Magnetite-cobalt ferrite nanoparticles for kerosene-based magnetic fluids

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Abstract

Due to the magnetic anisotropy introduced by the Co^{2+} ion in octahedral sites of cubic spinel ferrites, it is possible to tailor the magnetic properties by changing the cobalt content. Magnetic fluids with magnetite-cobalt ferrite nanoparticles given by the formula $Co_{(x)}Fe_{(3-x)}O_4$ with x = 0, 0.2 and 0.4 were prepared. Kerosene and oleic acid were used as liquid carrier and surfactant, respectively. Spherical magnetic nanoparticles were obtained by coprecipitation from metal salts and ammonium hydroxide; afterwards the magnetic fluids were obtained by a peptization process. Powder properties were characterized by X-ray diffraction (XRD), nitrogen adsorption–desorption isotherma (BET), vibrating sample magnetometry (VSM) and fluids by transmission electron microscopy (TEM), thermogravimetric analyzer (TGA), VSM and the short-circuited transmission line technique.

Introduction

It is well known that ferromagnetic cubic spinels (ferrites) are important technological materials and have been extensively investigated in order to improve their good soft magnetic properties. It is found that when the particle diameter is of a definite size, spinel ferrite nanoparticles may exhibit the so-called superparamagnetic (SP) properties. The chemical coprecipitation method is an economical way to produce ultrafine particles [1]. There are interesting applications of SP particles as in magnetic fluids. A magnetic fluid is a colloidal suspension of a distribution of single domain ferro–

ferrimagnetic particles dispersed in a liquid carrier and stabilized by means of a suitable organic surfactant. In this article we describe the synthesis of nanoparticles of $Co_{(x)}Fe_{(3-x)}O_4$ (x = 0:0, 0.2 and 0.4) as well as magnetic fluids using the nanoparticles obtained as the magnetic material while kerosene and oleic acid were the liquid carrier and surfactant, respectively.

Experimental

$Co_xFe_{3-x}O_4$ (x = 0:0, 0.2 and 0.4) nanopowders were synthesized by a chemical coprecipitation technique using 0.1M separate stocksolut ions of the following reagent grade chemicals: $FeCl_3 \cdot 6H_2O$ (JT Baker), $FeCl_2 \cdot 4H_2O$ (JT Baker) and $CoCl_2 \cdot 6H_2O$ (Aldrich). The stocksolut ions were prepared by dissolving appropriate amounts of the starting chemicals in distilled water. Appropriate amounts of stocksolut ions were mixed in a Pyrex baker using a mechanical stirrer at a velocity around 1000 rpm to obtain a $(Fe^{+2}:Fe^{+3})$ ratio of 2:3 while heating on a hot plate. When the temperature reached 70°C, the stirring velocity was increased up to 5000 rpm, to produce an effective reaction and then NH_4OH (JT Baker) at 10% was suddenly added. A black color, characteristic of the precipitated nanoparticles was observed. The precipitate was washed with distilled water several times to eliminate as much as possible the residual chlorides.

The washed precipitates were oven dried at 60 °C over a period of 3 days. From the XRD patterns the crystal structure of the obtained powders was determined using a D-5000, Siemens diffractometer. Magnetizations and coercive forces of the powders were carried out by means of a LDJ-9600 (VSM). Mean particle sizes in the powders were calculated by using BET.

To obtain magnetic fluids later, the powders were dispersed in a Pyrex baker containing distilled water with continuous stirring at 1000 rpm, while heating on a hot plate. When the temperature reached 80 °C, oleic acid (JT Baker) was added as a surfactant. After this, kerosene (Fluka) was added as a liquid carrier in three different stocks (x = 0:0, 0.2, 0.4). Three different magnetic fluids were obtained as a separated phase from the water excess after 30 min of stirring at 1000 rpm, on a hot plate at 80°C.

