Contents lists available at ScienceDirect



Journal of Magnetism and Magnetic Materials





Synthesis and characterization of a mixture of CoFe₂O₄ and MgFe₂O₄ from layered double hydroxides: Band gap energy and magnetic responses



Ulises A. Agú^{a,*}, Marcos I. Oliva^b, Sergio G. Marchetti^c, Angélica C. Heredia^a, Sandra G. Casuscelli^a, Mónica E. Crivello^a

^a CITeQ–CONICET, Universidad Tecnológica Nacional–Facultad Regional Córdoba, Córdoba, Argentina ^b IFEG–CONICET, Universidad Nacional de Córdoba, Córdoba, Argentina ^c CINDECA–CONICET, Universidad Nacional de La Plata, La Plata, Buenos Aires, Argentina

ARTICLE INFO

Article history: Received 20 December 2013 Received in revised form 12 June 2014 Available online 21 June 2014

Keywords: Ferrites Nanocrystals Band gap energy Magnetic responces LDH

ABSTRACT

A mixture of nanocrystals of cobalt ferrite and magnesium ferrite was obtained from Layered Double Hydroxides (LDH) through a co-precitation method with a theoretical molar ratio M^{2+} : Fe³⁺ = 3:1, where M^{2+} represents Mg^{2+} and/or Co^{2+} . The molar ratios between Co^{2+} : Fe^{3+} were 0.0 (0Co), 0.2 (5Co), and 0.4 (10Co). In order to assess the effect on the properties of the LDH and their oxides, the molar percentages were 0, 5 and 10%. Two different synthesis methods were evaluated; (i) ageing at room temperature (rt), and (ii) hydrothermal ageing at 200 °C in autoclave (ht), both methods needed 15 h of ageing. Then, these LDH were calcined in air atmosphere at 550 °C for 10 h. The calcined materials were characterized by X-ray diffraction (XRD), thermogravymetric analysis (TGA), temperature-programmed reduction (TPR), infrared spectroscopy with Fourier transform (FTIR), Diffuse Reflectance UV-visible spectroscopy (UV-vis-DRS), Mössbauer spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES). The magnetic response was analyzed using a vibrating sample magnetometer (VSM). The band gap energy of the iron oxides was determined through the UV-vis-DRS analysis. Through these studies it was possible to identify the presence of a mixture of cobalt ferrite and magnesium ferrite. Samples did not show hematite and cobalt oxides, but the presence of MgO in the periclase phase was determined. This magnesium oxide promoted a good dispersion of the ferrites. Moreover, when a single ferrite phase of Co or Mg was formed, a diminution of the crystal size with consequent enlarged values of band gap energy was observed. Thus, materials synthesized by room temperature ageing promoted the superparamagnetic behaviour of samples, attributed to the content of the cobalt ferrite structure in nanocrystals. In regard to the estimated band gap energy, all samples exhibited low levels. These results indicate that these solids would be suitable for photocatalysts use in all visible light range, and that they could be easily removed from the reaction medium by a simple magnetic separation procedure.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, oxides of iron have aroused particular interest in different areas of science and in their potential applications in many fields of technology such as medicine, redox reactions and applied physic [1–5]. In general, metallic oxides with spinel structure may be described by the general formula AB_2O_4 , where A and B represent divalent and trivalent cations, respectively. Both of them are transition metals and they are in tetrahedral (Td) and

* Corresponding author. E-mail address: uagu@scdt.frc.utn.edu.ar (U.A. Agú).

http://dx.doi.org/10.1016/j.jmmm.2014.06.046 0304-8853/© 2014 Elsevier B.V. All rights reserved. octahedral (Oh) sites in a cubic close packing of oxygen (Fig. 1). For a divalent spinel, two extreme distributions of cations between the Oh and Td available sites are possible: the "normal spinel" $A[B_2]O_4$ and the "inverse spinel" $B[AB]O_4$; in each case the cations in the Oh sites are between square brackets.

When the spinel contains iron it is called ferrite. In ternary spinels systems, Fe^{3+} combined with ion transition metals M^{+2} (MFe₂O₄) can be easily shifted between the Oh and Td sites [6,7].

Spinel presents a good thermal stability and acceptable catalytic and photocatalytic activity in redox reactions. In particular, MFe₂O₄ exhibits interesting magnetic, magneto-resistive, and magneto-optical properties, which are potentially useful for a broad range of applications [8]. In this sense, ferrites can be easily separated from the reaction medium by a simple magnetic separation procedure [9]. When the metal cation (M) is Mn, Mg, Zn, Ni, Co, just to name some, the resulting ferrites are among the most widely used magnetic materials [10]. Costa et al. [11] reported Fe–Mn and Fe–Co ferrites for the oxidation of organic contaminants in aqueous medium. Sreekumar et al., worked with ferrites based on Ni and Co as catalysts for the synthesis of o-cresol and 2,6-xylenol from phenol and methanol [12]. Moreover, due to the low band gap energy exhibited by systems with MFe₂O₄, these materials were employed in various studies as catalysts in photocatalytic reactions [11,13]. Those physical and chemical properties of the nanomaterials tend to be exceptionally closely dependent on their size, shape, composition and morphology.

The iron oxides, as ferrites, can be obtained by thermal decomposition of layered double hydroxides (LDH), also known as anionic clays or hydrotalcite-like compounds. LDH materials are considered a new generation of solids in areas such as anion exchangers, adsorbents, separation media, catalysis, polymer composites, and magnetic precursors [14].

The general chemical formula of these lamellar solids can be written as $[M_{(1-x)}^{2+} M_x^{3+}(OH)_2]$ $(A^{-x/n})_n mH_2O]$ where M^{2+} and M^{3+} are divalent and trivalent cations that occupy the center of $[M^{2+}/M^{3+}](OH)_6$ octahedral units like-brucite, and A is a compensation anion [15–17]. Fig. 2 shows the LDH structure. The partial replacement of the cations in the brucite-type layer with divalent or trivalent transition metal cations, with redox properties and ionic radius similar to Mg^{2+} or Al^{3+} , that can adopt an octahedral arrangement, leads to the obtainment of materials with specific catalytic activity due to the high dispersion of the active



Fig. 1. Black: oxygen. White and gray: 2+ and 3+ metals, respectively. Tetrahedral (A) and Octahedral (B) holds in the spinel FFC cell.

redox sites [18–21]. Iron-based layered double hydroxides (LDH), in which Fe^{2+} and/or Fe^{3+} in the brucite-type layer are partially replaced with other metal ions [22,23], have attracted much attention due to their suitable properties, such as anion exchange capacity and catalytic activity. When these materials are calcined at temperatures higher than 450 °C, a highly active homogeneous mixture of oxides is obtained, which have remarkable properties as catalysts and catalyst supports.

In this paper it is reported that a mixture of nanocrystals of cobalt ferrite and magnesium ferrite dispersed on the MgO matrix was obtained by calcinations in air of Co-Mg/Fe LDH synthesised by a co-precipitation method, using two ageing procedures: at room temperature (rt) and hydrothermal (ht). The Co content was changed in order to assess this effect on the structural properties of the LDH and the magnetic responses and band gap energy of the calcined materials. Due to their properties, these materials can be used as catalysts and photocatalysts for remediating water contaminated with organic compounds in solution.

