Nanotechnology 16 (2005) 506-511

# Cobalt doped $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: synthesis and magnetic properties

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Received 19 October 2004, in final form 31 December 2004 Published 21 February 2005 Online at stacks.iop.org/Nano/16/506

#### Abstract

We demonstrate here the wet chemical synthesis of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and the subsequent effect on magnetic properties with the variation in dopant concentration. It is observed that cobalt can be homogeneously doped into the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> lattice up to 5 mol% without any appreciable change in the particle size (~6 nm). Further increase in cobalt concentration (10 mol% here) resulted in an increase in particle size (~9 nm) due to possible adsorption of a cobalt layer on the surface of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles rather than complete doping in the iron oxide lattice. The ac susceptibility measurements revealed an increase in blocking temperature ( $T_{\rm B}$ ) with percentage variation in cobalt doping (2–10%), indicating substitution of Fe<sup>3+</sup> ions by Co<sup>2+</sup> ions in the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> lattice. The dc magnetization measurements showed an increase in saturation magnetization only up to 5%, beyond which it significantly diminished. The reduction in saturation magnetization is attributed to the contribution from surface anisotropy in cobalt coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

# 1. Introduction

Fine particle magnetism has become the subject of intense research today in view of fundamental research as well as industrial applications [1-4]. The proper understanding of the physical properties of single-domain magnetic nanoparticles is necessary prior to the possible technological applications. In this thrust area of research,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is a very popular material in the magnetic storage industry [5-11]. In comparison to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, it has been found that cobalt doped or cobalt modified  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can increase the coercivity to a large extent, which is a basic requirement for its use in high density recording. Besides high coercivity, cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> provides improved stability with respect to temperature and stress [12, 13]. The challenge still lies in obtaining cobalt doped into the lattice rather than surface modified iron oxide nanoparticles with high coercivity and low cobalt content for high density magnetic storage materials. The difficulty arises in identifying the cobalt doped into the lattice or into the surface

of iron oxide nanoparticles and cobalt ferrite nanoparticles, as they have similar crystal structures.

Also, the mechanism of the enhancement of coercivity in cobalt modified or doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is crucially dependent on the anisotropic occupation and orientation of the cobalt ions in the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> lattice and this is not well understood It has been proposed that the effective uniaxial so far. anisotropy rather than magneto-crystalline anisotropy is to be dominant in cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The crystalline anisotropy can be different for cobalt ions doped into the core of the particles and that of the surface doped particles. The anisotropy as well as the coercivity is dependent on the particle size, degree of cobalt doping and the distribution of cobalt ions, and more importantly on the nature of the surface of the particles [14-16]. Despite a number of studies on cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [17–20] in bulk form and cobalt ferrite nanoparticles [21, 22], less attention has been paid to the synthesis and studies of the magnetic behaviour of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in nanocrystalline form. Successful synthesis of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with high coercivity and improved stability with time and temperature can be a major

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breakthrough in the magnetic storage industry. In continuation with our earlier work on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles [23], we made an attempt here at the synthesis and magnetic response of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles by ac susceptibility and magnetization measurements.