The particle shape, size and morphology were observed by a TEM and the magnetization and coercive force of the fluids were obtained by VSM. Complex magnetic susceptibility measurements over the frequency range from 60MHz to 6GHz were carried out by the short-circuited coaxial transmission line technique [2] using an Agilent Vector NetworkAnal yzer 8753ES and a 50Ω coaxial line incorporating a coaxial cell. The cell containing the magnetic fluid sample and terminated in a standard short-circuit load was placed between the pole faces of an electromagnet, the axis of the cell being perpendicular to the polarizing field [3]. The polarizing field, H_s, was varied between 0 and 96kAm^{-1}. Automatic sweep measurements over the entire frequency range were made and from these measurements, the real and imaginary components of the complex magnetic susceptibility, $X(\omega)=X'(\omega)-iX''(\omega)$, were determined.

Results and discussion

XRD patterns of the $Co_xFe_{3-x}O_4$ (x = 0:0, 0.2, 0.4) nanoparticles are shown in Fig. 1, which indicates the spinel phase presence in the three samples as well as line broadening due to the nanometer size of the crystallites. The main difference between the magnetite and cobalt ferrite spectrums is the appearance of a small peakat 37.05°; it

can be seen in Fig. 1 when x = 0:4, and we can conclude that magnetite and cobalt ferrite are present.

The mean diameter of powder particles, fluids and solids percentage in fluids, are shown in Table 1. From a comparison of the mean diameter of powder and fluids we can see small differences which are due to the different characterization techniques used, but they follow the same behavior.
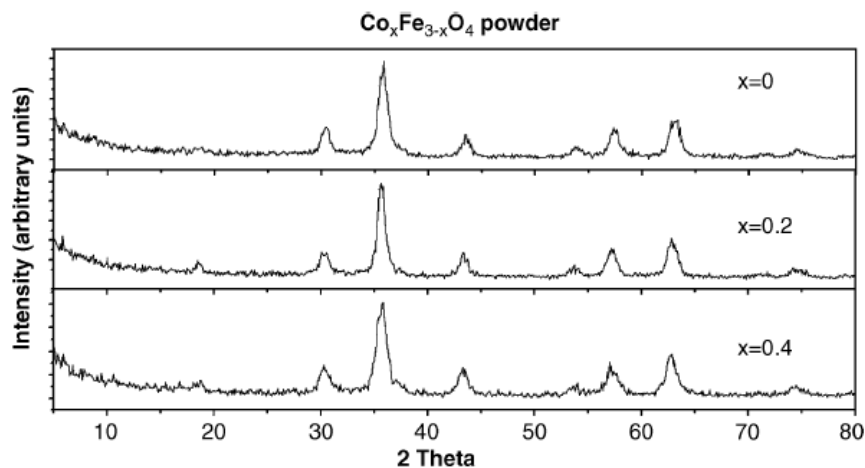

Fig. 1. XRD patterns of coprecipitated powder of $Co_xFe_{3-x}O_4$ system ($x = 0.0$, 0.2 and 0.4).

Table 1
Characteristics of $Co_xFe_{3-x}O_4$ ($x = 0.0$, 0.2, 0.4) nanoparticles and fluids

Sample	Mean diameter pw (BET) (nm)	Mean diameter fluid (TEM) (nm)	Solids in fluid (%)
Fe_3O_4	10.49	10.2, sd $\pm$ 3.22	23.67
$Co_{0.2}Fe_{2.8}O_4$	11.55	9.4, sd $\pm$ 2.06	20.84
$Co_{0.4}Fe_{2.6}O_4$	8.65	6.0, sd $\pm$ 1.38	23.79

(sd = standard deviation, pw = powder)

Table 2
Magnetic measurements data, VSM

Sample	Powder		Fluid	
	σ_{max} (emu/g)	H_C (Oe)	σ_{max} (emu/g)	H_C (Oe)
Fe_3O_4	56.7	14	13.7	16
$Co_{0.2}Fe_{2.8}O_4$	62.0	76	12.7	16
$Co_{0.4}Fe_{2.6}O_4$	56.8	76	13.0	14

Magnetic measurements of ferrite particles in powder and dispersed in kerosene were made using a VSM and are given in Table 2. Both powder and liquid samples show SP behavior [4]. The coercive force of powders was evaluated by measuring the hysteresis under an applied field of 16 kOe, and it was found that particles of samples with x = 0:2 and 0.4 relax through Brownian rotation for H_{DC}<76 Oe [5]; this is due to the contribution of cobalt ions in these samples which have a higher magnetocrystalline anisotropy. Magnetite shows almost the same coercive force for powder as for liquid. This means that magnetite relaxation is purely Néel in character, where the particles magnetic moment moves inside the particles. The coercive force in fluids is less than in powders, which means that magnetic particles can rotate almost freely inside the fluid. Maximum magnetization of the fluids coincides with the percentage proportion of solids in the fluids, as shown in Table 1.