2. Experimental

2.1. Sample preparation

The Layered Double Hydroxides (LDH) containing Co-Mg-Fe with different loads of Co⁺² were synthesized by a coprecipitation method at low supersaturation, using aqueous solutions of Mg(NO₃)₂ \cdot 9H₂O, Co(NO₃)₂ \cdot 9H₂O and Fe(NO₃)₃ \cdot 9H₂O as a source of metals. The M^{2+} :Fe³⁺ molar ratio was 3:1, where M^{2+} was Mg^{2+} and/or Co^{2+} . In order to assess the effect on the properties of the LDH and their mixture oxides, the molar percentage for Co was 0, 5 and 10%; the molar ratios between Co²⁺:Fe³⁺ were 0.0 (0Co), 0.2 (5Co), and 0.4 (10Co). In all cases, three solutions were prepared. The A solution contains the cations dissolved together in distilled water. The concentration of metals salts was 0.7 M. The B solution contains carbonates with 0.085 M concentration. A and B solutions were added simultaneously, dropwise, in a glass reactor vessel containing 50 mL of bidistilled water, at a dripping rate of 60 mL/h and under vigorous magnetic stirring. The pH was maintained constant (9.0 + 0.5) by continuously adding the third solution (NaOH 2 M). The resulting gel was aged by two different ways: (a) hydrothermal aging at 200 °C in autoclave (ht) in a teflon-lined stainless-steel and (b) at room temperature (rt). Both methods were carried out for15 h. The products obtained were separated by centrifugation at \sim 2800 rpm



Fig. 2. Schematic illustration of HDL structure.

 Table 1

 Chemical composition of the studied LDH and ferrites.

Sample	Molar percentage						Ferrites	
	Theoretical			ICP-OES			<i>х</i> :	1-x:
	Co ²⁺	${\rm Mg}^{2+}$	Fe ³⁺	Co ²⁺	${\rm Mg}^{2+}$	Fe ³⁺	COPe ₂ O ₄	Wgre ₂ O ₄
0Co _{ht}	0.00	75.00	25.00	0.00	68.25	31.75	0.00	1.00
0Co _{rt}				0.00	70.89	29.11	0.00	1.00
$5Co_{ht}$	5.00	70.00	25.00	4.97	58.41	36.62	0.27	0.73
5Co _{rt}				6.72	59.90	33.38	0.40	0.60
10Co _{ht}	10.00	65.00	25.00	7.14	64.71	28.15	0.51	0.49
10Co _{rt}				14.59	56.10	29.31	0.99	0.01

and washed with distilled water until sodium content was lower than 0.13% wt/wt. Then, the solids were dried at 90 °C for 10 h in air and they were named as precursors. All samples were calcined in air atmosphere at 550 °C for 10 h. The theoretical mole fractions in each sample are shown in Table 1. The samples calcined were named as XCo_Y , where "X" is the molar percentage for Co and "Y" the condition in which the synthesis gel was aged. The precursors were identified by adding the letter p to XCo_Y .

2.2. Materials characterization

The XRD powder patterns were collected on a PHILIPS PW3830 using monochromatized Cu K_{α} radiation (λ =1.54 Å) at a scan speed of 1/4 min in 2 θ and interfaced to a DACO-MP data acquisition microprocessor provided with the Diffract/AT software. The diffraction pattern was identified by comparing it with those included in the JCPDS (Joint Committee of Powder Diffraction Standards) data base.

The Thermogravimetric Analysis (TGA) was carried out in a Perkin Elmer UNIX TGA 7 instrument, under air atmosphere (20 mL/min) from 25 °C to 900 °C with a rate of 20 °C/min.

Spectroscopy Fourier transform infrared (FTIR) was performed on a JASCO FTIR 5300, with a nominal resolution of 4 cm⁻¹ and 16 scans; the sample was pressed into KBr pellets with a ratio of 1.53% wt/wt.

The reducibility of the materials was measured by temperature-programmed reduction (TPR) experiments in a QuantachromeChembet3000. In these experiments, the samples were heated at a rate of 10 °C/min in the presence of H₂ (5% H₂/N₂ flow, 20 mL/min STP), and the reduction reaction was monitored by the H₂ consumption.

Diffuse reflectance UV–visible spectra (UV–vis-DRS) were used to estimate the size of the particle, the electronic environment of metals, and to calculate the band gap energy (semiconductor character) of the calcined samples, using the Kubelka–Munk equation. The spectra of the ferrites modified were recorded using a spectrometer Jasco V-650, in the wavelength range 200–800 nm.

Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ⁵⁷Co in a Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 12 µm thick α -Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard. The spectra were evaluated using the Recoil spectral analysis software [24]. Although some spectra display magnetic relaxation, for simplicity, Lorentzian lines with equal widths for each component were considered. The spectra were folded to minimize geometric effects.

Inductively coupled plasma optical emission spectroscopy (ICP–OES) was used for determining the content of metals in the calcined materials. The measurements were performed with a Varian Spectra.

The magnetic measurements were performed in a conventional vibrating sample magnetometer (Lakeshore 7300) at room temperature varying the applied field between \pm 15 000 Oe. The powder samples were compacted applying 5 Tn to make a disk shaped sample of 5 mm diameter and 2 mm height to measure magnetization as function of the applied field as *M*(*H*).

The hysteresis properties, as coercivity and remanence, were obtained directly from the magnetization curves; these hysteresis curves were well fitted by the sum of two contributions: a ferromagnetic one (M_f) [25], and a superparamagnetic-like one (M_{sp}), [26] so the total magnetization (M_t) can be written as: $M_t = M_f + M_{sp}$.

$$M_f = \frac{2M_{\rm sf}}{\pi} \arctan\left[\frac{(H_i \pm H_{\rm ic})}{H_{\rm ic}} \tan\left(\frac{\pi M_r}{2M_{\rm sf}}\right)\right] \tag{1}$$

$$M_{\rm sp} = M_{\rm ssp} \left\{ \coth\left(\frac{\mu(H_i + H_i^*)}{k_B T}\right) - \frac{k_B T}{\mu(H_i + H_i^*)} \right\}$$
(2)

where $M_{\rm sf}$, $H_{\rm ic}$ and M_r are the effective ferromagnetic saturation magnetization, the coercitive field and the remanent magnetization, associated to the ferromagnetic contribution, respectively. $M_{\rm ssp}$, μ and H_i^* are the effective saturation magnetization, the mean magnetic moment of the activated clusters and a mean interaction field, introduced to account for the effect of eventual interactions between particles on the superparamagnetic-like component of the M(H) loops.

3. Results and discussion

3.1. X-ray diffraction

Fig. 3 shows the XRD pattern of the precursors. Most of the peak positions were matched with the ICDD (International Centre for Diffraction Data) PCPDFWIN data. The X-ray patterns showed a series of (0 0 l) peaks, such as (0 0 3), (0 0 6) and (0 0 9), appearing as narrow symmetric lines at low 2θ angles, associated to diffraction characteristics of the Layered Doubled Hydroxides in like hydrotalcite phase (PCPDFWIN 70-2151). However, the (1 1 0) and (1 1 3) diffraction planes were only observed in samples synthesized over rt ageing. They are associated to the formation of "*n*" layers and "*n* – 1" interlayers in the LDH structure, when *n* > 2. The absence of these planes in ht samples, suggest the formation of layers as film, in a slim structure [27].

The samples synthesized by rt ageing method showed a poor signal of the LDH phase due to a low-grade of crystallinity and/or a small crystal size. Furthermore, when the Co loading is increased, a ferrite phase (PCPDFWIN 77-1744/17-0465/82-1533) was detected.

Samples synthesized by the ht ageing method showed the formation of LDH lattice in all cases, in conjunction with the MgCO₃ phase (PCPDFWIN 83-1761). With the addition of a 5% theoretical molar load of Co, the hydrotalcite structure is enhanced. However, when the sample contains a 10% of Co (10Co_{ht}) a poor LDH lattice structure was observed. Moreover, in the X-ray diffractions patterns two intense signals, centered at 2θ =19 and 38°, were observed. They may be associated with the Co(OH)₂ as a segregated phase (PCPDFWIN 74-1057).

