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Nonclassical crystallization of amorphous iron nanoparticles by radio frequency methods

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Amorphous iron nanoparticles were synthesized using an aqueous reduction in iron(II) sulfate with sodium borohydride and sodium citrate. Various radio frequency (rf) exposure times were investigated in order to determine trends in nonclassical crystallization. RF times from 15 to 300 s revealed an increase in crystallite size from 5 to 60 nm, as determined by powder x-ray diffraction. Also, solvent optimization revealed that ethanol produced the largest trends for increasing crystallite size without total oxidation of the samples. Magnetic characterization by room temperature vibrating sample magnetometry and high resolution transmission microscopy was performed to verify magnetic properties and particle morphology. © 2010 American Institute of Physics. [doi:10.1063/1.3334169]

Single-crystal monodisperse ferromagnetic nanoparticles are an interesting area of research for their use in electronic and biomedical devices. Several papers have highlighted classical methods, such as the self-assembly of nanostructures, for producing crystalline monodisperse ferromagnetic materials.^{1–9} Amorphous metal nanostructures offer a non-classical approach to creating crystalline monodisperse nanoparticles by not relying on the nucleation and growth process but by inducing crystallization into pre-synthesized particles.¹⁰ This work shows a novel way to induce crystallization into amorphous metals by radio frequency (RF) techniques. RF methods allow for tunable more controlled heating to orient atoms from an amorphous state to a destabilized crystalline state within a nanostructure.^{11,12} Clusters of about 100 nm amorphous iron nanoparticles were synthesized by aqueous reduction using sodium borohydride and sodium citrate.¹³

The synthesis of Fe nanoparticles was carried out under ambient conditions. A borohydride to metal ratio and a metal to citrate ratio were kept constant at 2:1 and 10:1, respectively. In a typical experiment 4.60 mM iron(II) sulfate heptahydrate and 0.460 mM trisodium citrate dihydrate were mixed vigorously for 10 min using a magnetic stir-bar in 2 L of DI-H₂O to ensure total dissolution. Sodium borohydride (8.80 mM) was added to the mixture and allowed to react for 10 min. The particles were magnetically washed several times with ethanol. After washing, the particles were placed in a vacuum oven to dry overnight prior to rf exposure.

RF exposure was done on an Ameritherm HOTSHOT 2 kW rf generator. Approximately 0.1 g of the as-prepared powder was placed in a glass test tube. The solvent was then added to the test tube (5 ml) and mixed to disperse the particles. Initial and final temperatures of the solvent were recorded. After exposure the particles were collected by magnetic separation, and then washed with ethanol (three times).

The sample was then dried in a vacuum oven prior to characterization.

The dried powders were characterized by several techniques for the determination of phase, morphology, and temperature dependent magnetic properties. A typical high resolution transmission electron microscopy (TEM) image of the as-prepared amorphous nanoparticles is shown in Fig. 1. From the size distribution histogram (inset), an average particle size of 104 ± 1.9 nm could be estimated. A relatively small distribution of particle size was seen. About 50 particles were considered to obtain the size distribution histogram. Also, the image (inset) shows a lighter shell around the particles which is an amorphous Fe²⁺ determined by x-ray photoelectron spectroscopy (XPS).

High resolution photoelectron spectra were recorded using an ESCALAB 250 spectrometer. An Ar⁺ ion flood gun was used for charge compensation and an ion etch gun (3 kV, 3 mA) was used for depth profiling. XPS was conducted on the as-prepared particles to determine surface composition. Figure 2(B) shows the atomic percentage of Fe²⁺ and Fe⁰ as

FIG. 1. (Color online) TEM image of the as-prepared amorphous nanoparticles, (top right) image shows a thin layer of Fe²⁺ surrounding the nanoparticles, (bottom right) histogram of particle size for the as-prepared particles.

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FIG. 2. (Color online) (a) Depth profile of the Fe $2p$ XPS region spectra. (b) Atomic percentage vs etch level which shows an decrease in Fe^{2+} and an increase in Fe-metal as the etch level increases. This suggests that at the surface a layer of oxide is present on the particles.

FIG. 3. XRD patterns at various rf exposure times. From the graph it can be seen that as the exposure time increases the 45° Bragg diffraction peak increases.

FIG. 4. (Color online) Graph of particle size vs rf exposure time.

FIG. 5. (Color online) Graph of saturation magnetization vs rf exposure time with statistical significance, (top right) graph of ΔT vs rf exposure time.

a function of etch levels. From Fe $2p$ region scan, it can be seen that the surface of the particle consists mainly of Fe^{2+} and the concentration of Fe^{2+} decreases as the surface is sputtered, exposing a higher concentration of Fe^0 . The C $1s$ spectra reveal three peaks, which is consistent with a surface with adsorbed citrate. The peaks are consistent with a C—C, C—O, and C=O bonds. While the C $1s$ spectra speculates citrate on the surface, the exact type of interaction is uncertain because of the large scan area used in the analysis. Also, the surface roughness introduced by having spherical particles does not produce even surface etching.

Figure 3 represents a series of powder x-ray diffraction (XRD) patterns obtained on the dried powders at different rf exposure times. In Fig. 3, an increase in crystallinity is seen from no rf exposure to an rf exposure of 45 sec. The Scherrer equation was used to determine the crystallite size changes versus the rf exposure time (Fig. 4). For example, the crystallite size increases from 5 to 30 nm for particles with 0 to 45 s of rf exposure, respectively.

Figure 5 represents saturation magnetization versus rf exposure time. From this graph it can be seen that a decrease in saturation magnetization is seen as the rf exposure time is increased. The change in temperature of the solvent versus rf exposure time was also investigated (inset). From this graph a linear correlation is seen which can be explained by the particles heating in the rf field causing the solvent to increase in temperature. The error bars represent the uncertainty in the temperature measurements.

An aqueous synthesis of Fe(II) sulfate using sodium borohydride and sodium citrate produced spherical monodisperse amorphous nanoparticles which served as the starting material for the study of nonclassical crystallization. These results show promise in the area of rf techniques for the production well defined single-crystal nanoparticles for electronic and biomedical devices. Ethanol as a solvent helped to dissipate heat to and from the particles for crystallization which prevented agglomeration and oxidation. In this non-classical method, the rf technique provided enough energy to the Fe atoms to cause them to reorient to a more crystalline state.

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