#### 2. Experimental details

The nanoparticles of undoped and cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were synthesized by the wet chemical method. Cobalt chloride was used as the source of cobalt. For preparing  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles both ferrous and ferric ions were used in the synthesis procedure. The reason for using both ferrous and ferric ions in the precipitation was to form pure phase  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> that has the cation-deficient spinel  $(AB_2O_4)$  structure. In a spinel the cations on A and B sites have tetrahedral and octahedral coordination with oxygen respectively. Precipitation of pure Fe<sup>3+</sup> ions typically produces an amorphous hydrated oxyhydroxide that can be easily converted to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with all Fe<sup>3+</sup> ions having octahedral coordination. As a result some Fe<sup>3+</sup> should occupy tetrahedral sites to form spinel structure. By introducing Fe<sup>2+</sup> cations, which have a stronger preference for octahedral sites than Fe<sup>3+</sup> ion, the spinel structure is favoured during crystallization. The source of Fe<sup>2+</sup> ion was FeSO<sub>4</sub>:7H<sub>2</sub>O and that of Fe<sup>3+</sup> ion was anhydrous FeCl<sub>3</sub>. To synthesize  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> we have used a twostage process whereby magnetite Fe<sub>3</sub>O<sub>4</sub> was synthesized and then it was oxidized to obtain maghaemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). For the preparation of undoped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, first an ionic aqueous solution of FeSO4:7H2O and FeCl3 in the molar ratio of 1:2 was prepared. The molar ratio of (FeSO<sub>4</sub>:7H<sub>2</sub>O): (FeCl<sub>3</sub>):(H<sub>2</sub>O) was 1:2:1210. NH<sub>4</sub>OH solution (25%) was added to the aqueous solution of ferrous sulfate and ferric chloride dropwise, until the pH of the solution became 11. A black precipitate was produced instantly, which seems to be  $Fe_3O_4$ . This precipitate was then acidified to pH = 3by addition of (10.8 N) HCl. After acidification the black precipitate turned chocolate brown in colour, indicating the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [23, 24]. The solution was then centrifuged for precipitation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and dried at 100 °C in air for 30 min. For preparation of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles CoCl<sub>2</sub> salt was added to the aqueous solution of FeSO<sub>4</sub>, 7H<sub>2</sub>O and FeCl<sub>3</sub> in three different molar percentages, 2%, 5% and 10% respectively. Then NH<sub>4</sub>OH solution (25%) was added to the solution dropwise under continuous stirring, until the pH of the solution became 11, and was acidified with (10.8N) HCl to pH = 3. The precipitate of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was then collected by the same procedure as for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and dried at 100 °C for 30 min. Thus we obtained 2%, 5% and 10% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and used for further characterizations.

The crystal structures of the cobalt doped and undoped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were investigated by XRD (Rich Seifert S-3000P). The particle size and morphology of the nanoparticles were observed by transmission electron microscopy (Hitachi H-600). The ac susceptibility measurements (at frequency 33 Hz and magnetic field 100 Oe) of the cobalt doped and undoped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were made in the temperature range of 80–450 K. The dc magnetization measurement was carried out at room temperature using a

vibrating sample magnetometer (VSM) with a maximum field of 1 T.

#### 3. Results and discussion

#### 3.1. Microstructural and XRD studies

The transmission electron microscopic images of the pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> sample and those doped with 2%, 5% and 10% cobalt are presented in figures 1(a)-(d) respectively, insets of which represent the corresponding selected area diffraction patterns (SAED). It was observed that for cobalt doped samples up to 5%, the average particle size estimated from TEM did not show any appreciable change in comparison to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The average particle size estimated from TEM images figures 1(a)-(c) for pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> 2% and 5% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> respectively is  $\sim 6 \pm 0.5$  nm. The TEM micrographs in figures 1(a)-(c) also reveal a narrow size distribution of the nanoparticles. In contrast to 2% and 5% cobalt doped samples, the average particle size ( $\sim 9 \pm 0.5$  nm) for the 10% cobalt doped sample (figure 1(d)) is significantly increased compared to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The concentric rings in the SAED pattern of the undoped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, 2% and 5% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles indicated the polycrystalline nature of the nanoparticles. However, the rings become discontinuous with the increase in cobalt concentration beyond 5%, giving rise to textured growth of the nanoparticles as clearly observed for the 10% cobalt doped sample. The reason could be the possible adsorption of a thin cobalt layer onto the surface of the iron oxide nanoparticles rather than complete doping into the iron oxide lattice and hence the formation of partly crystalline phase.

The high resolution transmission electron micrographs (HRTEM) of 2% and 10% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles are shown in figures 2(a) and (b) respectively. Figure 2(a) shows the high magnification image of 2% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The lattice spacing was found from figure 2(a) to be 0.249 nm, which corresponds to a (311) planar spacing of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The average particle size obtained from the HRTEM (figure 2(a)) of 2% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles was  $\sim 6$  nm as mentioned earlier. We also observed the similar particle size for cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles up to 5% by HRTEM. The lattice image of 10% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (figure 2(b)) indicated 0.295 nm lattice spacing which corresponds to (220) planar spacing of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The average particle size obtained from the HRTEM (figure 2(b)) of 10% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles was  $\sim 9$  nm. It is to be mentioned that due to the very thin layer and amorphous character of the adsorbed cobalt on the nanoparticle surface, shell structure is poorly visible in the HRTEM image for 10% doped sample.

