Size-modulation of Thermally-annealed Nanosized Cobalt Ferrite Particles

P. P. C. Sartoratto\textsuperscript{a}, M. A. G. Soler\textsuperscript{b,*}, T. M. Lima\textsuperscript{a}, F. L. R. Silva\textsuperscript{b}, T. V. Trufini\textsuperscript{b}, V. K. Garg\textsuperscript{b}, A. C. Oliveira\textsuperscript{b} and P. C. Morais\textsuperscript{b}

\textsuperscript{a}Universidade Federal de Goias, Instituto de Quimica, Goiania-GO 74001-970, Brazil
\textsuperscript{b}Universidade de Brasilia, Instituto de Fisica, Brasilia-DF 70910-900, Brazil

Abstract

CoFe\textsubscript{2}O\textsubscript{4} nanoparticles were synthesized by co-precipitating Co(II) and Fe(III) ions in alkaline medium following temperature annealing, aiming to study the influence of the sintering temperature on the structure of the nanosized cubic ferrite. A group of powder samples were submitted to thermal treatment at 373, 623, 1023, 1273, and 1473 K during 30 minutes in atmospheric air. For the purpose of our investigation cobalt ferrite nanoparticles were evaluated by atomic absorption spectrophotometry, X-ray diffraction (XRD), Raman, and Mössbauer spectroscopy. The chemical composition of cobalt ferrite samples, expressed as the [Fe]/[Co] ratio, was found as 2.1. Our results reveal that the increase of the sintering temperature modifies the cation distribution profile, resulting in an improvement of the nanomaterial’s properties.

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1. Introduction

Nanosized iron oxides have been extensively studied due to the increasing interest in applications as different as high-density magnetic recording media and drug delivery systems [1,2]. The effective use of a magnetic nanoparticle (NP) for a given application is primarily based on its properties, such as morphological, compositional, and surface characteristics. Among nanosized iron oxides, cobalt ferrite (CoFe\textsubscript{2}O\textsubscript{4}) is especially interesting because of its high magnetocrystalline anisotropy, high coercivity, high values of magnetostriction coefficients, moderate saturation magnetization and high chemical and structural stability [3,4]. Bulk cobalt ferrite presents the inverse spinel structure with a collinear ferrimagnetic array. At room temperature the tetrahedral sites (site A) of bulk CoFe\textsubscript{2}O\textsubscript{4} are occupied by half of the Fe(III) ions whereas the octahedral sites (site B) are occupied half by Co(II) ions and half by Fe(III) ions. The presence of Co(II) in site B has been associated to the large anisotropy and high coercivity values observed in this material. However, in the case of nanosized particles the collinear arrangement of
spins can be distorted, especially when the nanocrystallite surface-to-volume ratio becomes significantly high. Details of the nanosized ferrite preparation route determine the final distribution of the metal ions in the spinel structure. Further, thermal annealing could affect compositional homogeneity, phase content and site occupancy of cobalt and iron ions among sites A and B. Then, the understanding of the NP surface properties, particle size, lattice constant, lattice strain, and cation distribution profile are key issues to tailor nanosized systems for specific applications. The aim of this study is to investigate the influence of the sintering temperature on the structure of cobalt ferrite NP prepared by co-precipitating Co(II) and Fe(III) ions in alkaline medium. To support our investigation X-ray diffraction (XRD), atomic absorption spectrophotometry, Raman and Mössbauer spectroscopy were employed.

2. Experimental

Cobalt ferrite NPs were synthesized by co-precipitating Co(II) and Fe(III) ions in alkaline medium using equal volumes of aqueous solutions of the divalent and trivalent ions at 0.1 mol/L and 0.2 mol/L, respectively [5]. The as-precipitated material (solid cobalt ferrite) was isolated by centrifugation and washed with distilled water. Portions of the solid precursor were then used for further annealing treatment. Each portion of the precursor was submitted to thermal treatment at 373, 623, 1023, 1273, and 1473 K, during 60 minutes in atmospheric air, and labeled S1, S2, S3, S4 and S5, respectively. The chemical composition of all samples (total iron and cobalt contents) was determined by atomic absorption. Information regarding the structure, lattice constant and average crystalline diameter of the samples was obtained by XRD. Diffractograms of the powder samples were recorded in the 2θ range of 10-80° using the Shimadzu XRD-6000 system equipped with a Cu Kα radiation source at 40 kV and 30mA while scanning the angle at 0.004°/s. The Raman spectra were recorded using a commercial double spectrometer equipped with a CCD detector. The 514 nm line of an Argon ion laser used for excitation of the samples was kept at 1 mW. Mössbauer spectra of all powder samples were recorded in the transmission geometry, using a ⁵⁷Co source in Rh matrix. The velocity was calibrated with a thin Fe foil.

