Synthesis and Characterization of Cobalt Ferrite $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ Nanoparticles by Raman Spectroscopy and X-Ray Diffraction

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Abstract

In this paper, ferrite nanoparticles of formula $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ (where $x = 0.0, 0.5$ and 1) have been synthesized, through the chemical co-precipitation method, in a basic medium through the use of Fe (III), Fe (II) and Co (II) solutions. The powders were characterized by Raman spectroscopy and X-Ray Diffraction (XRD). The diffractograms indicated the Co (II) ions occupied the tetragonal region, modifying considerably the distribution of the rest of the ions present in the inverse spinel structure. Raman spectra shows variations in the intensity of the characterized bands located at $460, 624$ and 672 cm^{-1} for each structure.

Keywords

Nanoparticles, Cobalt ferrites, Raman spectroscopy, Ion dispersion and displacement

Introduction

As nanoscience and nanotechnology progress, new sort of magnetic nanocrystals are being created, among these paramagnetic nanomaterials, ferrite nanoparticles stand out, due to their unique fascinating properties, such as magnetic, electronic and magneto-optic [1], which exhibit a good combination of high electric resistance and ferromagnetic behavior [2]. The novel physicochemical and electromagnetic properties, observed in the ferrite nanoparticles, are caused by the changes in the composition and size of the particles. These peculiar properties have led researchers to synthesize these materials [3]. The facility with which these materials can be synthesized and the stability of the same under diverse conditions, have caused great

interest in many industrial areas [4,5]. The study of magnetic nanocrystals has been fundamental for the comprehension of nanomagnetism, so it can be applied in different areas such as; medicine and biomedical science [6,7]. Can be a useful tool for the development of therapeutic agents, carcinogenic diagnostics [8], hyperthermia with magnetic fluids, contrast agents for magnetic resonance images [9,10] and antimicrobial agents [11].

The nanocrystal family belonging to the spinel and inverse spinel ferrites is represented by the molecular formula AB_2O_4 [1]. The magnetic properties of these oxides are mainly governed by the distribution and interaction of the cations in their both tetrahedral and octahedral networks [1], for example; the migration of the divalent ions such as

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Co, Ni, Mg and Zn form the CoFe_2O_4 , MgFe_2O_4 and MnFe_2O_4 nanoferrites [12].

The cobalt ferrite nanoparticles have been synthesized by the co-precipitation method through changing the adding sequences of the reactants, the concentrations of NaOH solutions, as well as the temperatures in the subsequent annealing treatment. The mechanism for the composition and size dependence of magnetic properties was studied in detail [13].

Magnetic CoFe_2O_4 nanoparticles with different sizes were obtained from the versatile coprecipitation process. Studying the temperature treatments or with the addition of tartrate ions, Fe nitrates or Co nitrates, nanoparticle sizes were tuned between 7 nm and 21 nm [14].

In this work, by using the co-precipitation method, magnetic nanoparticles of magnetite and cobalt ferrites were prepared. Co (II) accomplished gradual replacement of the metallic ions Fe (II), forming the general molecular system of nanoferrites $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$, where the stoichiometric relation of Co^{2+}

was used (0.0, 0.5, and 1.0) in the ferrite's crystalline network. Therefore, the influence of Co (II) ions in the inverse spinel structure is demonstrated through Raman spectroscopy and X Ray Diffraction techniques.

Description of the Method

Synthesis of cobalt ferrite nanoparticles

Currently there is a vast diversity of methods that can be used for the preparation of magnetic nanoparticles with sizes that of 10 nm approximately [15,16], the simplest and viable method is chemical co-precipitation. This method is based on an aqueous solution mixture of suspended salts in an alkaline medium (see Figure 1).

8 mmol of Fe (III) were dissolved in 5 ml of deionized water, this solution was then mixed with the quantities indicated in Table 1 for Fe (II) and Co (II), this was later dissolved in 5 ml of water slightly acidulated (pH = 4). For M1 4.0 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 2.5 mL of deionized water acidified with 0.5 ml of HCl 1.0 N. A solution

Table 1: Portions for the formation of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$.

