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Structural and magnetic properties of CoFe_2O_4 nanopowders, prepared using a modified Pechini method

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ABSTRACT

Cobalt ferrite nanopowders were synthesized by means of the sol-gel method, using citric acid as a chelating agent, and various alcohols as gelling agent: ethanol (ET), ethylene glycol (EG), polyvinyl alcohol (PVA), 1,3 propanediol (PD) and a mixture of PVA and EG. The simultaneous TG/DTA analysis revealed different thermal behaviours of the synthesized gels, depending on the gelling agent. The powders obtained at 500 °C and annealed at 700 °C and 1000 °C contain a single CoFe_2O_4 phase. Scanning electron microscopy (SEM) revealed the influence of the gelling agent on the morphology of cobalt ferrite particles. The coercivity and the saturation magnetization of the powders obtained at 500 °C showed a strong dependence on the crystallite size, determined by the nature of the gelling agent.

1. Introduction

Spinel ferrites are interesting materials, having ferrimagnetic and semiconductor properties that recommend them for several technological applications in magnetism, electronics and telecommunication [1]. Nanosized ferrites exhibit certain electric and magnetic properties that are different from those of microstructured materials. These materials can be tailored for special applications such as ferrofluids [2], magnetic drug delivery [3], high density information storage [4], photocatalysis [5], gas sensors [6] etc.

Cobalt ferrite (CoFe_2O_4) is a well-known magnetic material with special properties such as a high coercive force, mechanical hardness, and chemical stability. Thus, great efforts have been made for the synthesis and characterization of nanosized CoFe_2O_4 materials. There are many reports in the literature on various methods of synthesizing cobalt ferrite, such as hydrothermal synthesis [7], coprecipitation [8], sol-gel routes [9,10], solid state synthesis [11], microemulsion processes [12], mechanical alloying [13] and electrochemical synthesis [14].

Sol-gel synthesis is one of the methods used intensively for the synthesis of nanosized ferrite in general, and cobalt ferrite in particular. It starts from soluble precursors (cobalt and ferric salts), which are hydrolyzed and condensed into a gel, which is further dried into a xerogel. Subsequent heat treatments are needed to develop the final crystalline state [15]. Many variants of sol-gel synthesis for cobalt

ferrite nanopowders have been reported, resulted from the use of several modifying agents, such as: citric acid [16,17], polyvinyl alcohol [18], benzyl alcohol [19], ethylene-glycol [20,21], acting as ligands and reactants in the synthesis. Since the resulted xerogels burn when heated at relatively low temperatures, these methods have been named sol-gel auto-combustion. The sol-gel auto-combustion method requires a low temperature, a short amount of time, and produces nanopowders containing uniform particles with narrow size distribution. The porosity of the spinel ferrite produced by means of the sol-gel auto-combustion method is high, leading to an increase of resistivity [22].

This paper presents a comparative study on the preparation of cobalt ferrite nanopowders through the auto-combustion sol-gel method, using different alcohols: ethanol, ethylene glycol, polyvinyl alcohol, 1,3 propanediol, and a mixture of ethylene glycol - polyvinyl alcohol. The powders obtained were characterized using the FT-IR and XRD techniques, SEM microscopy and magnetic measurements.

2. Experimental

2.1. Materials and method

Cobalt ferrite nanopowders were synthesized through the sol gel method followed by auto-combustion. The starting materials were cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$]. The additives used were: ammonia solution 25%, citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$)

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Table 1
Quantities (mol) of raw materials used in synthesis.

Sample	Co(NO ₃) ₂ ·6H ₂ O	Fe(NO ₃) ₃ ·9H ₂ O	Citric acid	Gelling agent	
	Quantity/mol			Type	Quantity/mol
ET	0.0025	0.005	0.005	Ethanol	0.3
EG	0.0025	0.005	0.005	Ethyleneglycol	0.3
PD	0.0025	0.005	0.005	1,3propanediol	0.3
PVA	0.0025	0.005	0.005	PVA _{monomer}	0.0115
EG + PVA	0.0025	0.005	0.005	EG + PVA _{monomer}	0.3 + 0.0115

(CA), ethylene glycol (EG) (C₂H₆O₂), polyvinyl alcohol (PVA) (M = 20,000 g/mol), and 1,3 propanediol (PD) (C₃H₈O₂). All chemicals were reagent pure and used without further purification.

The stoichiometric amounts of metal nitrates (in molar ratio Co (II): Fe (III) = 1:2) were dissolved in a 1% aqueous solution of citric acid. The molar ratio of nitrates to citric acid was 1:3. A homogenous transparent solution was obtained after stirring for 10 min at 60 °C. An adequate amount of ammonia was added to the solution to adjust the pH value to about 8. The temperature of the solution was gradually increased up to 150 °C, when the gelling agent was added as aqueous solution: ethanol (ET), ethylene glycol (EG), polyvinyl alcohol (PVA), or 1.3 propanediol (PD) and a mixture of polyvinyl alcohol and ethylene glycol (EG-PVA); brown gels were obtained in these conditions. The gelling agent/(Co + Fe) molar ratio was 40:1 for the samples with ET, EG, and PD, while for the sample with PVA the ratio PVA_{monomer}/(Co + Fe) was 1,5. In the sample prepared with a mixture of ethylene glycol and polyvinyl alcohol the molar ratio gelling agent/(Co + Fe) = 41.5, while EG/PVA_{monomer} molar ratio was 26. The quantities of the raw materials used in synthesis are shown in Table 1.