Fig. 4 shows the XRD pattern of the metallic oxides. Thus, after calcination at 550 °C, the (003), (006) and (009) reflections disappeared. The MgO phase (periclase PCPDFWIN 78-0430) with the ferrite phase, (MFe₂O₄-PCPDFWIN 77-1744/17-0465/82-1533) were detected in all samples.

The diffraction signals were more intense and defined when the samples were obtained by ht ageing, indicating that a better structure was achieved in these calcined materials. This effect was more evident when the Co loading was increased to 10%.

Table 2

materials.



Fig. 3. X-ray diffraction patterns of the LDH precursors with different Co percentage, synthesized by both ageing methods. $Co(OH)_2$ (o); $Mg(CO_3)$ (Δ); MFe_2O_4 (*).



Fig. 4. X-ray diffraction patterns of calcined samples. PericlaseMgO (+), and $\mathsf{MFe}_2\mathsf{O}_4$ (*).

3.2. TGA and DTG

Thermal properties of the sample have been assessed by TGA–DTG. Regardless of the method of aging, the total weight loss was 40% for the precursors with a molar percentage, of 0 and 5% of Co, while for the sample with 10% of Co, the total weight loss was of the 30% (Table 2). All samples showed four and three peaks or steps on materials synthesized using ht and rt ageing, respectively. These steps are produced by the overlapping of various and simultaneous reactions [28]. The thermal decomposition of precursor materials LDH showed particulars events:

Sample	Event	Range (°C)	DTG maximun (°C)	Weight loss (%)	Weight total loss (%)
0Co_{ht}	I, II	Untill 161	-	5.19	5.19
	II, III	161-375	190	11.99	17.18
	III, IV	375-475	387	12.03	29.21
	IV	475-800	587	11.07	40.28
$0 \text{Co}_{\mathrm{rt}}$	I, II	Untill 214	-	14.43	14.43
	II, III	214-369	239	16.3	30.73
	III	369-800	406	10.2	40.93
5Co_{ht}	I, II	Untill 172	-	7.91	7.91
	II, III	172-388	218	9.02	16.93
	III, IV	388-485	395	11.06	27.99
	IV	485-800	621	15.01	43.00
5Co _{rt}	I, II	Untill 226	-	14.67	14.67
	II, III	226-393	250	17.47	32.14
	III	393-800	410	7.83	39.97
10Co_{ht}	I, II	Untill 160	-	4.43	4.43
	II, III	160-373	178	11.34	15.77
	III, IV	373-527	447	9.43	25.20
	IV	527-800	580	5.57	30.77
10Co _{rt}	I, II	Untill 180	-	12.68	12.68
	II, III	180-334	197	15.36	28.04
	III	334-800	364°C	5.19	33.23

Thermogravimetric analysis (TGA) and d (% mass loss)/dT (DTG) of precursor

- (I) Removal of water: usually attributed to the removal of water physically absorbed on the external surface of the crystallites [29], between 25 and 100 °C. Moreover, removals of interlayer water take place in 100–150 °C range.
- (II) Removal of the interlayer anion: the destruction of interlayer took place due to thermal decomposition of the compensation anion CO_2^{3-} with elimination of CO_2 [17], between 130 and 220 °C.
- (III) Removal of hydroxyl groups: destruction of hydroxide metallic layers with consequent formation of oxides [18,29], between 200 and 500 °C.
- (IV) Removal of $MgCO_3$ salt: due to thermal decomposition, compound also detected by XRD [30]. This occurs above 500 °C.

The decomposition of the samples can be represented by the following reactions:

$$\begin{split} & [\mathsf{M}^{2+}_{(1-x)}\mathsf{Fe}^{3+}_{x}(\mathsf{OH})_{2}](\mathsf{CO}_{3}^{-2})_{n/x}\mathsf{m}\mathsf{H}_{2}\mathsf{O}] \to [\mathsf{M}^{2+}_{(1-x)}\mathsf{Fe}^{3+}_{x}(\mathsf{OH})_{2}](\mathsf{CO}_{3}^{-2})_{n/x} \\ & + \mathsf{m}\mathsf{H}_{2}\mathsf{O}_{(g)} \end{split} \tag{1} \\ & [\mathsf{M}^{2+}_{(1-x)}\mathsf{Fe}^{3+}_{x}(\mathsf{OH})_{2}](\mathsf{CO}_{3}^{-2})_{n/x} \to [\mathsf{M}^{2+}_{(1-x)}\mathsf{Fe}^{3+}_{x}(\mathsf{OH})_{2}] + {}^{(n/x)}\mathsf{CO}_{2(g)} \\ & + {}^{n/(2x)}\mathsf{O}_{2(g)} \\ & [\mathsf{M}^{2+}_{(1-x)}\mathsf{Fe}^{3+}_{x}(\mathsf{OH})_{2}] + {}^{(1/4)}x\mathsf{O}_{2(g)} \to {}^{(x/2)}\mathsf{M}^{2+}\mathsf{Fe}^{3+}_{2}\mathsf{O}_{4} + [1 - {}^{(3/2)}x] \\ & \mathsf{M}\mathsf{O} + \mathsf{H}_{2}\mathsf{O}_{(g)} \end{split}$$

$$MgCO_3 \rightarrow MgO + CO_{2(g)} \tag{IV}$$

The events (I), (II), (III) are detected in all samples.

The first step is attributed to (I) and (II) event. The samples obtained by ht ageing showed a loss weight close to 5–8%. However, the samples synthesized by the rt ageing method showed an important weight loss close to 13–15% suggesting a higher water content in the LDH structure. The second peak or step is produced by the overlapping of simultaneous loss weight corresponding to the reactions (II) and (III). The thermal stability of LDH materials is attributed to the formation of multi-layer

structure. A low initial temperature of this range and a low DTG maximum are indicative of the lower thermal stability of the structure materials. In samples rt, a poor layer structure was detected, but extensive lattice in a multi-layers was determinate. In ht samples, according to XRD patterns, a slim layer structure was formed. Possibly, for this reason, the second step shows a lower DTG maximum in ht samples in comparison with the rt samples. In this regard, the weight loss corresponding to this step range is higher in rt samples than in ht samples.

The third step is produced by (III) event in rt samples, and (III)–(IV) events in samples obtained by ht ageing. A higher weight loss was observed in ht samples than in rt ageing samples, due to the thermal decomposition of MgCO₃ (phase also detected by XRD patterns). In this step, all samples showed an initial temperature of decomposition between 370 and 390 °C, except in p-10Co_{rt} where a minor value was observed (334 °C).

The fourth step was only observed in ht materials due to (IV) event. The range of temperature in this step was between 500 and 700 °C approximately, with a DTG maximum at ~ 600 °C. The highest weight loss in this step, of 15%, was detected in p-5Co_{ht} suggesting the major content of MgCO₃ in this precursor.

Species and structure of LDH precursor materials and phases in oxides suggested are in agreement with the results obtained from previous analysis and other results that will be discussed below.

3.3. Fourier transform infrared spectroscopy (FTIR)

Fig. 5 shows the FTIR spectra for all calcined samples. In all of them there are observed two bands at about 680 and 560 cm⁻¹, v_1 and v_2 , respectively. They could be originated by the stretching vibrations of the metal–oxygen bond, such as A–O–B of a spinel. The v_1 band is attributed to the ABO₃ vibration in the spinel lattice, where A denotes M²⁺ in the tetrahedral position (Td) [31], and the v_2 band is characteristic of BO₆ vibration, where B denotes M³⁺ in the octahedral position (Oh) of a spinel structure.