The XRD pattern (figures 3(a)-(d)) of pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and cobalt doped nanoparticles confirms the high crystallinity and phase purity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. There are no indications of the formation of other phases of iron oxides in our sample. The possibility of formation of a small amount of cobalt oxide and other cobalt compounds cannot be completely ruled out although there is as such no signature in the XRD data. We therefore did not consider the effect of other phases of cobalt compounds on the magnetic property results here. In



**Figure 1.** Transmission electron micrographs and electron diffraction patterns of undoped and Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: (a) undoped, (b) 2% Co, (c) 5% Co and (d) 10% Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.



**Figure 2.** High resolution transmission electron micrographs of (a) 2% Co and (b) 10% Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

the case of the 2% doped sample (figure 3(b)), the peak (400) is absent compared to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The same is observed for 5% and 10% cobalt doped samples (figures 3(c) and (d)). All the peaks in the XRD spectra of doped samples

are essentially of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. However, the peaks are shifted slightly to lower  $2\theta$  values with increasing percentage of cobalt doping compared to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which plausibly indicates the  $Co^{2+}$  substitution of  $Fe^{2+}$  ions in the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> lattice. For better clarification, we calculated the lattice parameters of the samples from the XRD pattern and plotted the lattice constant of doped samples with dopant concentrations as shown in figure 4. The lattice constant increased linearly with dopant concentration up to 5%, beyond which followed a marginal increase. This plausibly indicated that for the 10% cobalt doped sample, cobalt is not essentially fully doped in the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> lattice, rather either forming an adsorbed layer at the nanoparticle surface or remaining unreacted. It is worth mentioning that  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Co modified Fe<sub>2</sub>O<sub>3</sub> have similar crystal structures and lattice parameters and can be hardly distinguishable from pure XRD data [25]. However, in our case, cobalt doping is further evidenced by the data obtained through magnetic measurements.

# 3.2. AC susceptibility and magnetization studies

The effect of cobalt doping (2–10%) on the magnetic properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles is characterized by measurements of the temperature (*T*) dependence of the ac susceptibility ( $\chi$ ) and the magnetic field (*H*) dependence of the magnetization (*M*). The variation of  $\chi(T)$  with temperature for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and that of doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with various concentrations of cobalt is presented in figure 5 which shows an increase in  $\chi(T)$  with *T* attaining a maximum value at temperature *T*<sub>B</sub>, called the blocking temperature, beyond which it rapidly falls off. Such behaviour is a typical characteristic of the superparamagnetic relaxation of nanoparticles. Above *T*<sub>B</sub>, the single-domain magnetic moment of the particles becomes thermally unstable and



**Figure 3.** X-ray diffraction pattern of undoped and Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: (a) undoped, (b) 2% Co, (c) 5% Co and (d) 10% Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

undergoes superparamagnetic relaxation. Below the blocking temperature due to the large magnetic anisotropy, the particles become magnetically frozen and tend to align with the easy axis of magnetization, thereby causing a reduction in the magnetic susceptibility with decrease in temperature. Notably,  $T_B$  is increased with the increase in cobalt concentration and this confirmed that cobalt was doped into the iron oxide lattice. In discussing our results, we did not take into account the



Figure 4. Variation of lattice constant with cobalt concentration in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.



**Figure 5.** Plot of ac susceptibility versus temperature of undoped and Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: (a) undoped, (b) 2% Co, (c) 5% Co and (d) 10% Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

effect of particle size distribution on the blocking temperature and relaxation behaviour of magnetic nanoparticles [26]. The particle size distribution was found to be narrow here and an average particle size was considered while interpreting the results. Similar is the case for intensity of magnetization (per unit mass) with magnetic field as shown in figure 6. The results clearly indicate an increase in saturation magnetization up to 5% cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in comparison to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and then a decrease with further increase in dopant concentration as shown in figure 7. Although for the 10% cobalt doped sample saturation magnetization was found to decrease substantially, the blocking temperature  $T_{\rm B}$ increased for the all the doped samples. The increase in magnetization upon small cobalt doping could be understood on the basis of a very strong interaction between the Co<sup>2+</sup> spin and the lattice. The spin-lattice interaction favours the alignment of Co<sup>2+</sup> spins parallel to the cube edge of the spinel lattice. Now we seek a plausible explanation for the above results for cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles from the structural and relaxation dynamics point of view.