In the case of 1.3 propanediol, the gel burned at 150 °C, resulting in a dark brown powder. In order to obtain cobalt ferrite powder, the xerogels were annealed at 500 °C, when the auto-combustion of the gel started leading to a branch-like structured powder, due to the auto-propagation of the reaction within the gel structure.

The obtained products were milled in a mortar, resulting in fine powders. In order to study the influence of temperature on the evolution of the crystallisation process, the powders were annealed at various temperatures (500°, 700° and 1000 °C).

The gels obtained at 150 °C were characterized by FT-IR spectroscopy and thermal analysis in order to highlight the auto-combustion process. All powders obtained by annealing at different temperatures (500°, 700°, and 1000 °C) were characterized by FT-IR spectroscopy, X-ray diffraction, SEM microscopy and magnetic measurements.

2.2. Characterization techniques

Thermal analysis was performed on a 1500D MOM Budapest Derivatograph. The heating was achieved in static air, up to 500 °C, with a heating rate of 5 °C min⁻¹, on Pt plates using α-Al₂O₃ as inert material. The synthesized powders were characterized by means of FT-IR spectrometry using a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range of 400–4000 cm⁻¹. Phase analysis was achieved with a PANalytical X'Pert Pro MPD-type diffractometer using Cu-K_α radiation (λ_{Cu} = 1.54060 Å) and a 2θ-step of 0.016, from 20° to 100°. SEM images were recorded on a Quanta 3D FEG (FEI) microscope. The magnetic investigations on the powders were carried out at room temperature under AC (50 Hz) magnetic fields, with amplitudes of up to 160 kA/m, with a hysteresis graph described elsewhere [23].

3. Results and discussion

The gels obtained at 150 °C were studied by thermal analysis in

order to establish the temperatures where the combustion takes place. Fig. 1(a, b, c, d, e) presents the TG and DTA curves of all gels obtained at 150 °C.

The thermal curves of CoFe₂O₄ samples with ET (a), EG (b), PVA (c), EG-PVA (d), and PD (e) reveals the fast decomposition (burning) of the organic part of the xerogels, with a clear exothermic effect on the DTA curve (between 70% and 80% mass losses). The samples synthesized with ethanol burned completely in a single step, at around 200 °C – Fig. 1(a). The samples with EG, PVA and especially EG-PVA presented two stages of oxidative decomposition: first stage between 150 and 200 °C, due to the burning of the polymeric gel, and the second stage, between 250° and 350 °C, with a spread exothermic effect, due to the burning of residual organics. In the case of the CoFe₂O₄ sample with PD, the total mass loss was about 13%. This mass loss corresponds to a process in the temperature range of 300–400 °C, which takes place with a sharp but not very strong exothermic effect, due to the burning of residual carbon. This thermal behaviour confirms the burning of the gel during its heating at 150 °C.

Fig. 2 shows FT-IR spectra for cobalt ferrite xerogels obtained at 150 °C – Fig. 2(a) and the FT-IR spectra for samples heated at 500 °C – Fig. 2(b).

All FT-IR spectra of the gels exhibit a strong band located at 1390 cm⁻¹, which may be assigned to the anti-symmetric stretching and bending vibration of NO₃⁻ ions present in the system, together with the bands located at around 850 cm⁻¹, corresponding to their bending vibration [24]. This band may also overlap with the one characteristic to the symmetric vibrations of carboxylate groups, coordinated with metallic ions [25]. The other band characteristic to the anti-symmetric vibrations of –COO⁻ coordinated groups is located between 1560 and 1640 cm⁻¹, and overlaps with the band characteristic to the bending vibrations of the water molecule, at around 1630 cm⁻¹ [26]. The band located at around 3130 cm⁻¹ can be assigned to the vibrations of –OH groups from citric acid molecules but may also include the bands characteristic to the vibrations of C–H bonds (generally located in the 2800–3000 cm⁻¹ range) [27]. The FT-IR spectra of the CoFe₂O₄ gel with PD exhibit faint bands characteristic to –COO⁻ groups located at 1548 and 1394 cm⁻¹, and a strong band at 576 cm⁻¹, characteristic to the vibrations of M–O bonds in cobalt ferrite [26]. Thus, the FT-IR spectrum confirms the conclusion of the thermal analysis regarding the burning of CoFe₂O₄ with PD gel during thermal treatment at 150 °C.

The FT-IR spectra of the powders obtained at 500 °C – Fig. 2(b) – show very weak residual bands of incompletely burned organics. The strong band located at around 580 cm⁻¹ characteristic to the vibration of M - O bonds in cobalt ferrite proves the formation of cobalt ferrite in all samples. The FT-IR spectrum (2) of the CoFe₂O₄ sample with PVA shows a shoulder at around 640 cm⁻¹, presumably due to the formation of a secondary phase besides cobalt ferrite, possibly Co₃O₄, with characteristic absorption bands at around 660 and 570 cm⁻¹ [28].

All powders obtained by means of the sol-gel method using different alcohols: ET (a); EG (b); PVA (c); EG-PVA (d), PD (e) were subjected to heat treatment at 500 °C, 700 °C and 1000 °C for 2 h and then

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