

Magnetic nanocomposites: preparation and characterization of Co-ferrite nanoparticles in a silica matrix

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Abstract

Magnetic nanocomposites of Co-ferrite nanoparticles dispersed in silica matrix ($\text{CoFe}_2\text{O}_4/\text{SiO}_2$) have been prepared by the sol-gel technique using tetraethylorthosilicate (TEOS) as precursor of silica, and metallic nitrates as precursors of ferrite. Samples prepared in powder form have been dried at 100 °C for 3 h and calcined for 2 h at temperatures between 500 and 1000 °C. Co-ferrite particles were formed in the matrix pores and the nucleation of these particles was observed with the increase in the calcining temperature. TEM measurements showed that the nanoparticles had a fairly uniform morphology and an average particle size of approximately 5 nm. The combination of different Co-ferrite concentrations and calcining temperatures allowed to obtain samples with saturation magnetization ranging from 0.7 to 21.8 emu/g.

Keywords: Sol-gel process; Cobalt ferrite; Silica; Nanocomposite materials; Magnetic measurements; X-ray diffraction.

Introduction

The interest in nanocomposites consisting of nanometric magnetic particles embedded in an insulating matrix such as silica has grown considerably in recent years due to new magnetic properties presented by these kinds of materials [1]. These materials presented considerable differences in the changes in magnetic properties when compared with their equivalent pure and bulk materials. Magnetic

nanocomposites have potential application in magnetic recording media, information storage, bioprocessing, and magneto-optical devices [2]. Different nanoparticles, such as Fe [3], Ni [4], Y-Fe₂O₃ [5], NiZn-ferrite [6] dispersed in silica, have been synthesized by the sol–gel process. The sol–gel process offers some advantages in making silica composite materials containing highly dispersed magnetic nanoparticles; the process facilitates a good and homogeneous dispersion of the particles into the silica matrix.

The present work deals with preparation and characterization of sol–gel-derived Co-ferrite particles dispersed over a silica matrix with magnetic properties. The aim of the work was to study the influence of some preparation variables such as ferrite concentration and calcination temperature of the gels in order to obtain nanosized Co-ferrite particles.

Experimental

The starting chemicals used in this work were iron nitrate (Fe(NO₃)₃·9H₂O, 99%, Aldrich), cobalt nitrate (Co(NO₃)₂·6H₂O, 98%, Aldrich), tetraethylorthosilicate (Si(OC₂H₅)₄, TEOS, 98%, Aldrich) and ethanol (98%, JT Baker). The weight ratios of the Co-ferrite/silica compositions chosen in this work were 20/80, 30/70, 40/60 and 50/50. The TEOS:Ethanol:H₂O and Fe:Co molar ratios were controlled at 1:4:11.67 and 2:1, respectively. For every composition, an appropriate amount of iron and cobalt nitrates were dissolved in ethanol, followed by the addition of TEOS and water, after which a clear solution was obtained. Soft pieces of the gels were obtained after about 4 days. The gels were put into an oven for further drying at 100 °C for 3 h. Those pieces were ground to a fine powder. They were then calcined at temperatures between 500 and 1000 °C for 2 h in air atmosphere to form Co-ferrite/SiO₂ nanocomposites.

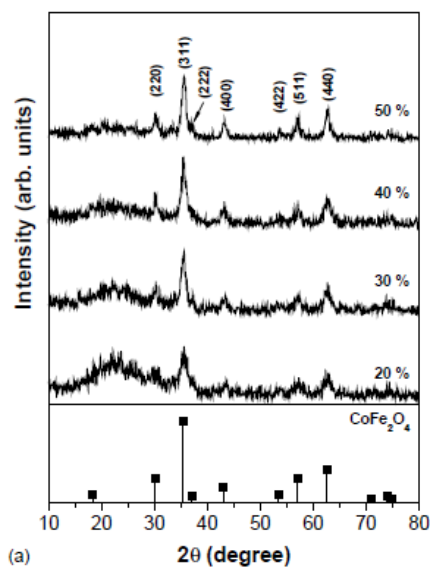
The phases in the nanocomposite were identified using a powder X-ray diffractometer Siemens D-5000 (25mW, 35 kV, Cu K α). A transmission electron microscope (TEM, JEOL JEM-1200EXII) was employed for studies of particle size and morphology of Co-ferrite in SiO₂. The magnetic properties of the nanocomposites were measured using a vibrating-sample magnetometer (VSM, Lakeshore 7300) with a maximum field of 15 kOe.

Results and discussion

Fig. 1a shows the XRD patterns of the Co-ferrite/silica samples calcined at 900 °C. The decrease in silica amorphous evidence ($2\theta = 23^\circ$) and the evolution of crystallinity of Co-ferrite phase with increasing ferrite content can be seen. By increasing the Co-ferrite content, the characteristic diffraction lines of CoFe₂O₄ gradually grow and it seems to be the only phase evidenced by XRD. The position of all the peaks coincided with the characteristics peaks of the standard CoFe₂O₄ phase [7]. Fig. 1b shows the X-ray diffraction patterns for the sample with 40 wt.% of CoFe₂O₄ calcined at 800, 900 and 1000 °C. The characteristic peaks of CoFe₂O₄ increase in intensity with the temperature of calcination treatment. No diffraction lines of other phases can be observed. The increase of the calcination temperature and the Co-ferrite content result in higher crystallization without changes in the obtained phases.