Nomenclature	Compound	%Cobalt nominal	Fe (III) mmol nominal	Fe (II) mmol nominal	Co (II) mmol nominal
M1	Fe_3O_4	0	8	4	0
M2	$\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$	50	8	2	2
M3	CoFe_2O_4	100	8	0	4

containing 8.0 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 2.5 mL of deionized water acidified with 0.5 mL of HCl 1.0 N was added under vigorous stirring. The M2 were synthesized using the described methodology, except that the 4.0 mmol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was replaced by 2.0 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2.0 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Accordingly, for M3 4.0 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was replaced by 4.0 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The solutions were mixed and vigorously agitated for 10 minutes at a stable temperature (between 20 and 25 °C). Later, drop by drop, 100 ml of NaOH at 3.0 M were slowly added as a precipitating agent. During the precipitation, the solution's colour changed to black, distinctive of this material. This indicates the formation of a ferrofluid. The next step is to raise the temperature to 90 °C and maintain it for an hour while it is being vigorously agitated. Later, the solution has to be cooled down at room temperature and washed three times with deionized water. Once the sample is washed, the next procedure is to let it dry for 24 hours at 90 °C, and then the sample is pulverized in a mortar so it can finally be characterized by Raman spectroscopy and XRD.

Cobalt ferrites nanoparticles characterization

The characterization of the magnetic nanoparticles is important, for this reason, the Raman

spectroscopy and the X-Ray Diffraction were used to obtain information at a molecular level. Characterizations of the ferrite nanoparticles morphology and elemental composition were analysed on a SEM HITACHI S-3400N fitted with an electron dispersive X-ray (10 Kv and 30 pA; image magnification 1500X and the work distance of 10.5 mm). In addition, the atomic ratio of cobalt and iron was determined by a Perkin Elmer Optima 7000 DV ICP-OES Spectrometer. Where the Raman spectroscopy, is a non-destructive method that does not require sophisticated preparation to analyse samples, for the case of the magnetic nanoparticles. In addition, it is a powerful and sensible tool for the analysis of thin films and powders. This technique is useful to comprehend the microstructure in nanomaterials, structure transition, network distortion, charge and reticle of lattice couplings, the distribution of local cation and the magnetic arrangement [1,12].

In this research, a near infrared laser with a wavelength of 785 nm was used to produce the laser beam, and, to obtain information from the samples, an Ocean Optics spectrogram model QE65000 was adjusted to an interval of 0 to 2100 cm^{-1} , with a spectral resolution of 3-4 cm^{-1} . The integration time and the fixed potency of the laser were 125 seconds and 35 mW, respectively.

Figure 2: The upper Raman spectra shows four active modes of ($A_{1g} + E_g + 2T_{2g}$) expected for ferrite (M1), at bottom is clear that when Cobalt is included, A_{1g} is splitted into two variant components, labelled as $A_{1g}(1)$ and $A_{1g}(2)$. $T_{2g}(2)$ have changes too. No clear evidence of $T_{2g}(1)$ and E_g are present for M2 and M3 spectra.

Regarding the X-Ray Diffraction instrument, a Rigaku UIV of 40 kV and 30 mA, with a wavelength corresponding to the Cu K α radiation, which is $\lambda = 1.5406 \text{ \AA}$, was used to obtain the diffractograms, which were mapped from 5 to 80° in 2 θ with a step of 0.02°.

Results and Discussion

The Ferrite Raman spectrum (M1) possesses a group of factors (phonon modes belonging to the inverse spinel structure) such as; A1g(R), Eg (R), T1g, 3T2g (R), 2A2u, 2Eu, 4T1u (IR) and 2T2u [14]. When analysing the group of factors, only a certain range of the spectrum can be observed with the instrument, which consists of four active Raman modes 1A1g+1Eg+2T2g [17,18]. Which correspond to the bands of 306, 393, 495, y 669 cm⁻¹, respectively [19].

In Figure 2, The upper Raman spectra shows four active modes of (A1g + Eg + 2T2g) expected for ferrite Fe₃O₄ (M1) [20], at bottom is clear that when Co²⁺ substitutes the Fe²⁺ ions A1g is splitted into two variant components, labelled as A1g(1) and A1g(2), as expected for CoFe₃O₄ [21], T2g(2) have changes too. Although, there are no clear evidence about T2g(1) and Eg in M2 and M3 spectra.