**Figure 6.** Plot of magnetization with magnetic field at room temperature of undoped and Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (2–10%) nanoparticles.

(This figure is in colour only in the electronic version)



Figure 7. Plot of saturation magnetization with cobalt concentration measured at room temperature.

The relaxation behaviour of nanoparticles is often expressed by Néel theory [27],

$$\tau = \tau_0 \exp(KV/k_{\rm B}T) \tag{1}$$

with  $\tau$  the superparamagnetic relaxation time,  $\tau_0$  a relaxationtime constant ( $\sim 10^{-10}$  s), *K* the anisotropy constant, *V* the particle volume and  $k_B$  the Boltzmann constant respectively. It is known that the blocking temperature increases with increasing particle size and so also the relaxation time  $\tau$ . However, in our case, with increase in cobalt doping up to 5%, although  $T_B$  increased, the particle size as observed from TEM remains unchanged  $\sim 6 \pm 0.5$  nm. The reason



**Figure 8.** Variation of effective anisotropy constant ( $K_{eff}$ ) with cobalt concentration; inset shows the plot of cobalt concentration versus blocking temperature.

behind the increase in blocking temperature could be the different anisotropy constant, and K in equation (1) should be replaced by an effective anisotropy constant  $K_{\text{eff}}$ . The values of  $K_{\rm eff}$  with percentage cobalt concentration are shown in figure 8 and are found to be comparable with the cobalt ferrite nanoparticles [28]. The magnetic behaviour of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> largely depends on the distribution of Co<sup>2+</sup> ions in the spinel lattice. On the basis of our experimental results obtained, we believe that up to 5% dopant concentration Co<sup>2+</sup> ions are homogeneously distributed in the whole particle volume. They are supposed to be distributed on both the tetrahedral (A) site and octahedral (B) site in the spinel structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The more homogeneous incorporation of the Co<sup>2+</sup> ions resulted into an increase in magnetization of the nanoparticles due to induced uniaxial anisotropy in the magnetization direction. It is assumed that magnetic anisotropy exhibited by the fine particles is uniaxial in character rather than cubic in bulk [21]. In case of 10% doped sample, there is an increase in particle size and cobalt are supposed to be adsorbed as a thin layer ( $\sim$  nm) on the surface of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, rather doped into the core of the nanoparticles. The distribution of cobalt atoms on the surface of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles may largely differ from the core. The blocking temperature is predominantly determined by the core (size), whereas the surface anisotropy has the strong effect on the magnetization and coercivity of the nanoparticles. The decrease in magnetization for 10% cobalt doped sample could therefore be attributed to the surface magnetic anisotropy reducing the saturation magnetization value. The spin relaxation at the surface may not coincide with the magnetization direction of the core and thereby reduces the effective magnetization. Similar results are obtained earlier for coated nanoparticles by several authors [29, 30].

## 4. Conclusion

Briefly, we have presented here the synthesis and magnetic behaviour of cobalt (2–10 mol%) doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The microstructural characterizations revealed no appreciable change in particle size ( $\sim 6$  nm) in 2–10% doped samples compared to pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. However, an increase in particle size ( $\sim 9$  nm) for 10% doped sample is observed. Although the ac susceptibility  $\chi(T)$  versus T curves reflected the characteristics of the superparamagnetic relaxation of cobalt doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with an increase in blocking temperature for all 2-10% doped sample, dc magnetization measurements showed an increase in saturation magnetization only up to 5%. In the case of the 10% doped sample the dc magnetization is found to be significantly reduced compared to that of obtained for the 2-5% doped sample. The reduction in dc magnetization indicated that beyond 5% cobalt is essentially adsorbed on the surface of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles rather than doped into the core of the nanoparticles. The results were explained on the basis of different magnetic anisotropy and relaxations exhibited by doped and coated nanoparticles.

# Acknowledgments

The authors would like to thank Dr P K Mukhopadhyay and Dr U K Singha of the S N Bose National Centre for Basic Sciences, Kolkata, for their constant cooperation in measuring the ac susceptibility of the samples. The authors are grateful to Mr N Chaudhuri, IACS, for the TEM images.

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