Journal of Magnetism and Magnetic Materials 410 (2016) 47–54

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetic properties evolution of the $Co_xFe_{3\text{-}x}O_4/SiO_2$ system due to advanced thermal treatment at 700 °C and 1000 °C

Thomas Dippong [a,*], Erika Andrea Levei [b], Claudiu Tanaselia [b], Mihai Gabor [c], Mircea Nasui [c], Lucian Barbu Tudoran [d], Gheorghe Borodi [e]

[a] Technical University of Cluj-Napoca, North University Center of Baia Mare, Department of Chemistry and Biology, 76 Victoriei Street, 430122 Baia Mare, Romania
[b] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath Street, 400293 Cluj-Napoca, Romania
[c] Technical University of Cluj-Napoca, Physics and Chemistry Department, Center for Superconductivity, Spintronics and Surface Science, 28 Memorandumului Street, 400114 Cluj-Napoca, Romania
[d] Babes-Bolyai University, Faculty of Biology and Geology, 44 Bilascu Street, 400015 Cluj-Napoca, Romania
[e] National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Street, 400293 Cluj-Napoca, Romania

ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form
1 February 2016
Accepted 4 March 2016
Available online 5 March 2016

Keywords:
Cobalt ferrite
Silica
Gels
Nanocrystallites
Magnetic properties

ABSTRACT

The $Co_xFe_{3-x}O_4$ ($x=0.5$–2.5) system embedded in the silica matrix was synthesised by sol–gel method using cobalt nitrate, iron nitrate, 1.4-butanediol and tetraethyl orthosilicate. Five different Co/Fe molar ratios in the presence of diol and one without diol were used for the synthesis. The obtained gels were subjected to thermal treatment at 700 °C and 1000 °C. The oxide species formed in the silica matrix, the optimum temperature for the $CoFe_2O_4$ phase formation, the evolution of nanocrystallites size and magnetic properties with the calcination temperature were studied. The formed oxide species were studied using X-ray diffraction, Fourier transformed infrared spectrometry, the Co/Fe molar ratio was confirmed using inductively coupled plasma optical emission spectrometry, the nanocrystallites size, shape and clustering was identified by transmission electron microscopy and scanning electron microscopy, while the formation of magnetic phases was investigated by hysteresis and magnetization derivatives measurements.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material used in many industrial applications due to its high coercivity, moderate magnetization, strong anisotropy, good mechanical hardness and chemical stability. Its uses are extended to audio, videotape and high-density digital recording disks, catalysis, magnetic resonance imaging, lithium ion batteries, sensors and actuators, biosensors, hyperthermia treatment and antitumor applications [1–3].

Microstructure, particle size, surface to volume ratio, intra- and inter-granular pores and purity are determinant for the ferrite properties, so special attention is given to the design of the synthesis method [4,5]. For special magnetic properties such are superparamagnetism and spin canting, the reduction of particle sizes is one of the main determinant factors [5].

Considering that the final properties of nanoparticles depend upon material morphology, which itself depends on nanoparticle size, dispersion and distribution through the matrix, the preparation techniques for nanocomposite materials have developed rapidly in the last years, to support a variety of applications [6]. The proposed synthesis methods for cobalt ferrite preparation include thermal decomposition, coprecipitation, reverse micelles, micro-emulsion procedures, alkaline reduction, sonochemical reactions, electrodeposition, electrospinning, sol–gel techniques, host template, solvo/hydrothermal method, combustion method, and mechanical alloying. However, the fabrication of stoichiometric and chemically pure spinel ferrite powders with controlled size and distribution of nanoparticles is not possible within all approaches [7–15].

This work presents the evolution of the magnetic properties (coercive field, saturation magnetization) of the $Co_xFe_{3-x}O_4$ system embedded in silica matrix at different calcination temperatures. Compared to other studies [16–18] for the synthesis of the $Co_xFe_{3-x}O_4$ system a diol with longer chain (1.4-butane diol) and a wider range of the Co/Fe molar ratio were used. The obtained oxides were characterized by X-ray diffraction (XRD), Fourier transformed infrared spectrometry (FTIR), inductively coupled plasma optical emission spectrometry (ICP-OES), transmission

---

* Corresponding author.
E-mail addresses: dippong.thomas@yahoo.ro (T. Dippong), erika.levei@icia.ro (E.A. Levei), mihai.gabor@phys.utcluj.ro (M. Gabor), lbarbu@hasdeu.ubbcluj.ro (L. Barbu Tudoran), borodi@itim-cj.ro (G. Borodi).

http://dx.doi.org/10.1016/j.jmmm.2016.03.020

Table 1
Characteristics of the synthetized precursors.

Quantity [mol]							***x***	**t_{gel} [h]**
Sample	**$Co(NO_3)_2\cdot 6H_2O$**	**$Fe(NO_3)_3\cdot 9H_2O$**	**NO_3^-**	**Diol**	**TEOS**	**H_2O**	**$Co_xFe_{3-x}O_4/SiO_2$**	
D0	0.01	0.02	0.08	0	0.08	0.2	1.0	187
D1	0.01	0.05	0.17	0.17	0.17	0.2	0.5	259
D2	0.01	0.02	0.08	0.08	0.08	0.2	1.0	283
D3	0.01	0.01	0.05	0.05	0.05	0.2	1.5	283
D4	0.01	0.005	0.035	0.035	0.035	0.2	2.0	172
D5	0.01	0.002	0.026	0.026	0.026	0.2	2.5	259

