Magnetic interactions and hysteresis loops study of Co/CoFe$_2$O$_4$ nanoparticles

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Abstract

Co/CoFe$_2$O$_4$ nanoparticles with the mean size of 8.8, 10.8 and 16.9 nm were prepared by thermal decomposition of metal salts in the presence of citric acid. The X-ray diffraction patterns and Rietveld refinements confirmed coexistence of Co-ferrite and metallic cobalt phases in the nano-powders. Scanning electron microscope images showed an increase in particles aggregates mean diameter with increasing the annealing temperature. Magnetic hysteresis loops showed a demagnetization jump at low fields, which was attributed to different reversal fields of ferrite and the cobalt phases. Field-dependent behavior of maximum magnetization (M_{max}), remanence (M_r), squareness (S) and coercivity (H_c) were studied through minor loops measurements. The calculated S value of the loops showed a maximum, between anisotropy and coercive fields. A sharp increase in H_c of larger particles was observed with increasing the applied field when compared to smaller particles. Henkel plots showed that the samples are interacting. Negative deviation of Henkel plots from linear behavior and negative δm plots revealed the dominant role of dipole–dipole interactions in the nano-aggregates.

1. Introduction

Spinel ferrites nanoparticles with the general formula of AFe$_2$O$_4$ (A: Mn, Fe, Ni, Co, etc.) exhibit unique physical properties which make them suitable for different environmental, industrial and biomedical applications [1,2]. Although, the Fe$_3$O$_4$ particles have attracted great attention in MRI and drug delivery, magnetic hyperthermia, etc. [3,4]; being magnetically one of the hardest materials, CoFe$_2$O$_4$ is also well known between spinel ferrites. The anisotropy constant of CoFe$_2$O$_4$ is about one order of magnitude larger than Fe$_3$O$_4$. Therefore, Co-ferrite nanoparticles show large magnetocrystalline anisotropy [5], which has attracted considerable interest for potential application in memory disks, where the superparamagnetic (SPM) particles are not appropriate [6].

A/AFe$_2$O$_4$ composites show interesting properties compared to single ferrite phase. Zhao and Jiang prepared Co/CoFe$_2$O$_4$

nanobelts using a solvothermal method [7]. They found high saturation magnetization of $M_s = 110$ emu/g and coercivity of $H_c = 387$ Oe for the composite system which may be attractive for different potential applications. Ong et al. observed an exchange bias field of $H_E = 1190$ Oe in Fe/Fe$_3$O$_4$ core–shell magnetic nanoparticles [8]. They obtained $H_E = 133$ Oe for Fe$_3$O$_4$ hollow shell, which is less than that of Fe/Fe$_3$O$_4$. Dong et al. showed that because of cyclic stability the Cu/CuFe$_2$O$_4$-graphene composite is a good candidate for use as anode materials of lithium-ion batteries [9]. Xi et al. studied the microwave absorption of Co$_3$Fe$_7$–Co coated CoFe$_2$O$_4$ and found improved microwave absorption properties of the composite sample compared to single CoFe$_2$O$_4$ phase [10].

Quesada et al. found the coercivity and remanence of CoFe$_2$O$_4$/FeCo composite smaller than that of CoFe$_2$O$_4$ while the saturation magnetization is higher [11]. Their results can well justified by considering the hard/soft behavior of CoFe$_2$O$_4$/FeCo and higher M_s of FeCo than CoFe$_2$O$_4$. In a similar work, Leite et al. studied the exchange coupling interaction in CoFe$_2$O$_4$/FeCo nanocomposite. They showed

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that the exchange coupling between the magnetic hard phase and the soft phase in the composite sample leads to magnets with 115% higher energy products than the value obtained for single $CoFe_2O_4$ phase [12]. Lavorato et al. studied the exchange coupling energy in $CoO/CoFe_2O_4$ core–shell nanoparticles and showed that the interface interactions between antiferromagnetic CoO and ferromagnetic $CoFe_2O_4$ phases increase the total energy barrier [13]. The increase of energy barrier can affect the blocking temperature, coercivity, activation volume, remanence etc. In addition, they claimed that exchange coupling between CoO core and $CoFe_2O_4$ shell can increase the magnetization thermal stability of $CoFe_2O_4$ phase up to room temperature [14]. Because of these interesting properties, the A/AFe_2O_4 composite materials are considered for different applications including permanent magnets, recording media, microwave absorption, biomedical etc. [15].

To the best of author knowledge, there are few detailed studies of magnetic properties of $Co/CoFe_2O_4$ nanoparticles in literature. In this work, the $Co/CoFe_2O_4$ nanoparticles system was investigated through different structural and magnetic characterizations.

2. Experimental

$Co/CoFe_2O_4$ nanoparticles were prepared by a thermal decomposition method. A stoichiometric amount of cobalt acetate ($Co(C_2H_3O_2)_2 \cdot 4H_2O$, Merck, 99%), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck, 99%), and citric acid ($C_6H_6O_7$, Merck, 99.5%) powders were mixed and were ground in a mortar and pestle for 5 min. Obtained powders were annealed at different temperatures (200, 250, 300 and 350 °C) for 1 h in the air atmosphere. The samples were named as C200, C250, C300 and C350.