The hysteresis loops of the samples with different concentrations of Co-ferrite in silica are shown in Fig. 2a. Apparent superparamagnetic behavior is always observed for all samples at room temperature. The saturation magnetization values increase up to a maximum of 21.8 emu/g obtained for sample with 50 wt.% of Co-ferrite. The saturation magnetization value is, in all cases, far from the reported value for bulk

CoFe_2O_4 (80 emu/g) [8]. Finite size effects have been reported as being responsible for the reduction of the saturation magnetization of nanoparticles [9]. Hysteresis loops at room temperature (Fig. 2b) show a drastic change in shape from the initial gel calcined at 500 °C, which is paramagnetic, to that of the sample calcined at 700 °C, which is clearly superparamagnetic at this temperature. An increase in saturation magnetization with the temperature takes place up to 700 °C, indicating a gradual increase in the particle size. From 700 to 1000 °C the sample exhibits hysteresis, and both coercivity and remanent magnetization increase with the calcining temperature. This type of behavior is entirely consistent with a model of particle growth in the system in such a way that the differences in the magnetic parameters are associated with changes in particle size [10].



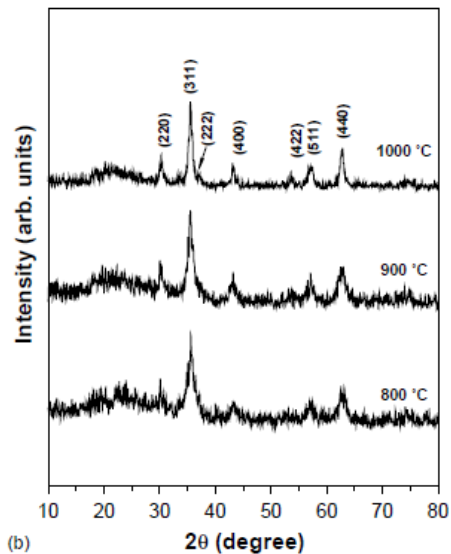


Fig. 1. XRD patterns for the samples with different Co-ferrite content: (a) after calcining at 900 °C for 2 h and (b) for the sample with 40 wt.% of CoFe_2O_4 calcined at 800, 900 and 1000 °C for 2 h.

TEM observation shows that the spherical Co-ferrite nanoparticles are homogeneously distributed within the silica matrix in all the samples. Fig. 3 shows the TEM micrograph of the Co-ferrite/silica nanocomposite with 40 wt.% of CoFe_2O_4 . The nanoparticles of CoFe_2O_4 exhibit a narrow particle distribution, with sizes ranging from 3 to 10 nm and an average size of about 5 nm.

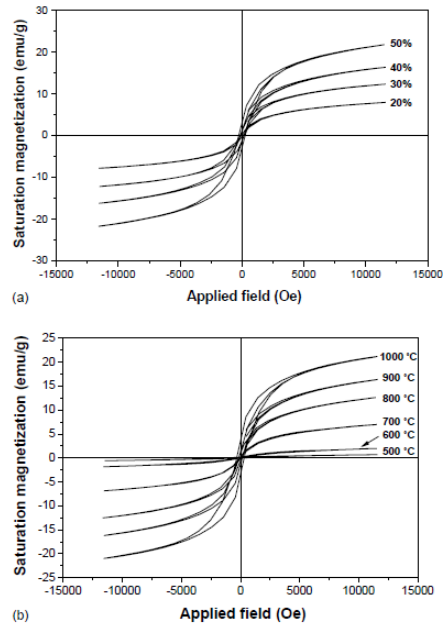


Fig. 2. Hysteresis loops of the samples with different concentrations of Co-ferrite in (a) silica and (b) for the sample with 40 wt.% of CoFe_2O_4 calcined at different temperatures.

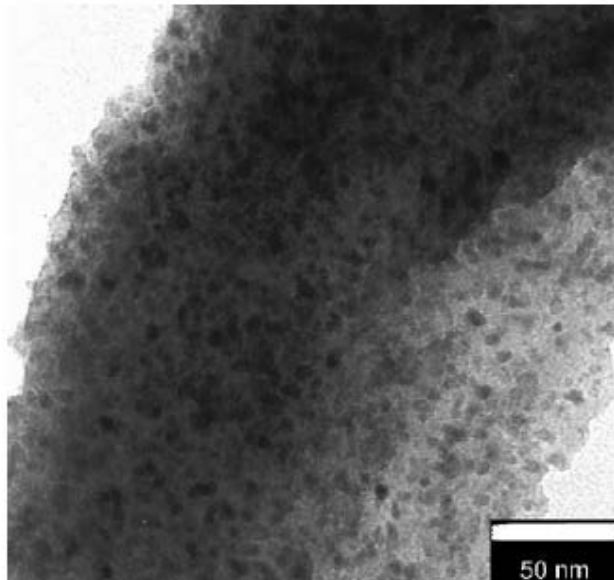


Fig. 3. TEM micrograph for the sample with 40 wt.% of CoFe_2O_4 calcined at 900 °C.

Conclusions

In summary, Co-ferrite/silica nanocomposites with magnetic properties have been obtained using the sol–gel process. By changing the preparation variables such as the Co-ferrite content and the calcination temperature, nanocomposites with different saturation magnetization values and particle sizes can be prepared. The saturation magnetization for all the samples was lower than that of CoFe_2O_4 bulk phase owing to the particle sizes obtained. The magnetic properties of these nanocomposites indicate that this material has good potential for important technological applications, e.g. in information storage, bioprocessing and magneto-optical devices.

Acknowledgements

The authors wish to acknowledge CONACYT, Mexico, for the support given to carry out this work under the project J35161-U.

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