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Magnetic properties of the nanocomposite $CoFe_2O_4$/FeCo-FeO at a high H/T regime

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ABSTRACT

The low temperature magnetic properties of nanopowders of $CoFe_2O_4$ and of $CoFe_2O_4$/FeCo-FeO with average particle size of about 6 nm were investigated for temperatures down to 5 K and for applied magnetic fields up to 350 kOe. Highly enhanced coercive fields were obtained for the $CoFe_2O_4$ nanoparticles. The values of the saturation magnetization M_S and of the anisotropy constant K_1 were also found to be enhanced for the nanocomposite powder sample. The overall results are discussed in terms of a particle model which takes into account a thin amorphous layer present in the $CoFe_2O_4$ particles and due to a FeCo-FeO layer grown during an annealing procedure. Moreover, the temperature dependence of K_1 was found to be in good agreement with a model proposed by Tachiki.

1. Introduction

Cobalt ferrite materials are known to exhibit very high cubic magnetocrystalline anisotropy K_1 characteristic of hard magnets which, in turn, is strongly influenced by the size and morphology of the particles. For instance, at room temperature bulk cobalt ferrite specimens can exhibit K_1 values [1] in the range of $2.1 - 3.9 \times 10^6$ ergs/cm$_3$ while values about three times larger (9×10^6 ergs/cm$_3$) has been reported for nanopartiles of $CoFe_2O_4$ with average particle size of 40 nm. By applying high magnetic field ($H \leq 140$ kOe) Franco et. al. [2] found that the temperature dependence of K_1 is strongly influenced by the value of H used for determining K_1. This is in agreement with current theoretical models which predicted that H might indeed influence the distribution and the dynamics of the magnetic moments within the sites of crystalline structures. [3,4] Moreover, exchange coupling through an interface was also found to drastically modify the magnetic properties of nanocomposites by combining the high magnetic moments of a soft-magnetic phase with the high anisotropy of a hard magnetic material. [5,6] Magnetic nanoparticles have become important lately for applications such as treatment of cancer by hyperthermia [7] while the exchange-spring coupling is expected to increase the *BH* product of a magnet. [8].

In this work, nanoparticles of $CoFe_2O_4$ and of nanostructured particles of $CoFe_2O_4/FeCo - FeO$ were prepared and their magnetic properties investigated in broad ranges of temperature (5–300 K) and applied magnetic field (± 350 kOe). An unusually large value for the coercive field H_c was obtained for the cobalt ferrite nanoparticles while the exchange-spring phenomena was observed in the nanocomposite $CoFe_2O_4/FeCo - FeO$. The law of approach to saturation [9] (LA) was employed for determining the anisotropy constant K_1 and the saturation magnetization M_S. The values of K_1 for the nanostructured particles $CoFe_2O_4/FeCo - FeO$ were found to be enhanced by a factor of two compared to the values obtained for nanoparticles of $CoFe_2O_4$.

2. Experimental procedure

The $CoFe_2O_4/FeCo - FeO$ nanoparticles were obtained from a single-phase $CoFe_2O_4$ powder prepared by an ionic coordination technique. [10] X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for determining the average particle size of the $CoFe_2O_4$ powder yielding 6.3 nm. The composite layer of $FeCo - FeO$ was produced on the top of the nanoparticles of $CoFe_2O_4$ as described next. First, the FeCo layer with a thickness that is determined by the length of time a hydrogen flux passes through the cobalt ferrite powder at a given temperature is produced. This procedure has been described in details in Ref. 8. The ferromagnetic iron-cobalt layer is actually formed when the oxygen atoms of $CoFe_2O_4$ are removed from the iron-cobalt ferrite core. Next, the FeO phase is obtained by allowing the $CoFe_2O_4 - FeCo$ particles to be oxidized in air. Again, the length of time and the temperature determine the amount of