From the TEM micrographs we found the particles to be small, uniform and spherical in shape. Mean diameters obtained are shown in Table 1.

Fig. 2 shows the real (solid lines) and the imaginary (dash dot lines) components of the complex magnetic susceptibility for a magnetite in kerosene magnetic fluid, measured in the frequency range from 60MHz to 6GHz for polarizing fields, H_s. These results were obtained using the short-circuited coaxial transmission line technique. Considering the particles sizes, Néel relaxation and ferroresonance are both contributing to the susceptibility in the studied frequency range. The resonance frequency is determined when the real part of the complex magnetic susceptibility goes from positive to negative values (crossing through the zero value).
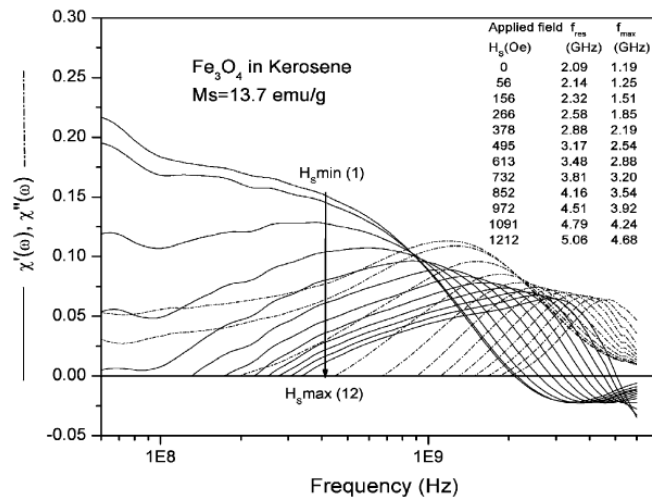
Fig. 2. Plot of real (solid line) and imaginary (dash dot line) part of susceptibility against frequency in Hz, for 12 polarizing fields, of: (1) 0.0; (2) 4; (3) 12; (4) 21; (5) 30; (6) 39; (7) 48; (8) 58; (9) 68; (10) 77; (11) 87, and (12) 96 kA m^{-1}, for kerosene-based magnetic fluid of Fe$_3$O$_4$ nanoparticles.

Resonance frequencies, f_{res}, in the range 2.09–5.06 GHz, and maximum absorption frequencies, f_{max}, in the range 1.19–4.68 GHz, were obtained as a function of the bias polarizing field which was varied from 0 to 96 kAm^{-1}. We can see that increasing Hs produces a shift of f_{res} and f_{max} to higher values and that the higher the polarizing field, the lower the difference in the values of f_{res} and f_{max}. The resonance frequency can be fitted as a linear function of the bias polarizing field in accordance with the well-known ferroresonance formula $\omega_{res}=y(H_A+H_s)$, where y is the gyromagnetic ratio and HA is the anisotropy field. From these fitting a mean anisotropy field of 61kAm^{-1} was obtained.

Conclusions

A coprecipitation chemical method was used to synthesize nanoparticles of Co$_x$Fe$_{3-x}$O$_4$ ($x = 0{:}0$, 0.2 and 0.4), and three different kerosene-based magnetic fluids were produced with these magnetic nanoparticles. The materials produced were characterized by different techniques and results were reported. It was found that the

magnetite and cobalt magnetic fluids indicated the presence of Néel and Brownian relaxation, respectively. For the magnetite magnetic fluid, resonance frequencies in the range 2.09–5.06GHz and maximum absorption frequencies in the range 1.19–4.68 GHz, were obtained for Hs ranging from 0 to 96 kAm^{-1}. A mean anisotropy field of 61 kAm^{-1} was also obtained.

Acknowledgements

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