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Temperature-dependent structure of Tb-doped magnetite nanoparticles

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High quality 5 nm cubic Tb-doped magnetite nanoparticles have been synthesized by a wet-chemical method to investigate tailoring of magnetic properties for imaging and biomedical applications. We show that the Tb is incorporated into the octahedral 3+ sites. High-angle annular dark-field microscopy shows that the dopant is well-distributed throughout the particle, and x-ray diffraction measurements show a small lattice parameter shift with the inclusion of a rare-earth dopant. Magnetization and x-ray magnetic circular dichroism data indicate that the Tb spins are unpolarized and weakly coupled to the iron spin lattice at room temperature, and begin to polarize and couple to the iron oxide lattice at temperatures below 50 K. Broadband ferromagnetic resonance measurements show no increase in magnetic damping at room temperature for Tb-doped nanoparticles relative to undoped nanoparticles, further confirming weak coupling between Fe and Tb spins at room temperature. The Gilbert damping constant, α , is remarkably low for the Tb-doped nanoparticles, with $\alpha = 0.024 \pm 0.003$. These nanoparticles, which have a large fixed moment, a large fluctuating moment and optically active rare-earth elements, are potential high-relaxivity T1 and T2 MRI agents with integrated optical signatures. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4907332]

Rare-earth ions have been incorporated into magnetic oxides^{1–4} and magnetic metals^{5–7} to modify crystalline structure, magnetic anisotropy, optical properties, and magnetic damping. Rare-earth ions can have large spin and orbital moments and, since the moments reside in the f-shell, the orbital moment is often not quenched when the ion is in a lattice. The strong spin-orbit coupling along with a large local moment then causes a large increase in anisotropy and magnetic damping.⁸ Weak exchange or superexchange between Tb³⁺ and neighboring magnetic ions can result in fluctuating spins embedded in a ferrimagnetic structure. Incorporation of rare-earth ions can also lead to strong temperature dependence of the magnetic properties near room and physiological temperatures.⁹

While there have been extensive studies of rare earth doping in bulk materials and thin films, the details of where the rare earth dopants are incorporated in nanoparticles and their effects on magnetic and optical properties are still poorly understood.^{3,4} Here, we investigate Tb doped magnetite nanoparticles and show that the Tb³⁺ ions are incorporated in the octahedral sites, with some clustering and preference for the surface. Tb³⁺ goes into the magnetite lattice despite the large ionic radii mismatch: 78.5 pm for high-spin Fe³⁺ and 106.3 pm for Tb³⁺.¹⁰ The octahedral site, which is larger than the tetrahedral site, can nominally accommodate cations up to ~86 pm, which indicates Tb³⁺ incorporation requires local

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lattice distortion. The ionic size favors incorporation of Tb into larger octahedral and surface sites. The addition of Tb-precursor changes the growth habit from spherical to cubic particles. In contradistinction with Tb-doped garnets and Tb-doped magnetic metals, the anisotropy and magnetic damping are largely unaffected at room temperature, which indicates that the Tb spins are decoupled from the Fe spin lattice at room temperature. Magnetization data show Tb spins begin to polarize and couple to the Fe spins at temperatures below 50 K.

In a typical synthesis,³ 0.47 mmol Iron(III) acetylacetonate (Fe(acac)₃), 0.093 mmol Terbium(III) acetylacetonate hydrate (Tb(acac)₃), 1.12 mmol 1,2-hexadecanediol were mixed with 10 ml diphenylether and degassed for approximately 45 min. The reaction was placed under a slight positive nitrogen pressure and heated to 100 °C, where 1.0 mmol oleylamine was rapidly injected, followed by 1.0 mmol oleic acid. All chemicals were purchased from Sigma,²⁷ and used as received. The reaction was refluxed at 260 °C for 22 h. After cooling, the particles were cleaned from the reaction mixture by addition of excess ethanol and centrifugation, and redispersed in hexanes.

High-resolution transmission electron micrographs (TEMs) of the Tb-doped and undoped nanoparticles are shown in Fig. 1. The cubic morphology of the Tb-doped particles is clearly seen, and image simulations of the magnetite structure with glide translations overlaid on the particles show excellent agreement with the particle lattice.¹¹ Previous work on ferrite nanoparticles¹² has shown that the growth habit can be controlled by growth rate, which is modified by dopant incorporation. Histograms of particle size taken from TEM micrographs give mean sizes and

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FIG. 1. TEM images of (a) undoped and (b) Tb-doped magnetite particles. Insets show simulations of the magnetite crystal structure. Scale bars represent 2 nm.