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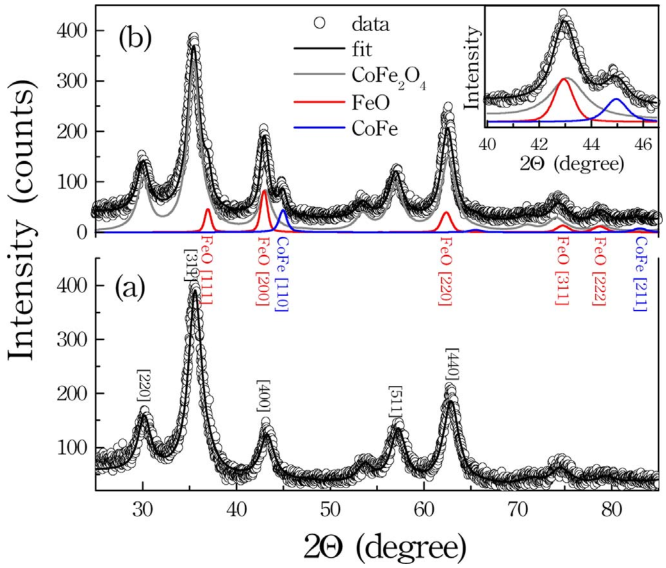

Fig. 1. X-ray diffractograms for pure $CoFe_2O_4$ (a) and for $CoFe_2O_4$/CoFe – FeO (b). All the peaks observed by XRD were properly indexed by using the three proposed crystalline phases. The open circles are experimental data and the solid lines are fits obtained by Rietveld refinement. The inset in Fig. 1(b) is a blow-up for 2θ in the range 40–47.

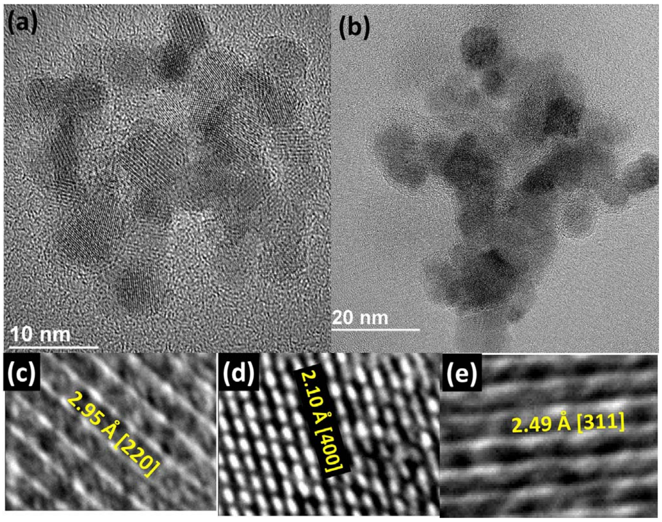

Fig. 2. TEM images for (a) CoFe2O4 and for (b) CoFe2O4/CoFe-FeO. Details of the first layers were also obtained by using high resolution TEM for a nanoparticle of $CoFe_2O_4$ (c–e).

FeO present in the nanoparticle. [11] In the current work, the FeCo phase was obtained by reducing the $CoFe_2O_4$ powder under an hydrogen flux of 50 SCCM for 10 min at a temperature of 573 K. The antiferromagnetic phase FeO was formed when the hydrogen flow was turned off at a temperature of 493 K and kept in air for 25 min. Next, the hydrogen flow was reconnected till the end of heat treatment.

The symmetry of the three crystalline phases are cubic, crystallographically compatible and these phases did grow within a distance of the order of a lattice parameter far from each other. This is one of the requirements for the exchange coupling occur among magnetic/structural phases which, in turn, is the mechanism responsible for the exchange-bias and the exchange-spring phenomena. [12] The magnetization data were obtained by using a vibrating sample magnetometer and they were recorded in intervals of magnetic field of about $\Delta H = 150$ Oe.