Figure 2, shows also a remarkable difference between M2 and M3 respect to M1, Raman bands of M2 and M3 are less intense than Raman bans of M1, but with the particularity that A1g is splitted into to modes. For M1 which only contains half of the amount of Co (II) in relation to Fe (II), A1g(2) is shifted to lower energy bands, around 624 cm⁻¹, and A1g(1) is shifted to higher energy bands, around 672 cm⁻¹. In this case, A1g(2) intensity < A1g(1) intensity.

For the case of M3 which contains the 100% of Co, also are appreciable the A_{1g}(2) and A_{1g}(1) modes, but A_{1g}(2) intensity > A_{1g}(1) intensity. Thus, the changes in the intensity of vibrational modes in this particular case, could indicate the redistribution of cations in the tetrahedral spaces (T) of Fe³⁺ to the octahedral spaces (O) of Co²⁺, which alters the symmetry of the crystalline structure [22].

Figure 3, shows the best Lorentzian fits on M1, M2, and M3 spectrums. Inspection of Lorentzian curves on T_{2g}(2), A_{1g}(1) and A_{1g}(2) depict important variations, with little shift center, and changes in peak intensities as Cobalt increased. Table 2, shows the peak center variations of T_{2g}(2), A_{1g}(1)

and A_{1g}(2), and the relative intensities of the A_{1g}(1) and A_{1g}(2) modes.

A_{1g}(1) and A_{1g}(2) demonstrate the stretching vibrations of the Fe-O and Co-O bonds in tetrahedral sites. The cation redistribution can be noticed by comparing the relative intensities of the A_{1g}(1) and A_{1g}(2) modes. From Figure 3 and Table 2, M3 sample has higher value in the relative intensity that agrees with the high percentage of Co(II). Consequently, A_{1g}(2) is associated to the Co-O bonds [23]. While M2 sample has a lower value in the relative intensity, indicating that A_{1g}(1) mode depends on the interaction of Fe-O bonds [24].

Table 2: Raman modes for Cobalt Ferrite nanoparticles.

Sample	Raman peak (cm ⁻¹)	Raman peak (cm ⁻¹)	Raman peak (cm ⁻¹)	Ratio of Intensity
	T _{2g} (2)	A _{1g} (2)	A _{1g} (1)	$I_{A_{1g}(2)} / I_{A_{1g}(1)}$
M1	495.128	---	669.577	---
M2	471.661	610.899	673.298	0.132
M3	461.837	622.410	680.747	5.133

Figure 4: XRD Diffractograms of the grinding process.

T_{2g}(2) mode demonstrate the variations of the spinel structure, from Figure 3 and Table 2 is noticeable the shift to lower energy bands as Co increases. It is associated with the decreased of particle size in the sample [25].

On the other hand, in Figure 4, the diffraction patterns of the ferrite nanoparticles X-Rays can be observed. When analysing and indexing the diffractograms, it was observed that these matched with the magnetite standard by checking with the DRX 99-203-7367 card, this one also indicates that they possess an inverse spinel structure. The asterisk peaks of M1 diffractogram in Figure corresponding to other iron oxides phases (as goethite and maghemite). Similarly, to the analysis of the Raman spectra, the analysis for the diffractograms starts with the sample M1, which serves as a starting point. When comparing the patterns for M1, M2 and M3, a slight displacement in the 2 θ angle was observed, due to the progressive substitution of Fe (II) over Co (II). To gather more information from the diffractograms, the greater intensity profiles were measured to obtain an approximate size of the ferrite nanoparticle, by making use of Debye Scherrer's equation ($D = 0.9 \lambda / \beta \cos \theta$), where D is the crystal size, λ is the wavelength of X-ray, θ is

the Braggs angle in radians, and β is the full width at half maximum of the peak in radians. The results for the measurements of the next samples; Fe₃O₄, Co_{0.5}Fe_{2.5}O₄ and CoFe₂O₄ (M1, M2 and M3 respectively), were; 13.02, 17.38, 13.29 nm, respectively.