When the band at 560 cm⁻¹ is analysed, a displacing with the Co loading is observed. The above-mentioned band is associated with the AOB₃ vibrations in the spinel lattice, but it may be also associated with the stretching vibrations of the bond between the surface cation-oxygen, which is affected by the available oxygen in the oxide. The characteristic diffraction signals observed by XRD of MFe₂O₄ are weekly, but as this displacing is associated with the cristalinity at the sample, it can be inferred that the MFe₂O₄ is present in small crystals. The absorbance band at higher values is likely to be due to the presence of Co situated in the environment oxygen octahedral.

Florea et al., observed two bands at 540 and 480 cm⁻¹, characteristics of well crystallized hematite [32]. These bands are not present in our samples, suggesting that pure iron oxide is not segregated. This result is in agreement with the observation made by XRD.

In all samples, an absorption band of around 450 cm^{-1} (v_3) usually associated with the stretching vibration of bond metaloxygen in the octahedral structure in the ferrite was observed [33], suggesting the presence of MFe₂O₄.

The absorption region between 420 cm⁻¹ (v_4) and 405 cm⁻¹ (v_5) can be due to the distortion A–O bond.

3.4. Analysis of temperature-programmed reduction (TPR) of calcined materials

The TPR analysis was used to obtain information about the reducibility and the state of metals in the calcined materials (Fig. 6).

The band centered to 450-520 °C could be assigned to the reduction of Co²⁺ to Co⁰ as it can be observed in the reaction (V)



Fig. 5. FTIR spectra of samples calcined, synthesized by both methods.

[34], in conjunction with the reduction of Fe^{3+} to Fe^{2+} (VI) [35], both metals present in ferrite phase. The wide range of this reduction band could be attributed to the particle size effects and the different Co content for each sample.

The H_2 consumption above 520 °C would correspond to the reduction of Fe $^{2+}$ in oxides phase, to $\alpha\text{-Fe}$ (VII–VIII). On the other hand, Mg^{2+} preserves their oxidation state in all reduction process.

 $Co^{II}Fe_2^{III}O_4 + H_2 \rightarrow Fe_2^{III}O_3 + Co + H_2O$ (V)

 $Mg^{II}Fe_2^{III}O_4 + H_2 \rightarrow {}^{2/y}Mg_{1-y}^{II}Fe_y^{II}O + H_2O + (3-2/y)MgO$ (VI)

 $Mg_{1-y}^{II}Fe_{y}^{II}O+yH_{2}\rightarrow y(\alpha-Fe)+(1-y)MgO+yH_{2}O$ (VII)

$$Fe_2^{III}O_3 + 3H_2 \rightarrow 2(\alpha - Fe) + 3H_2O \qquad (VIII)$$

Similar TPR profiles were observed in previous works by Xin and col. [36], where the reduction processes of complex oxides $(Mg^{2+}-Fe^{3+}-O \text{ and } Mg^{2+}-Fe^{3+}-Al^{3+}-O)$ derived from their HDL as precursors, were studied. The TPR technique suggests that Co is present as Co²⁺ in the ferrite phase, in accordance with others physico-chemical analysis.

3.5. Diffuse reflectance UV-visible (UV-vis-DRS)

In order to investigate further the structural characteristics of the oxides prepared, the UV–vis-DRS spectra were recorded in the region 200–800 nm (Fig. 7).

The bands around 210 and 270 nm are ascribed to $\text{Fe}^{3+} \leftarrow 0$ charge transfer bands of isolated iron ions in tetrahedral (Td) and octahedral (Oh) coordination, respectively [37]. The peak around \sim 330 nm is assigned to isolated Fe^{3+} in either periclase $\text{Mg}_{1-y}\text{Fe}_y\text{O}$ or ferrite [35,38]. The absorption bands observed at 360 and 480 nm, are attributed to small oligonuclear (FeO)_n clusters [35,39].

Moreover, the absorption region between 200 and 300 nm could be also assigned to the charge transfer between oxygen and Co^{2+} ions in Td symmetry [40]. In this range, there is a superposition with the iron-oxygen charge transfer bands. The spectra



Fig. 6. Temperature-programmed reduction analysis of calcined samples.



Fig. 7. UV-vis-DRS of calcined materials.

of the samples synthesized by both methods of aging with a molar percents of 5 and 10% of Co $(5Co_{ht,rt} \text{ and } 10Co_{ht,rt})$, shown an enlargement of the absorption band between 550 and 800 nm. Thus these materials exhibit an absorption band at 575 nm and a shoulder at 720 nm. This multiple absorption can be attributed to the presence of CoFe₂O₄ in nanoparticles, where Co²⁺ ions are in Td symmetry (575 nm) and Oh symmetry (shoulder at 720 nm), in

coordination with Fe^{3+} ions [41]. Moreover, the shoulder at 720 nm could be attributed to the presence of Co^{+3} in Td position. However, this oxidation state was not observed by other analysis which may be due to the small particle size, the extremely small quantity or the absence of this species. Similar observations were made by Zacharaki et al. [42] with cobalt spinel and modified cobalt spinel by XRD. The analysis of UV–vis-DRS suggests that mixture ferrites of MFe₂O₄, where M is Co²⁺ or Mg²⁺, are present as nanoparticles in two structures: (a) normal spinel ferrite, where Fe³⁺ ions are in position Oh and M ions are in position Td, (b) inverse spinel ferrite with Fe³⁺ in position Th and Oh, and M in Oh position.

3.6. Mössbauer spectroscopy

In order to get insight about the iron species present in the calcined samples, the Mössbauer spectra at room temperature were obtained (Figs. 8 and 9). Their hyperfine parameters are listed in Tables 3 and 4. Sample $0Co_{ht}$ shows an intense central doublet with two broad peaks at both sides. Besides, the background appears curved and the "valleys" between lines 1 and 2 and 5 and 6 did not get to the baseline. These aspects are characteristics of systems with superparamagnetic relaxation, typical of the presence of very small magnetic crystals. Therefore, this complex behavior was fitted with three sextets and one doublet. Two sextuplets are magnetically blocked (red lines) and the other one (cyan line) was relaxing and it was simulated using the relaxation model of two states of Blume and Tjon [43]. The doublet (green line) would correspond to species with superparamagnetic relaxation.

Sextuplets magnetically blocked have hyperfine parameters assignable to Fe³⁺ ions located in tetrahedral (A) and octahedral (B) sites of MgFe₂O₄ spinel [44]. Hyperfine magnetic fields appear slightly decreased in comparison with the bulk values: 7% for A sites and 9% for B sites. This effect can be explained by the magnetic collective excitations phenomenon present in small magnetic crystals [45]. The presence of a sextuplet with hyperfine parameters typical of α -Fe₂O₃ is not detected. Therefore, the presence of this species as a segregated phase can be discarded. Consequently, the relaxing sextuplet and the doublet can be assigned to MgFe₂O₄ spinel too but with different fluctuation speed of the magnetization due to different crystal sizes. Taking into account that Mg²⁺ ions are diamagnetics, the magnetic coupling in MgFe₂O₄ is produced only between Fe³⁺ ions. As a consequence, the magnetic anisotropy is relatively low, and it is common to find superparamagnetic behaviour of this compound. In this way, Chen et al. [46] have found that $MgFe_2O_4$ nanoparticles with 20 nm of size, show superparamagnetic behavior. On the other hand, the doublet parameters are very similar to that reported by Ferreira et al. [47] for this species.