3. Results and discussions

X-ray diffraction (XRD) data are shown in Fig. 1 for the powder samples of pure $CoFe_2O_4$ and for the nanostructured $CoFe_2O_4$/CoFe – FeO particles. The X-ray diffractograms were refined by using the Rietveld method and the MAUD program (Material Analysis Using Diffraction). The space groups used in the refinement were Fd-3 m:1, Pm-3 m and Fm-3 m for, respectively, the crystalline phases of $CoFe_2O_4$, CoFe and FeO. The inset in Fig. 1(b) is a blow-up of the XRD spectra for 2θ in the range 40–47 degree. It show in more detail the influence of each of the phases to the overall fit represented by the solid black line. The average size of the cobalt ferrite was estimated to be D_m=6.3 nm and this value did not vary significantly throughout the heat treatments because the annealing temperature (573 K) was sufficiently low for allowing thermally activated atomic diffusion.

Transmission electron microscopy images for $CoFe_2O_4$ and for $CoFe_2O_4$/CoFe – FeO are shown in Fig. 2(a) and (b), respectively. The size of the particles for $CoFe_2O_4$ where found to be disperse in the range 5.2–7.9 nm while the average values was found to be close to 5.9 nm. This value is in good agreement with the one obtained by XRD which was 6.3 nm. The value of D_m for the $CoFe_2O_4$/CoFe – FeO powder sample was found to be 7.4 nm. This value is close to the one obtained for $CoFe_2O_4$ and it is a clear indication that the heat treatment did not influenced the particles size in a significant way. Due to the large density of particles and to their large values of magnetization, the images show some blur. However, while focusing on some of them it is possible to determine lattice parameters of about 2.95, 2.10 and 2.49 Å. These values correspond to the ones expected for the [220,400] and [311] planes, respectively, for the $CoFe_2O_4$ crystalline phase. Images of selected parts of a particle are shown in Figs. 2(c)–(e).

Fig. 3 shows representative hysteresis loops for $CoFe_2O_4$ and for $CoFe_2O_4$/CoFe – FeO measured for $T = 5$ and 300 K, and for H in the range ± 350 kOe. Both samples were found to be superparamagnetic at room temperature. The magnetization measured at the highest applied field at 5 K was 290 emu/cm^3 well below the expected value for bulk samples of $CoFe_2O_4$ (480 emu/cm^3). The actual magnetization data was measured in emu/g. Latter, it was converted to emu/cm^3 by using the density of mass obtained from the X-ray refinement data. The reduction in the magnetization of nanoparticles has been associated to the presence of a magnetic thin amorphous shell grown during the synthesis procedure. Indeed, it is not difficult to show that a random anisotropic amorphous layer with an average thickness $\delta\,[=(D_m/6)(\Delta M/M_s)$, $D_m = 5.9$ nm, $\Delta M = 190$ emu/cm$_3$ and $M_s = 480$ emu/cm$_3$] of about 0.4 nm can account for the total reduction in the magnetization of the cobalt ferrite nanoparticles. The presence of

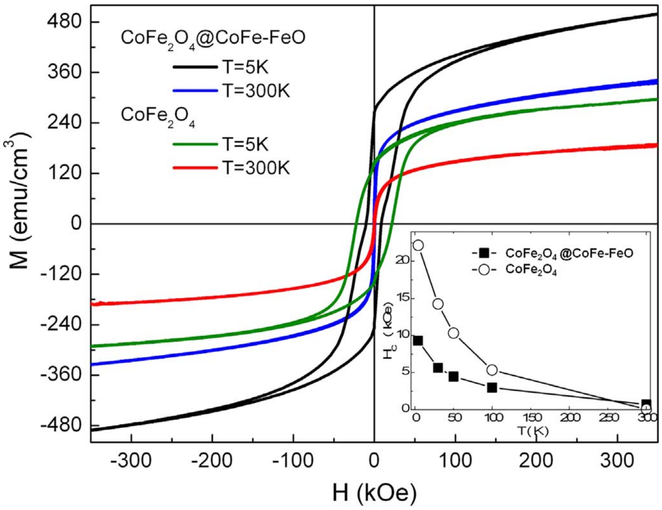

Fig. 3. Hysteresis loops for $CoFe_2O_4$ and for $CoFe_2O_4$/CoFe – FeO, for $T = 5$ and 300 K. The inset shows the T-dependence of the coercive field H_c for both samples.