3. Results and Discussion

The iron/cobalt molar ratio, obtained by atomic absorption spectrophotometry, show that the precursor sample presents [Fe]/[Co] = 2.1. Analysis of the XRD patterns of all powder samples investigated revealed cubic spinel (Fd3m) structure, consistent with typical cobalt ferrite. Fig. 1 shows the XRD patterns of samples S1 through S5. The line broadening (FWHM) of the (311) X-ray diffraction peak provided the estimation of the average diameter ($D_{XRD}$) of the nanoparticulated materials. The $D_{XRD}$ for samples S1 through S4 are 14, 14, 35 and 57nm, respectively. The average diameter for sample S5 was too big to be estimated from the XRD data. Nevertheless, the unit cell parameter calculated for S1 through S5 samples are respectively 8.379, 8.344, 8.361, 8.391 and 8.396 Å. It is observed that as the annealing temperature increases the unit cell parameter value tend to the value reported for bulk cobalt ferrite (8.396 Å) [6]. The inset of Fig.1 displays the variation (β cosθ)/λ versus (sinθ)/λ for samples S1-S4, where β is the FWHM and θ is the Bragg angle for the (3 1 1), (4 0 0), (5 1 1), and (4 4 0) diffraction peaks. It is possible to observe that the angular coefficient of the linear plots presents a continuous decrease as the annealing temperature increases, suggesting that the strain within the particles reduces significantly with annealing temperature [7] from 1.2×10⁻² for sample S1 (373K) down to 3.2×10⁻³ for sample S4 (1273 K), as calculated from the Williamson-Hall method [8].
Fig. 1 XRD patterns of samples S1 through S5, annealed at 373, 623, 1023, 1273 and 1473 K, respectively. The inset is the plot of \((\beta \cos \theta)/\lambda\) versus \((\sin \theta)/\lambda\).

Figure 2 shows the Raman spectra of samples S1 through S5. Raman features showed in the spectral region from 150 to 800 cm\(^{-1}\) are assigned to vibrational modes from the NP crystalline structure. The fitting procedures, using Lorentzian-like components, showed the presence of seven structures at 300, 447, 472, 543, 601, 645 and 681 cm\(^{-1}\), for S1 sample. The peaks were identified considering the Raman active symmetry modes expected for a cubic spinel \(\text{O}_h^6(\text{Fd}3\text{m})\) spacial group and compared with the data available in the literature for nanosized cobalt ferrite. The highest frequency Raman mode (695 cm\(^{-1}\)) in sample S5, annealed at 1473 K, was assigned to the tetrahedral position (site A) whereas the peak at 473 cm\(^{-1}\) is related to the octahedral position (site B) [9,10]. As observed in Fig. 2, the Raman features indicate the presence of a stable crystalline structure, as the annealing temperature increases. The Mössbauer spectra recorded at 77 K present slightly asymmetric magnetic hyperfine patterns, similar to the ones previously observed in cobalt ferrite NPs. The curve fitting of the spectra was obtained with two well-defined sextets. The first sextet, with the largest hyperfine field value, was assigned to Fe(III) ions located in sites A of the cubic spinel structure. The second sextet was assigned to Fe(III) ions occupying sites B [11]. The Mössbauer hyperfine parameters obtained at 77 K are listed in Table 1.

Fig. 2 Raman spectra of S1 through S5 samples at 1 mW laser intensity
Table 1: Hyperfine Field ($H$), Relative Intensity ($I_{rel}$), Isomer Shift (IS) and Quadrupole Splitting (QS). Values obtained from Mössbauer Spectra of Samples S1 through S5 at 77 K.

<table>
<thead>
<tr>
<th>sample</th>
<th>site</th>
<th>$H$ (kOe)</th>
<th>$I_{rel}$</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>A</td>
<td>529</td>
<td>29</td>
<td>0.50</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>505</td>
<td>71</td>
<td>0.40</td>
<td>-0.07</td>
</tr>
<tr>
<td>S2</td>
<td>A</td>
<td>531</td>
<td>23</td>
<td>0.51</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>507</td>
<td>77</td>
<td>0.40</td>
<td>-0.05</td>
</tr>
<tr>
<td>S3</td>
<td>A</td>
<td>540</td>
<td>39</td>
<td>0.50</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>512</td>
<td>61</td>
<td>0.39</td>
<td>-0.06</td>
</tr>
<tr>
<td>S4</td>
<td>A</td>
<td>541</td>
<td>42</td>
<td>0.51</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>513</td>
<td>58</td>
<td>0.38</td>
<td>-0.06</td>
</tr>
<tr>
<td>S5</td>
<td>A</td>
<td>543</td>
<td>42</td>
<td>0.50</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>515</td>
<td>58</td>
<td>0.38</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

Mössbauer parameters listed in Table 1 fall within the values reported in the literature for cobalt ferrite NPs. When the temperature increases from the liquid Nitrogen temperature one observes a strong asymmetrical broadening of the sextet lines and the onset of a doublet whose intensity increases as the intensity of the sextets reduce. Such behavior is characteristic of superparamagnetic relaxation and the approach used to fit the spectra consists of a superposition of a magnetic hyperfine field distribution with a quadrupolar doublet. Such behavior was observed in the Mossbauer spectra recorded for samples S1 and S2 at 300 K.

4. Conclusions

In summary, the influence of the sintering temperature on the structure of nanosized cobalt ferrite was investigated. The average grain size increased monotonically from 14 to 57 nm as the annealing temperature increases from 373 to 1273 K. Annealed samples at lower temperatures presented superparamagnetic behavior at room temperature. The XRD studies of annealed cobalt ferrite NPs revealed no change in the crystalline phase while matching perfectly with the standard reported data. Further, as the annealing temperature increases Raman trends indicate the presence of a stable crystalline structure. Our results also reveal that the increase of the sintering temperature modifies the cation distribution profile.

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References