Sample $0Co_{rt}$ shows six broad peaks with a curved background. The central doublet has disappeared. This spectrum was fitted with three sextuplets: two of them completely blocked (red interactions) and the other one relaxing (cyan interaction). All sextuplets can be assigned in the same way that in $0Co_{ht}$. A lower diminution of the hyperfine magnetic fields with reference to bulk compound (4% for A sites and 6% for B sites) was detected. This result, in conjunction with the disappearance of doublet, would indicate that the average particle size in $0Co_{ht}$ is lower than in $0Co_{rt}$. A narrowing of the size distribution in $0Co_{rt}$, without important changes in the average crystal sizes, would be compatible with the present results too.

The Mössbauer spectra of $5Co_{ht}$, $5Co_{rt}$ and $10Co_{ht}$, have six broad peaks and two small central peaks (Figs. 8 and 9). Besides, the background appears curved. On the other hand, the spectrum of $10Co_{rt}$, only shows four broad peaks, with low intensity, and a



Fig. 8. Mössbauer spectroscopy of ht series calcined materials.

very strong central doublet (Fig. 9). In order to get a good fitting, in all spectra there were used six interactions: five sextuplets (one of them relaxing) and one doublet.



Fig. 9. Mössbauer spectroscopy of rt series calcined materials.

The two sextuplets with the higher magnetic hyperfine fields (blue interactions) can be assigned to $CoFe_2O_4$ following the methodology described below. Ferreira et al. [48] refined Mössbauer spectra of $CoFe_2O_4$ considering that Fe^{3+} ions can be located in five different sites: in A sites and in B sites, with 6 (B1 sites), 5 (B2 sites), 4 (B3 sites) and (3+2+1) (B4 sites) Co^{2+} ions as nearer neighbors. In the present samples, the signals belonging to this species are very weak, as a consequence, it is not advisable to use so many interactions. Therefore, we use:

- A sextuplet for Fe³⁺ ions located in A sites. They have the lowest isomer shift and the highest magnetic hyperfine field,
- A second sextuplet in which there are included all Bi sites. Their hyperfine parameters were estimated using a weighted average of all these sites taking into account the theoretical relative population of each site, following the model proposed by Ferreira et al. [48].

The values of the hyperfine parameters obtained by fitting with this procedure show a good agreement with that found in the literature for $CoFe_2O_4$. The presence of $FeCo_2O_4$ was discarded

Table 3 Mössbauer parameters of $0Co_{ht}$ and $0Co_{rt}$ samples measured at 25 °C.

Species	Parameters	0Co _{ht}	0Co _{rt}
Fe^{3+} in A sites of MgFe ₂ O ₄	H (T) δ (mm/s) 2ε (mm/s) %	42.9 ± 0.1 0.28(*) 0(*) 9 + 1	$\begin{array}{c} 44.5 \pm 0.1 \\ 0.27(*) \\ 0.04 \pm 0.01 \\ 17 + 1 \end{array}$
Fe^{3+} in sites B of MgFe ₂ O ₄	H (T) δ (mm/s) 2ε (mm/s) %	45.2 ± 0.2 0.38(*) 0(*) 5 ± 1	46.5 ± 0.1 0.36(*) 0.01 ± 0.01 12 ± 1
$MgFe_2O_4$ magnetic partially blocked	H (T) δ (mm/s) 2ε (mm/s)	5 ± 1 40.6 ± 0.3 0.3(*) 0(*) 67 ± 2	12 ± 1 41.8 ± 0.1 0.3(*) 0(*) 71 + 1
$MgFe_2O_4$ (sp)	$\Delta (mm/s)$ $\delta (mm/s)$ %	0.74 ± 0.02 0.34 ± 0.01 19 ± 1	

H: Hyperfine magnetic field in Tesla.

 δ : Isomer shift (all the isomer shifts are referred to α -Fe at 25 °C).

2*e*: Quadrupole shift.

∆: Quadrupole splitting.

(*): Parameters held fixed in fitting.

(sp): Superparamagnetic.

Table	4
-------	---

Mössbauer parameters of $5Co_{ht},\,5Co_{rt},\,10Co_{ht}$ and $10Co_{rt}$ samples measured at 25 $^\circ C.$

since, as it was explained previously, the other characterization techniques used did not detected Co^{3+} .

The other three sextets (red and cyan interactions) were assigned to $MgFe_2O_4$ in the same way that for OCo_{ht} and OCo_{rt} .

The doublet could be assigned to superparamagnetic $CoFe_2O_4$ and/or MgFe₂O₄ species. A measure at low temperature is necessary to distinguish between both possibilities. However, in 10Co_{rt}, a significant change occurs in the value of the quadrupole splitting and the percentage of this signal is notoriously increased. Taking into account that these changes are produced when the Co loading is duplicated, while in 10Co_{rt} the percentages of the sextuplets assigned to $CoFe_2O_4$ decreases the doublet could be assigned, mainly, to superparamagnetic $CoFe_2O_4$.

It is important to remark that the present results did not allow us to discard the substitution of Co^{2+} by Mg^{2+} in $CoFe_2O_4$ and of Mg^{2+} by Co^{2+} in $MgFe_2O_4$, mainly in interphase regions. If these substitutions occur, depending on the crystallographic site (Td or Oh) substituted, a decrease in the magnetic hyperfine field could be detected. But, at the same time, in all samples the reduction of the magnetic hyperfine field is present due to the existence of very small particles. Therefore, the superposition of effects prevents us from obtaining deeper conclusions.

3.7. ICP-OES of precursor materials

The theoretical composition of the samples and experimental values obtained by ICP–OES are shown in Table 1. Sample $10Co_{rt}$ has the highest Co incorporation, with respect to the theoretical value of the precursor material.

The phase MFe₂O₄ has a stoichiometric molar ratio $A^{2+}:B^{3+} = 1:2$ ($A^{2+}B_2^{3+}O_4$). However, in the present work the molar ratio $M^{2+}:Fe^{3+}$ used in the precursor materials synthesized was 3:1. Therefore, after calcination, the excess of M^{2+} employed is segregated as isolated oxides. The previously described physicochemical analysis, (XRD, UV–vis-DRS, FTIR, TPR and Mössbauer spectroscopy) indicated that Co maintained the oxidation