standard deviations of $d = 5.0 \text{ nm} \pm 1.4 \text{ nm}$ and d = 4.6 nm \pm 1.0 nm for Tb-doped and undoped nanoparticles, respectively. Fig. 2 shows the X-ray diffraction spectra of the doped and undoped samples along with a model spectrum for ideal magnetite nanocubes. The X-ray data confirm high quality magnetite nanoparticles are present (here, we do not differentiate between magnetite and $\gamma - Fe_2O_3$) in the Tb-doped sample with a lattice constant of $0.8386 \text{ nm} \pm 0.0003 \text{ nm}$ compared to $0.8365 \,\mathrm{nm} \pm 0.0003 \,\mathrm{nm}$ for the undoped sample, showing an increase in the lattice parameter of approximately 0.25%, consistent with the incorporation of the large radii Tb^{3+} ions. Some additional non-magnetite diffraction lines are observed in the undoped control sample. These sharp peaks are from salt precipitates and are present when samples are not fully cleaned before drying. Single-particle energy dispersive X-ray spectra,¹³ taken in a 200 kV TEM, indicate a ratio of Tb:Fe of approximately 1:6 within a nanoparticle, and no Tb on the surrounding grid. The measured Tb:Fe ratio is slightly less than the 1:5 molar ratio used in the reaction.

High-angle annular dark-field (HAADF) images, taken in the scanning transmission mode of the TEM, are shown in Fig. 3. The Tb atoms, which have a high atomic number, scatter the electrons to larger angles and appear as bright white spots in the image. The Tb appears to be dispersed throughout the particles although some clustering and preference for the surface can be observed (higher intensity along the nanoparticle edges in the HAADF images).



FIG. 2. X-ray diffraction spectra using Cu Kα radiation, for undoped, doped, and ideal magnetite nanoparticles.



FIG. 3. HAADF image of Tb-doped nanoparticles. Tb atoms appear as bright white spots.

To confirm the location of the Tb in the magnetite lattice, x-ray magnetic circular dichroism (XMCD) spectra were taken. XMCD spectra, taken at 300 K, for the doped and undoped samples are shown in Fig. 4. A field of 0.5 T was applied to orient the magnetic moment and the difference spectra between right and left circularly polarized radiation are plotted for the Tb M4 and M5 edges (corresponding to excitations from the 3d to 4f states) in Fig. 4(a) and the Fe L2 and L3 edges (corresponding to excitations from 2p to 3d states) in Fig. 4(b). The Tb XMCD spectrum at 300 K shows a weak signal in comparison to the 60% theoretical value expected at 0 K.¹⁴ For the Fe L-edge data, a clear suppression in the peak at 708 eV is observed. This peak is associated with the Fe³⁺ in the octahedral site, and the loss of signal in this position indicates Tb substitution at that site.¹⁵

Fe L Edge MCD (%) Tb M Edge MCD (%) 51 01 5- 0 5 01 51 - 2- 1- 0 1 7 (a) Tb doped Fe₃O₄ Tb₂O₃ reference 1230 1250 1280 1240 1260 1270 (b) Tetrahedral Tb doped Fe₃O₄ Undoped Fe₃O₄ Octahedral 3+ 21 Octahedral 710 715 700 705 720 725 730 **Referenced Photon Energy (eV)**

FIG. 4. XMCD spectra at 300 K for (a) Tb M-edge in Tb-doped and reference sample and (b) Fe L-edge in Tb-doped and undoped samples. The Fe L-edge spectra show suppression of signal from Fe in the octahedral 3+ sites. The Tb M-edge data show weak polarization (a paramagnetic Tb₂O₃ spectrum is shown for comparison).



FIG. 5. (a) and (b) Magnetization versus field for Tb-doped and undoped magnetite nanoparticles at 1.8 K and 300 K. (c) Moment versus field at 1.8 K for doped, undoped magnetite nanoparticles and Tb(acac)₃ precursor showing that Tb-doped particles do not saturate at 1.8 K, 7 T. (d) Saturated moment at 7 T for doped and undoped samples versus temperature.

These XMCD data indicate that the Tb is incorporated into the crystalline lattice as opposed to a separate surface phase.

The effect of Tb-doping on the magnetic structure of the magnetite nanoparticles was further determined using SQUID magnetometry, electron paramagnetic resonance (EPR), and broad band ferromagnetic resonance (FMR). Figs. 5(a) and 5(b) show the magnetization vs. field curves for the nanoparticles dispersed in paraffin at 300 K and 1.8 K. There is no hysteresis at room temperature showing that both the undoped and doped nanoparticles are superparamagnetic. The onset of hysteresis occurs at blocking temperatures of 32K and 18K for the doped and undoped nanoparticles, respectively. The Tb-doped magnetization at 1.8 K does not saturate up to the maximum measurement field of 7 T, as shown in Fig. 5(c), indicating the presence of weak antiferromagnetic coupling of Tb with its nearest neighbor cations. Paramagnetic Tb³⁺ ions at 1.8 K would show magnetic saturation well below 7 T as shown in Figs. 5(c). Fig. 5(d) shows the moment at 7 T versus temperature for the doped and undoped samples. The undoped nanoparticles show a saturation magnetization temperature



FIG. 6. Tb L-edge polarization versus temperature showing a rapid increase in polarization below 50 K.

dependence that resembles bulk magnetite with the addition of a small paramagnetic component whose moment becomes appreciable at low temperatures, consistent with surface spins seen in many nanoparticle systems.¹⁶ A large fraction of the Tb-doped sample is unsaturated at room temperature and subsequently becomes magnetized below 50 K.