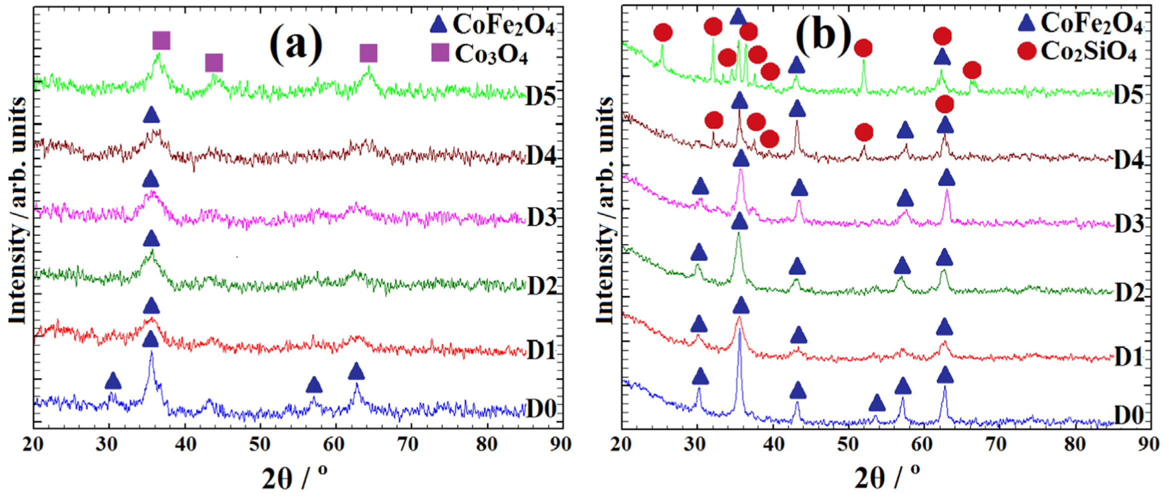

Fig. 1. X-ray diffraction pattern for D0, D1, D2, D3, D4, D5 at 700 °C (a) and 1000 °C (b).

Table 2
Average crystallites sizes calculated using Scherrer equation.

Crystallite size average diameter [nm]				
Sample	**700 °C**		**1000 °C**	
	Co_3O_4	**$CoFe_2O_4$**	**$CoFe_2O_4$**	**Co_2SiO_4**
D0	–	10.3	21.3	–
D1	–	4.6	9.0	–
D2	–	3.8	11.3	–
D3	–	4.4	12.0	–
D4	–	5.0	25.0	48.0
D5	68.0	–	34.0	10.9

electron microscopy (TEM) and scanning electron microscopy (SEM). The properties of the oxidic system embedded in the silica matrix were compared to that of the bulk oxidic system [19].

2. Materials and methods

The $Co_xFe_{3-x}O_4$ system was synthesized through a sol–gel method using iron nitrate ($Fe(NO_3)_3$ $9H_2O$), cobalt nitrate ($Co(NO_3)_2$ $6H_2O$), 1,4-butanediol, and tetraethyl orthosilicate (Table 1).

After gelation, the gels were heated to 400 °C for 5 h and then the formed carboxylate compounds were calcined at 700 °C and 1000 °C for 5 h.

Spectrum BX II (Perkin Elmer) FTIR spectra recorded on pellets of 1% (w/w) sample/KBr was used for the identification of oxidic phases. XRD analysis was performed at room temperature, using a Shimadzu XRD-6000 instrument, operating at 40 kV, 30 mA with CuK_α radiation ($\lambda = 1.54178$ Å) and graphite monochromator. The Co and Fe content in the calcined samples was analysed using a Perkin-Elmer Optima 3500 DV ICP-OES, after sample digestion (50 mg of sample, 21 ml aqua regia and dilution to 100 ml with ultrapure water). For the nanocrystallites shape and clustering, a JEM1010 TEM (Jeol), equipped with digital image recording system and photographic film image with high resolution scanner (Mega View III CCD camera, 1.2Mp-Olympus Soft Imaging System, DE and Mega View III CCD camera, 1.2Mp-Olympus Soft Imaging System, DE respectively) was used. The SEM measurements were carried out using a JSM 5510 LM SEM (Jeol). The magnetic measurements were carried out using a LakeShore 7400 Vibrating Sample Magnetometer.

3. Results and discussion

The XRD diffractograms of $Co_xFe_{3-x}O_4$ ($x = 0.5–2.5$) system embedded in the silica matrix, after calcination at 700 °C and 1000 °C are presented in Fig. 1. The samples from 1000 °C show better crystallization and differentiated peaks than those from 700 °C. Sample D0 has the best differentiated XRD peaks, probably due to the formation of $CoFe_2O_4$ spinel (JCPDS file no. 22-1086) at relatively low temperatures, due to the lack of diol that inhibit the formation of carboxylate precursor and favour the direct formation of the oxides. In D1 ($x = 0.5$), D2 ($x = 1$) and D3 ($x = 1.5$) gels, the $CoFe_2O_4$ cubic spinel is much better highlighted after calcination at 1000 °C [20,21]. In the case of D4 ($x = 2$) that contains an excess of Co, $CoFe_2O_4$ with low crystallization degree was identified at 700 °C, while at 1000 °C the presence of Co_2SiO_4 olivine (JCPDS file no. 87–0053) lines were identified along those of $CoFe_2O_4$ spinel. The presence of Co_2SiO_4 olivine can be explained by the reaction of CoO excess with the SiO_2 matrix. In the case of D5, where Co/Fe