Species	Parameters	5Co _{ht}	5Co _{rt}	10Co _{ht}	10Co _{rt}
$\mathrm{Fe^{3+}}$ in A sites of MgFe ₂ O ₄	H (T) δ (mm/s) 2ϵ (mm/s) γ	$\begin{array}{c} 44.6 \pm 0.1 \\ 0.27 \pm 0.01 \\ -0.02 \pm 0.01 \\ 27 \pm 1 \end{array}$	$\begin{array}{c} 43.0 \pm 0.1 \\ 0.27 \pm 0.01 \\ -0.02 \pm 0.02 \\ 20 + 1 \end{array}$	$\begin{array}{c} 44.5 \pm 0.1 \\ 0.28 \pm 0.01 \\ -0.02 \pm 0.01 \\ 22 \pm 1 \end{array}$	$\begin{array}{c} 42.9 \pm 0.2 \\ 0.27 \ (*) \\ -0.02 \ (*) \end{array}$
Fe^{3+} in B sites of MgFe ₂ O ₄	% Η (T) δ (mm/s) 2ε (mm/s) %	27 ± 1 46.5 ± 0.1 0.27 ± 0.01 0.04 ± 0.01 24 ± 1	$20 \pm 1 44.9 \pm 0.1 0.25 \pm 0.01 0.06 \pm 0.02 14 + 1$	22 ± 1 46.4 ± 0.1 0.26 ± 0.01 0.03 ± 0.01 27 ± 1	7 ± 1 45.5 ± 0.2 0.27 (*) 0.04 (*) 11 + 1
$[Co_xMg_{1-x}]Fe_2O_4$ magnetic partially blocked	H (T) δ (mm/s) 2ϵ (mm/s) %	$ \begin{array}{c} 2 + \frac{1}{2} \\ 41.8 (*) \\ 0.3 (*) \\ 0 (*) \\ 38 + 1 \end{array} $	40.5 0.3 (*) 0 (*) 54 + 2	$\begin{array}{c} 27 \pm 1 \\ 41.8 (*) \\ 0.3 (*) \\ 0 (*) \\ 37 \pm 1 \end{array}$	$ \begin{array}{c} 11 \pm 1 \\ 40.5 \\ 0.3 (*) \\ 0 (*) \\ 43 \pm 2 \end{array} $
Fe^{3+} in A sites of $\mathrm{CoFe_2O_4}$	$ \begin{array}{l} & \\ H (T) \\ \delta (mm/s) \\ 2e (mm/s) \\ \end{array} $	$ \begin{array}{c} 30 \pm 1 \\ 49.3 \pm 0.4 \\ 0.22 (*) \\ 0.06 (*) \\ 2 + 1 \end{array} $	3+12 47.5 ± 0.3 0.22 (*) 0.06 (*) 3+1	49.5 ± 0.2 0.22 (*) 0.06 (*) 2 ± 1	45 ± 2 48.7 ± 0.6 0.22 (*) 0.06 (*) 1 ± 1
Fe^{3+} in B sites of $\mathrm{CoFe_2O_4}$	H (T) δ (mm/s) 2ε (mm/s) %	2 ± 1 48.2 ± 0.1 0.41 (*) -0.2 (*) 7 + 1	46.3 ± 0.2 0.41 (*) -0.2 (*) 7 ± 1	2 ± 1 48.2 ± 0.1 0.41 (*) -0.2 (*) 8 ± 1	47.1 ± 0.3 0.41 (*) -0.2 (*) 1+1
MgFe ₂ O ₄ (sp) and/or CoFe ₂ O ₄ (sp)	Δ (mm/s) δ (mm/s) %	$0.\overline{63} \pm 0.03$ 0.34 ± 0.02 2 ± 1	0.8 ± 0.1 0.33 ± 0.05 2 ± 1	0.71 ± 0.02 0.33 ± 0.01 4 ± 1	0.53 ± 0.01 0.37 ± 0.01 37 ± 1

H: Hyperfine magnetic field in Tesla.

 δ : Isomer shift (all the isomer shifts are referred to α-Fe at 25 °C).

2*e*: Quadrupole shift.

 Δ : Quadrupole splitting.

(*): Parameters held fixed in fitting.

(sp): Superparamagnetic.

state 2+ (Co²⁺) after calcination process of the precursor materials. Moreover, the presence of isolated oxides such as hematite or CoO_x [49] was not detected, suggesting the existence of mixture oxides in MFe₂O₄ phase, where M is a 2+ metal. Taking into account that the experimental Co:Fe molar ratio, determined by ICP–OES, was less than 0.5, the missing M²⁺ quantity to obtain an stoichiometric ferrite must have been provided by Mg²⁺ ions. The excess of Mg would be segregated as MgO. In this sense, the mass balance for this metal is calculated based on the following equation:

$$\%Mg_{total} = \%Mg_{ferrite} + \%Mg_{ox}$$
(3)

 Mg_{total} represents the percentage of Mg in the samples, % $Mg_{ferrite}$ percentage of Mg in the ferrite phase, and Mg_{ox} the percentage of Mg as oxide isolated. Considering the stoichiometric ratio in the ferrites, the following equation was obtained:

$$\frac{A^{2+}}{B^{+3}} = \frac{\% Co_{ferrite} + \% Mg_{ferrite}}{\% Fe_{ferrite}} = 0.5$$
(4)

where %Fe_{ferrite} and %Co_{ferrite} are the molar percentages of the respective metals in the samples, a system of two equations with two unknown quantities was obtained. The fractions of $CoFe_2O_4(x)$ and MgFe₂O₄ (1-*x*), as well as the amount of isolated magnesium oxide (MgO) present in calcined materials, can be obtained. This suggests that iron prefers to combine with Co^{2+} , instead of Mg²⁺, in order to produces the ferrite (Table 1).

Therefore, it may be considered the general formula of spinel ferrites obtained as: MFe₂O₄, where M is Co²⁺ or Mg²⁺. The resultant system of phases in the calcined materials consisted in a mixture of CoFe₂O₄(x) and MgFe₂O₄(1-x) dispersed over a matrix of MgO with periclase structure.

The color of the samples is a simple indication of whether iron oxides are or not present in the samples [37]. Samples without Co, synthesized through both methods evaluated (OCo_{ht} and OCo_{rt}), exhibited a reddish brown color due to the large load iron present in the material. When the load of Mg in the synthesis was substituted by 5% Co of the total employed metals (5Coht and 5Co_{rt}), the samples showed brown color, suggesting that Co cations were substantially incorporated on the samples. However, if the load of Co increases up to 10%, the ageing method employed plays an important role; since the color of 10Co_{rt} was pale brown due to the incorporation of Co and iron presents in small crystals, indicating that the mixture oxides were well dispersed over an extensive MgO matrix [50]. On the other hand, 10Co_{ht} showed an off black color due to the incorporation of Co and iron in large crystals of the samples. These observations were consistent with the results obtained by other analysis techniques.

3.8. Band gap energy of calcined materials in connection with their structural properties

The physical and chemical properties of the nanomaterials tend to be exceptionally closely dependent on their size, shape, composition and morphology [51]. In this sense, the band gap energy (E_g) of oxides is strongly dependent of the composition and the crystal size of the materials due to quantum confinement effects [52]. Moreover, both aspects strongly affect the magnetic behavior of materials too. The average crystallite size may be estimated from the values of the full width at half-maximum (FWHM) of the peaks at 2θ =31° and 57.1° by means of the Scherrer in Eq. (5):

$$Dc = \frac{K\lambda}{\beta(\theta)\cos\theta}$$
(5)

where *Dc* is the crystallite size (average diameter of crystal), *K* is a shape factor (0.89), λ is the wavelength of the radiation used

(0.15418 nm), θ is the Bragg diffraction angle, and $\beta(\theta)$ is the FWHM. The results obtained are informed in Table 6 where smaller crystals of MFe₂O₄ were obtained by the room temperature ageing method. Moreover, when a pure ferrite of magnesium or cobalt was identified, a smaller crystal was determinate close to 7 nm.

Through the measure of UV–vis-DRS, it was determined the band gap energy (E_g) of the calcined materials. The evaluation of E_g for all calcined samples was calculated using the Kubelka–Munk (K–M) Eq. (6):

$$F(R) = \frac{(1-R)^2}{2R}$$
(6)

where *R* is the reflectance (%) from the converted UV–vis adsorption spectra. *F*(*R*) is proportional to the extinction coefficient. This equation is usually applied to highly light scattering materials and absorbing particles in a matrix. By plotting the K–*M* equation as a function of the energy in eV, the band gap of semiconductor particles can be obtained. In this work, it was used the method known as the Tauc method [53] plotting: $(F(R) h\nu)^2$ versus $h\nu$.

One of the characteristics of the semiconductor nanocrystals is the increase of the valence conduction band gap E_g with the decrease of *Dc*, where *Dc* denotes the size of nanocrystals [54].