Figure 5 shows a typical bright field SEM image of the sample, where numerous faceted particles with size of ~50 μ m and agglomerates of particles smaller than 5 μ m are distinguished. Dynamic light scattering (DLS), using a Nanotracs 252 Particle Size Analyzer, showed that the particle size is beginning with 2.375 nm for M1, 2.385 nm for M2 and 2.556 nm for M3.

The presence of cobalt in ferrite particles composition from SEM was corroborated by energy-dispersive X-ray spectroscopy (EDS) analysis, which displayed particles content to be 37.17% Fe and 62.83% O for M1, 13.31% Co, 31.59% Fe and 55.10% O for M2, and 20.82% Co, 23.60% Fe, and 55.58% O for M3. The elemental composition of cobalt in ferrite nanoparticles was also corroborated by ICP-OES, where nanoparticles were previously digested in concentrated hydrochloric acid. ICP-OES showed M2 and M3 nanoparticles to content 12.87% and 19.96% atomic Co, % for M2 and M3 respectively, in accordance to EDS, that's it, Co and

Figure 5: SEM micrographs, corresponding to: a) M1; b) M2 and c) M3.

Table 3: Content of Fe, O and Co for the samples.

Sample	EDS Analysis			ICP-OES Analysis		
	%Fe	%O	%Co	%Fe	%O	%Co
M1	37.17	62.83	-	Unrealized	Unrealized	-
M2	31.59	55.10	13.31	Unrealized	Unrealized	12.87
M3	23.60	55.58	20.82	Unrealized	Unrealized	19.96

Fe having a near $\frac{1}{4}$ and $\frac{1}{2}$ molar ratio for M2 and M3 respectively, see Table 3. These results corresponded to with cobalt ferrites nanoparticles $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ (where $x = 0.6, 1, 1.8$) obtained by a very simple non-aqueous one-pot process [25].

Regarding magnetic properties, Figure 1b displays the magnetic hysteresis loops of the ferrite NPs. The data such as saturation magnetization (M_s), the coercive field (H_c), and the remanence (M_r) of the NPs can be extracted from the loops. The M_s of 23.7, 56.4, and 43.8 emu/g was determined for M1, M2, and M3, respectively. The H_c of 2.6, 618, and 251 Oe was determined for M1, M2, and M3, respectively. The M_r of 0.05, 7.5 and 14.0 emu/g was determined for M1, M2, and M3, respectively. The H_c and M_r values near zero for the M1 NPs indicate their superparamagnetic nature at room temperature. For the cobalt ferrites, the hysteresis loops reveal their ferrimagnetic nature, where the M2 NPs are magnetically harder than the M3 NPs. Variations of coercive fields of the cobalt ferrites NPs, where a maximum was found, and it was explained that M2 is magnetically harder than M3 and, in agreement with our results [26] Figure 6.

Conclusions

In this research three ferrite compounds (M1, M2 and M3) were synthesized, differing from one another in their Co(II) and Fe(II) percentages, through co-precipitation methodology. These compounds were characterized through Raman Spectroscopy and X-Ray Diffraction and their magnetic properties were determined thorough magnetometry. The characterization of the compounds helped to observe and determine valuable information from the phenomenon that is caused by the substitution of Fe^{2+} ions from their octahedral spaces by the Co^{2+} . It was determined that the substitution of Fe^{2+} ions by Co^{2+} ions cause fluctuations in the intensity of the vibrational modes, intensity seems to decrease for T2g(2) as the percentage of Co(II) increases and Fe(II) decreases, this is due to the band 460 cm^{-1} being dependent on the interactions with the Fe-O bonds. Changes in intensity and peak center shift on the A1g(2) and A1g(1) modes demonstrating the stretching vibrations of the Fe-O and the Co-O bonds in the tetrahedral sites. It can be associated with the changes in the particle size, that agrees with the finding out analysis of the diffractograms by DLS.

Figure 6: Hysteresis curve with specific magnetization at room temperature for M1, M2 and M3 NPs.

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