Temperature-dependent XMCD data is shown in Fig. 6. The polarization of the Tb L-edge vs. temperature demonstrates a stronger, although still small, dichroism at temperatures below 50 K. The reference Tb_2O_3 powder demonstrated no changes vs temperature. These data indicate that the Tb is paramagnetic at room temperature and begins to align at low temperatures.

Broadband FMR linewidths, measured using a co-planar wave guide technique^{17,18} at 300 K, on unoriented dried powders, are shown in Fig. 7. The linewidths were determined



FIG. 7. Magnetic resonance linewidths as a function of frequency for Tb-doped and undoped magnetite nanoparticles. The lines are fits in the saturated region, marked by vertical dotted lines. The inset shows a measured resonance at 40 GHz with a Voigt fit.

by fitting the magnitude of the microwave transmission parameter S_{12} to a Voigt function (see inset in Fig. 7). Here, we assume that the ensemble is made up of non-interacting single-domain particles with the Gaussian component of the linewidth, ΔB_{IN} , due to the dispersion in magnetic anisotropy energies and axes and the Lorentzian component, ΔB_{LLG} , due to the intrinsic Landau-Lifshitz-Gilbert (LLG) susceptibilities. The inhomogeneous broadening should be independent of frequency, f, while the LLG linewidths should increase with frequency as $\Delta B_{LLG} \cong \frac{2\alpha}{v} 2\pi f$, where α is the Gilbert damping parameter and γ is the gyromagnetic ratio. Voigt fits confirm a relatively frequency independent Gaussian linewidth and a monotonically increasing Lorentzian linewidth.¹³ At intermediate frequencies, above magnetic saturation but when $\Delta B_{LLG} \leq \Delta B_{IN}$, the measured Voigt linewidth is given by $\Delta B \simeq 0.53 \Delta B_{LLG} + \Delta B_{In}$.¹⁹ The inhomogeneous linewidth, for the case of random uniaxial particles with an anisotropy field magnitude B_k , can be approximated by $\Delta B_{In} \cong \frac{3}{2}B_k$, which is the difference in resonant field values for nanoparticles with their easy axis aligned with and perpendicular to the applied field.^{20,21} The Gilbert damping constant, α , and average anisotropy field magnitude, B_k , therefore, can be approximated from the slope and zero-frequency intercept of the linear fit to the linewidth data above the saturation frequency (defined as the frequency at which the resonant field induces a moment of 90% of its saturated moment). The saturation frequency/field for the Tb-doped and undoped nanoparticles are 22 GHz/0.78 T and 27 GHz/0.96 T, respectively. For fields below saturation, the linewidth narrows due to thermal fluctuations, an effect often referred to as "anisotropy melting." 20-22

The measured 300K inhomogeneous linewidths (the intercepts in Fig. 7) are $59 \text{ mT} \pm 4 \text{ mT}$ and $74 \text{ mT} \pm 3 \text{ mT}$ corresponding to average anisotropy fields of $39 \text{ mT} \pm 8 \text{ mT}$ and $49 \text{ mT} \pm 10 \text{ mT}$ for the Tb-doped and undoped magnetite nanoparticles, respectively. The Gilbert damping coefficients, given by the slopes in Fig. 7, are 0.024 ± 0.003 and 0.031 ± 0.002 for the Tb-doped and undoped magnetite nanoparticles, respectively. The changes in damping and anisotropy fields are rather small in contrast to rare earth doping in bulk garnets,²³ which show rapid increase in damping and anisotropy with small amounts of Tb at room temperature. These data further support the conclusion that the Tb is in a paramagnetic state substantially decoupled from the Fe spin lattice at room temperature. The Gilbert damping constant, α , is quite small, considerably less than what is often reported for maghemite/magnetite in the literature.^{24,25} Our nanoparticle data are in good agreement with published data²⁶ showing that there is a strong thickness dependence of the damping in epitaxial magnetite films with the damping decreasing to a limiting value of $\alpha = 0.0370 \pm 0.001$ as the film thickness goes to zero.

In summary, we have described the synthesis of high quality Tb-doped magnetite nanoparticles with cubic morphology and have shown that the Tb is incorporated into the octahedral 3+ sites. Magnetization, XMCD, and FMR data demonstrate that the Tb spins are weakly coupled to the Fe spin lattice at room temperature and begin to polarize and couple at low temperatures.

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