Samples OCo_{ht} and OCo_{rt} showed similar Dc and low E_g values. This result could be attributed to the high molar ratio of MFe₂O₄/MgO (Table 5) since, as it is well known, some spinel ferrites exhibit low band gap energy [55,56]. The samples with the highest Co loading, $10Co_{ht}$ and $10Co_{rt}$, showed the lowest (1.73 eV) and the highest (2.48 eV) E_g values obtained, respectively. Both samples exhibited a similar low MFe₂O₄/MgO (Table 6), close to 0.25. The highest E_g observed in $10Co_{rt}$ was attributed to nanometric size of the ferrite crystals, mainly as CoFe₂O₄, where Dc observed is close to 6.5 nm.

The correlation between E_g and CoFe₂O₄/MgO molar ratio is shown in Fig. 10. A minimum value of the E_g was observed for the CoFe₂O₄/MgO ratio between 0.10 and 0.15. On the other hand, when the ferrite crystal size decreases, the E_g value increases (Fig. 11).

3.9. Magnetic measurements of calcined materials

The room temperature hysteresis loops of products obtained by calcination materials are shown in Figs. 12 and 13.

The magnetic responses of materials calcined are attributed to oxides iron formed by the thermal transformation process. In these sense, the magnetic response observed for both series samples (ht and rt) are weak and are not saturated with the magnetic field applied. Moreover, all of them show magnetic coercivity at room temperature, characteristic of ferromagnetic and/or superparamagnetic systems with magnetic interaction due to small particles size.

The coercitive field, remanent magnetization and magnetization at 15 kOe of the samples obtained by the hydrothermal aging method (ht) are higher to the parameters of samples aged at room temperature (rt), due to the major particle size obtained by this aging method. The magnetization curves are well described by the superposition of a superparamagnetic component and a small ferromagnetic one component. The parameters obtained to both methods by fitting using Eqs. (1) and (2) are shown in Table 6, where it can been observed that the saturation magnetization and the coercivity of the nanoparticles ferrites increases with increasing particle size [57]. Moreover, when the Co content increased, the magnetic parameters are increased, except by the sample $10Co_{rt}$, which could be due to the smaller crystals of cobalt ferrite identified by previous analyze.

Table 5

Band gap energy (E_g), Crystal size (Dc), CoFe₂O₄/MgO, MgFe₂O₄/MgO and MFe₂O₄/MgO molar ratios in calcined materials.

Sample	E_g (eV)	Dc [nm]	CoFe ₂ O ₄ /MgO	MgFe ₂ O ₄ /MgO	MFe ₂ O ₄ /MgO
0Co _{ht}	2.37	7.2	0.00	3.34	3.34
0Co _{rt}	2.27	7.1	0.00	1.15	1.15
5Co _{ht}	1.74	20.0	0.11	0.30	0.41
5Co _{rt}	1.80	14.6	0.13	0.20	0.33
10Co _{ht}	1.73	18.0	0.12	0.12	0.24
10Co _{rt}	2.48	6.5	0.26	0.00	0.26

Table 6

Estimated values of magnetic properties.

Sample	$M_{\rm sf}^{a}$ [emu/g]	$M_r^{\rm b}$ [emu/g]	$H_{\rm ic}^{\ \rm c}$ [Oe]	$M_{\rm ssp}^{\rm d}$ [emu/g]	$\mu^{\mathbf{e}} \left[\mu_{\mathrm{B}} \right]$	H_i^{*f} [Oe]
0Co _{ht}	1.958	0.152	90	4.171	823	0
0Co _{rt}	1.277	0.060	36	3.809	1,026	0
$5Co_{ht}$	1.708	3.454	315	9.765	10,447	- 351
5Co _{rt}	1.197	0.024	65	2.830	12,118	0
10Co _{ht}	2.856	5.761	260	16.725	12,840	-305
10Co _{rt}	1.321	0.026	40	4.413	617	0

^a Effective ferromagnetic saturation magnetization.

^b Remanent magnetization.

^c Coercitive field.

^d Effective saturation magnetization.

^e Magnetic moment.

^f Mean of interaction field by nanoclusters.



Fig. 10. Eg values [eV] vs. CoFe₂O₄/MgO determinate in all samples.

4. Conclusions

Mixtures of nanocrystals of MgFe₂O₄ and CoFe₂O₄ into MgO matrix were obtained by calcination of layered double hydroxides (LDH). They were synthesized by a co-precipitation technique, with different theoretical Co loadings (0%, 5%, 10%), using two ageing methods and employing carbonate as interlayer anion. The materials obtained at room temperature ageing showed a poor LDH structure and multi-layer, due to small crystal size. When the precursor materials were ageing by hydrothermal treatment, the production of MgCO₃ in conjunction with a better layer structure



in slim lattice was detected. Moreover, the highest Co loading used produced $Co(OH)_2$ as a segregated phase.

With respect to the metal contents in calcined samples, the major incorporation of Co was achieved by room temperature ageing. For this reason, a greater ratio $CoFe_2O_4/MgO$ was obtained by this ageing method, suggesting that the structural preference of iron is to combine with Co^{2+} with respect to Mg^{2+} in order to produce ferrite.

The physical-chemical analysis of all calcined material suggested the presence of nanocrystals of mixture ferrites of Co and Mg, in normal and inverse spinel structure, while the smallest crystals were obtained by the ageing at room temperature method.

The band gap energy and the superparamagnetic response in samples synthesized by aging at room temperature could be mainly related with the nanocrystal size detected. When a single ferrite phase of Co or Mg was formed, a diminution of the crystal size with consequent enlarged values of band gap energy was observed.



Fig. 13. Magnetic Response of OCort, 5Cort, 10Cort.

However, the results obtained indicate that these solids would be suitable for their use as photocatalysts in all visible light range.

Acknowledgements

U.A. to the CONICET doctoral fellowship. This work was supported by CONICET (PIP 11220090100490) and UTN-FRC of Argentina) (PID 25/E187). We thank to geol. Julio D. Fernández (UTN-FRC, Córdoba, Argentina) for helping to record FTIR spectral, and Marianela Pía Zannier (engineering student) for their valuable help in experimental activities. The authors are grateful to the "Programa de movilidad docente" of Education Ministry of Argentine Republic.

References

- [1] J. Roelofs, A. van Dillen, Y.K. de Jong, Catal. Today 60 (2000) 297-303.
- [2] K. Simeonidis, S. Mourdikoudis, M. Moulla, I. Tsiaoussis, C. Martinez- Boubeta, M. Angelakeris, C. Dendrinou-Samara, O. Kalogirou., J. Magn. Magn. Mater. 316 (2007) 1-4.
- [3] V. Rives, O. Prieto, A. Dubey, S. Kannan., J. Catal. 220 (2003) 161-167.
- [4] F. Prinetto, D. Tichit, R. Teissier, B. Coq., Catal. Today 55 (2000) 103-116.
- [5] S. Murcia-Mascarós, R. Navarro, L. Gómez-Sainero, U. Costantino, M. Nocchetti, I.L.G. Fierro., J. Catal. 198 (2001) 338-347.
- [6] K. Sreekumar, T. Mathew, B. Davassy, R. Rajgopal, R. Vetrivel, B. Rao., Appl. Catal., A 205 (2001) 11-18.
- [7] K. Sreekumar, T.M. Jyothi, M.B. Talawar, B.P. Kiran, B.S. Rao, S. Sugunan, J. Mol. Catal. A: Chem. 152 (2000) 225.
- [8] N. Bao, L. Shen, Y. Wang, P. Padhan, A. Gupta., J. Am. Chem. Soc. 129 (2007) 12374-12375.
- R. Costa, M. Lelis, L. Oliveira, J. Fabris, J. Ardisson, R. Rios, C. Silva, R. Lago., J. [9] Hazard. Mater. B 129 (2006) 171-178.
- [10] M. Sugimoto., J. Am. Ceram. Soc. 82 (1999) 269-280.
- [11] R. Costa, M. Fontes Lelis, L. Oliveira, J. Faabris, J. Ardisson, R. Rios, C. Silva, R. Lago., Catal. Commun. 4 (2003) 524-529.
- [12] K. Sreekumar, S. Sugunam., J. Mol. Catal. A: Chem. 185 (2002) 259-268.
- [13] C.h. Hsueh, Y. Huang, C.h. Wang, C.h. Chen, J. Mol. Catal. A: Chem. 245 (2006) 78-86.