X-Ray diffraction (XRD) patterns were obtained using a Philips EXPERT MPD diffractometer with Cu-kα ($\lambda = 0.154$ nm) radiation. Nanostructural and morphology of the samples were studied using a Tescan Mira 3 field emission scanning electron microscope (FESEM) equipped with an energy-dispersive X-ray spectrometer (EDXS) and a Philips/FEI model CM120 transmission electron microscope. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) with a maximum field of ± 20 kOe.

3. Results and discussion

Fig. 1a shows XRD pattern of $Co/CoFe_2O_4$ nanoparticles prepared at different annealing temperatures. There is no obvious Bragg reflection in XRD pattern of C200 sample. Small broad peaks can be seen in XRD pattern of C250 sample. With increasing the annealing temperature, the peaks become intense, thinner and more obvious. The XRD results of C300 and C350 samples revealed coexistence of crystalline spinel structure (PDF Card 22-1086) and metallic Co (PDF Card 01-1259). Average crystallites size, $\langle D \rangle_{XRD}$, the lattice constant (a) and volume of unit cell (V) were obtained using the following formulas:

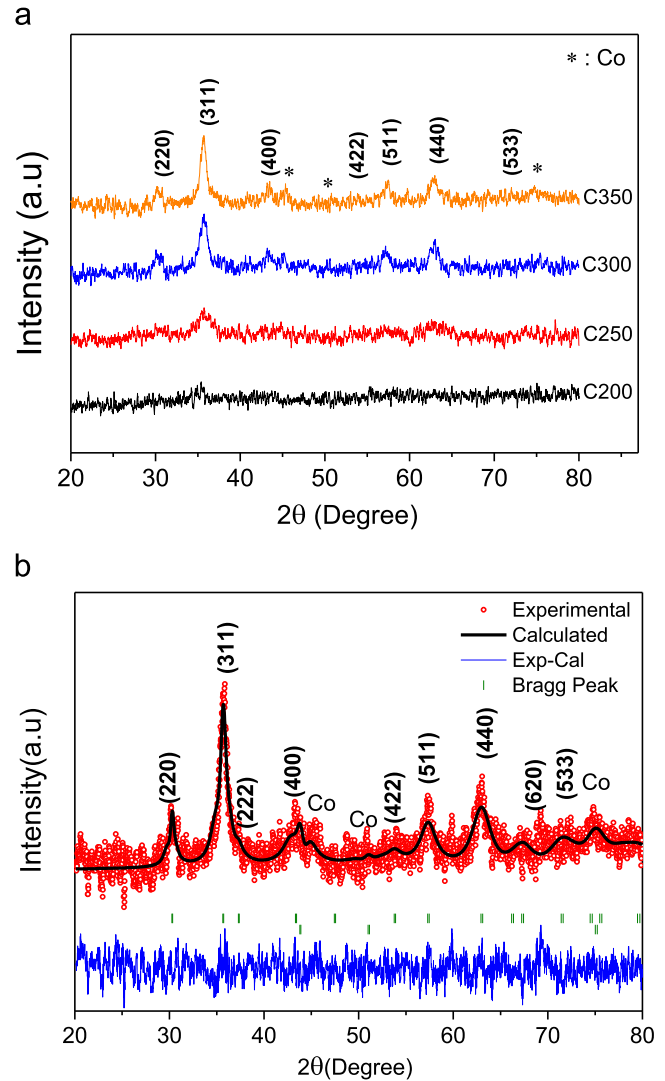$$\langle D \rangle_{XRD} = \frac{K\lambda}{\beta \cos \theta} \qquad (1)$$

Fig. 1. (a) X-Ray diffraction pattern of $Co/CoFe_2O_4$ nanoparticles prepared at different annealing temperatures. (b) Rietveld refined XRD pattern of C350 sample. The hollow spheres are experimental data, the solid black line represents the Rietveld refinement, and the zigzag line shows the residuals.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}, \qquad V = a^3 \qquad (2)$$

In the Debye-Scherrer's formula (Eq. 1), K (~ 0.9) is the Scherer's constant and related to the shape of crystallites, λ is wavelength of the X-ray, β is full-width at half-maximum (FWHM) of the diffraction peaks and θ is Bragg's angle. The parameter d in Eq. 2 is Bragg's distance of planes and the h, k, l are Miller indices. It can be seen from Table 1 that the crystallites size increases with increasing the annealing temperature. The obtained $\langle D \rangle_{XRD}$ values are smaller than the reported single domain limit (40 nm) for cobalt ferrite nanoparticles [16], which suggests single domain behavior in the samples.

For a deep study of the structural properties, the XRD patterns were analyzed using Rietveld method. As an example, the Fig. 1b shows Rietveld refinement of XRD data of the C350 sample. The refinement results confirmed two phases structure of the powders. The fit parameters are presented in Table 1. The calculated weight