inspection of the center of the particle reveals traces of the (110) planes resulting from ordering on the top and bottom of the particle with a third orthogonal direction of the c-axis. Impingement of the orthogonal variants of the tetragonal transformation would result in the second type of APB as the transformation continues. Unfortunately, this particle tilted out of its zone-axis orientation after 60 min at 500°C in Fig. 1(d). In addition to the FCC-to-$L1_0$ phase transformation, FePt nanoparticle coalescence during annealing has also been extensively studied. Perhaps significantly, annealing in a reducing environment [Ar-H_2 (9:1)] reduces coalescence [7].

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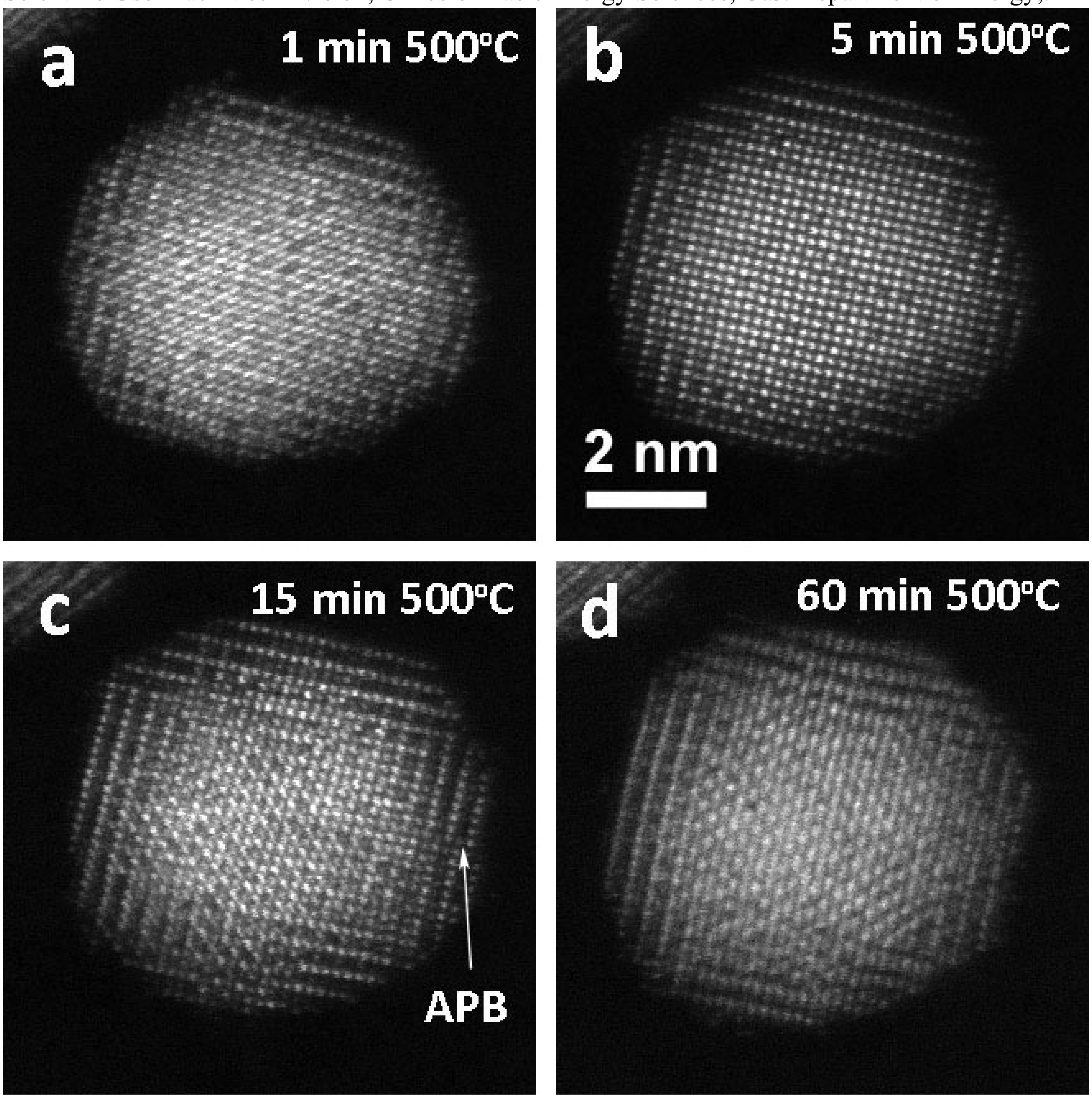

Fig. 1. HAADF STEM images from a 6.4-nm diameter FePt nanoparticle of composition 48at.%Fe – 52at.%Pt exhibit atomic-number contrast from the $L1_0$-ordered structure after annealing at 500°C.

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