- [14] X. Zhang, D. Wang, S. Zhang, Y. Ma, W. Yang, Y. Wang, S. Awaji, K. Watanable., J. Magn. Magn. Mater. 322 (2010) 2023-2027.
- [15] F. Cavani, F. Trifiró, A. Vaccari, Catal. Today 11 (1991) 173-301.
- [16] A. Vaccari, Appl. Clay Sci. 14 (1999) 161-198.
- [17] O. Ferreira, O. Alves, D. Gouveia, A. Souza Filho, J. de Paiva, J. Filho, J. Solid State Chem. 177 (2004) 3058-3069.
- [18] M. Crivello, C. Pérez, J. Fernández, G. Eimer, E. Herrero, S. Casuscelli, E. Rodrìguez-Castellón., Appl. Catal., A 317 (2007) 11-19.
- [19] R. Zăvoianu, R. Ionescu, O.D. Pavel, R. Bîrjega, E. Angelescu., Appl. Clay Sci. 52 (2011) 1-10.
- [20] S. Albertazzi, F. Basile, A. Vaccari, Interface Sci. Technol. 1 (2004) 497-546.
- [21] G. Busca, U. Costantino, T. Montanari, G. Ramis, C. Resini, M. Sisani, Int. J. Hydrogen Energy 35 (2009) 5356-5366.
- [22] C. Ruby, M. Usman, S. Naille, K. Hanna, C. Carteret, M. Mullet, Appl. Clay Sci. 48 (2008) 195-202.
- [23] Feng Li, Junjie Liu, David G. Evans, Xue Duan, Chem. Mater. 16 (2004) 1597-1602.
- [24] V. Lagarec, D. Rancourt, Mössbauer Spectral Analysis Software Dep. of Phys, University of Otawa, 1998 (Version 1.0).
- [25] M. Stearns, Y. Cheng, J. Appl. Phys. 75 (1994) 6894–6898.
 [26] P. Allia, M. Coisson, M. Knobel, P. Tiberto, F. Vinai, Phys. Rev. B: Condens. Matter 60 (1999) 12207-12218.
- [27] X. Kong, S.h. Shi, J. Han, F. Zhu, M. Wei, X. Duan., Chem. Eng. J. 157 (2010) 598-604.
- [28] V. Rives., Mater. Chem. Phys. 75 (2002) 19-25.
- [29] J. Pérez-Ramirez, G. Mul, J.A. Moulijn., Vib. Spectrosc. 27 (2001) 75-88.
- [30] J. Bouzaid, R. Frost., J. Therm. Anal. Calorim. 89 (2007) 133-135.
- [31] S. Christoskova, M. Georgieva, D. Mehandjiev., Mater. Chem. Phys. 60 (1999) 39_43
- [32] M. Florea, M. Alifanti, V. Parvulescu, D. Mihaila-Tarabasanu, L. Diamendescu, M. Feder, C. Negrila, L. Frunza., Catal. Today 141 (2009) 361-366.
- [33] L.M. Salah, Phys. Status Solidi 271 (2006) 203-207.
- [34] H. Lin, H. Chiu, H. Tsai, S. Chien, C. K. Wang, Catal. Lett. 88 (2003) 169–174.
 [35] Y. Ohishi, T. Kawabata, T. Shishido, K. Takaki, Q. Zhang, Y. Wang, K. Nomura,
- K. Takehira., Appl. Catal., A 288 (2005) 220-223.
- [36] X. Ge, M. Li, J. Shen., J. Solid State Chem. 161 (2001) 38-44.
- [37] T. Kawabata, N. Fujisaki, T. Shishido, K. Nomura, T. Sano, K. Takehira, J. Mol. Catal. A: Chem. 253 (2006) 279-289.
- [38] A. Heredia, M. Oliva, U. Agú, C. Zandalazini, S. Marchetti, E. Herrero, M. Crivello., J. Magn. Magn. Mater. 234 (2013) 38-46.
- [39] V. Elías, M. Oliva, S. Urreta, S. Silvetti., K. Sapag, A. Navarro, S. Casuscelli, G. Eimer., Appl. Catal., A 381 (2010) 92–100.
- [40] Verónica R. Elías, Eliana G. Vaschetto, Karim Sapag, Mónica E. Crivello, Sandra G. Casuscelli, Griselda A. Eimer, Top. Catal 54 (2011) 277-286.
- [41] Younes Brik, Mohamed Kacimi, Mahfoud Ziyad, F. Bozon-Verduraz, J. Catal. 202 (2001) 118-128.
- I. Zacharaki, C. Kontoyannis, S. Boghosian, A. Lycourghiotis, C.h. Kordulis., [42] Catal. Today 143 (2009) 38–44.
- [43] M. Blume, J.A. Tjon, Phys. Rev. 165 (1968) 446-456.
- [44] E. De Grave, A. Govaert, D. Chambaere, G. Robbrecht, Physica B 96 (1979) 103-110
- [45] S. Mørup, H. Topsøe, Appl. Phys. 11 (1976) 63-66.
- [46] Q. Chen, A.J. Rondinone, B.C. Chakoumakos, Z.J. Zhang, J. Magn. Magn. Mater. 194 (1999) 1-7.
- [47] O.P. Ferreira, O.L. Alves, D.X. Gouveia, A.G. Souza Filho, J.A.C. de Paiva, J. Mendes Filho, J. Solid State Chem. 177 (2004) 3058-3069.
- [48] T.A.S. Ferreira, J.C. Waerenborgh, M.H.R.M. Mendonca, M.R. Nunes, F.M. Costa, Solid State Sci. 5 (2003) 383-392.
- [49] Huang-Kuan Lin, Hui-Chi Chiu, Hsin-Chi Tsai, Shu-Hua Chien, Chen-Bn Wang, Catal. Lett. 88 (2003) 169-174.
- [50] A. Heredia, M. Oliva, C. Zandalazini, U. Agú, G. Eimar, S. Casuscelli, E. Herrero, C. Pérez, M. Crivello., Ind. Eng. Chem. Res. 50 (2011) 6695-6703.
- D. Mathew, R. Juang, Chem. Eng. J. 129 (2007) 51-65.
- [52] M. Li, J.C. Li., Mater. Lett. 60 (2006) 2526-2529.
- [53] R. López, R. Gómez., J. Sol-Gel Sci. Technol. 61 (2012) 1-7.
- [54] R. Viswanatha, S. Sapra, B. Satpati, P. Satyam, B. Devb, D. Sarma, J. Mater. Chem. 14 (2004) 661-668.
- [55] A. Mantilla, F. Tzompantizi, J. Fernández, J. Díaz Góngora, R. Gómez, Catal. Today 150 (2010) 353-357.
- [56] P.P. Hankare, R. Patil, A. Jadhav, K. Garadkar, R. Sasikala., Appl. Catal., B 107 (2011) 333-339.
- C. Liu, A. Rondinone, Z. Zhang., Pure Appl. Chem. 72 (2000) 37-45 (Nos. 1-2). [57]