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Unexpected magnetic properties explained by the homogeneity of mixed ferrites

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ABSTRACT

In this work, we report on magnetic nanoparticles of $Co_xFe_{3-x}O_4$ ($x \leq 1$, step 0.2) ferrites synthesized by a solvothermal chemical route based on theoretical study on Fe-Co-O alloys. Both, X-Ray Diffraction (XRD) and Selected Area Electron Diffraction (SAED) indicate the presence of both the hematite and the magnetite in the sample before any substitution ($x = 0$). The substitution of iron by cobalt ($x > 0$) gives spinel structure of space group Fd-3m for all samples. Magnetization curves, recorded by a Vibrating Sample Magnetometer (VSM), are the sign of two exchange-coupled magnetic phases ($x > 0$). This was in disagreement with XRD and SAED analyses which showed only one structural phase. Large (~250 nm and less) rectangular and small spheroidal nanoparticles have been found by Transmission Electron Microscopy (TEM). The increase of cobalt content favors the formation of monodisperse nanoparticles. Following a subsequent heat treatment, a fraction of the as prepared samples (depending on x) has been transformed into hematite phase with a disappearance of the exchange-coupling behavior. *In situ* Micro-Raman analyses were necessary to investigate on the growing of the nanoparticles and the ferrite-hematite transformation. We have also deduced, that the synthesized phase with the cobalt ferrite one (till $x < 1$) was the magnetite Fe_3O_4. Then, we have pointed out the effect of performing local spectroscopy and the effect of having mixed ferrites on the structural and the physical properties.

1. Introduction

Spinel ferrite magnetic nanoscale systems have attracted the interest of a wide scientific international community in recent years due to their large field of applications such as in biomedicine [1], electronics [2], catalysis [3], photocatalysis and sensors [4].

$Co_xFe_{3-x}O_4$ cobalt ferrite (CF) is one of the most promising members of the spinel systems because the cobalt amount x may control the coercive field and the saturation magnetization. The magnetic anisotropy is also directly related to the Russell–Saunders coupling (L-S coupling) magnitude which is governed by the difference between the orbital momentum of $Co^{2+}$and Fe^{3+} ($L = 0$) [5]. The control of these intrinsic structural properties can therefore open up fascinating perspectives for high density storage media [6] and electronic properties of next generation devices [2].

In the past decades, cobalt ferrite nanoparticles (CF NPs) have been successfully synthesized by mean of several physical and chemical routes. Nakagomi et al. [7] synthesized $Co_xFe_{3-x}O_4$ by combustion reaction method. They found, combining X-ray diffraction,^{57}Fe Mössbauer and Raman spectroscopies that samples with cobalt contents $x \leq 0.4$ present two different structural phases including the hematite α-Fe_2O_3 (rhombohedral structure, space group R-3c). Sichu et al. [8] observed, for similar systems prepared by water-in-oil micro-emulsion method, that lower contents of cobalt (x) favor the formation of the maghemite γ-Fe_2O_3 as a second phase whereas the higher cobalt content promotes pure CF spinel structure. Since both Co-ferrite and γ -Fe_2O_3 crystallize in the same space group Fd-3m and have close cell parameters, their distinction is out of the threshold of the XRD tool. Recently, under heat treatment up to 900 °C, it has been shown [9] that $Co_{0.6}Fe_{2.4}O_4$revealed the presence of two phases, the hematite and the cobalt ferrite. However, the authors cannot precise which phase is present before the annealing, the maghemite or the magnetite or probably both of them regarding their same symmetry as well as

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the CF. Sorescu et al. [10] examined a similar substitution using a hydrothermal synthesis route but did not exhibit any additional phase. From a theoretical point of view, Jung et al. [11] studied the phase diagram of Fe-Co-O based oxide systems and they demonstrated that low molar ratio of Co/(Co+Fe) leads to CF with α/γ-Fe_2O_3depending on the temperature. Therefore, it is quite delicate to elaborate a pure cobalt ferrite system for low cobalt content.

Recent studies highlight the important role played by the synthesis technique affecting homogeneity of the product, particle size distribution, shape, structural and magnetic characteristics [12,13].

Despite the large number of papers devoted to cobalt ferrites, which underlined their fascinating properties, there are relatively few systematic studies reporting on their chemical composition and the structural homogeneity of nanoparticles.

In this work, we point out the presence of two phases in cobalt ferrites powder synthesized by a solvothermal route. Structural investigations have been made by combining both external heat treatment and *in situ* micro-Raman under laser irradiations. As the iron oxide (magnetite or maghemite) transition to the hematite under high Raman laser irradiation has been widely investigated [14,15,16] we explored here this methodology to indirectly highlight the effect of the chemical composition on the phase evolution, the structural and magnetic properties of samples. The structural and morphological characterizations of the nanoparticles were done by X-ray Diffraction (XRD) and Transmission Electron Microscopy (MET). These two techniques allow showing how these properties are strongly correlated. The magnetic measurements were carried out at different temperatures and under different fields. Finally, the limitations of XRD and TEM techniques are discussed and compared to the sensitivity of Raman spectroscopy to characterize the variation of chemical composition.

2. Experimental section

2.1. Cobalt ferrite nanoparticles synthesis

The samples were prepared by a solvothermal chemical route developed by Pinna et al. [17] for magnetite nanoparticles and adapted to synthesize cobalt ferrites by Ajroudi et al. [18]. Five compositions have been elaborated $Co_xFe_{3-x}O_4$with x = 0, 0.2, 0.4, 0.6 and 0.8 labeled, Co0, Co02, Co04, Co06 and Co08, respectively.

Annealing treatments were performed at 400 and 900 °C for 6 and 8 h, respectively, in a Nabertherm furnace in air with a temperature rate 5 K/min.

2.2. Structural characterizations

The crystal structure, particle size and morphology of the samples were determined by XRD and TEM. The XRD measurements were carried out with a Siemens D5000 X-ray powder diffractometer using Cu Kα irradiation (λ-Kα_1 = 1.5406 Å and λ-Kα_2 = 1.5444 Å). XRD patterns were collected in the range of Bragg angles between 20 and 80° with a scanning rate of 0.02°/20 s. The TEM analyses were performed with a FEITecnaiG2 microscope (200 kV) mounted with a super twin objective lens of 0.25 nm point-to-point resolution. Magnetic measurements were done using a 7T Mini Cryogen Free Vibrating Sample Magnetometer (VSM) at different temperatures and under an applied magnetic field up to 70 kOe.

Raman analyses were performed at room temperature using a T64000 Jobin-Yvon-Horiba spectrometer equipped with the diffraction grating 600 lines/mm under a microscope (Olympus Bx41) with a 100 × objective. Raman spectra were recorded between 150 and 2000 cm^{-1}using an exciting argon-krypton ion laser (Innova 70C) operating at 514.5 nm. Measurements were carried out with different laser output powers (between 7 and 300 mW) in order to probe the structural properties of CF NPs.

3. Results and discussion

3.1. Structural and morphological details

Fig. 1 displays the XRD patterns for Co0, Co02 and Co06. Co0 sample, expected to be pure magnetite, gives a XRD pattern with a distinguishable additional hematite α-Fe_2O_3(R-3c) phase with a ratio to magnetite estimated at 40% using Rietveld calculations. The profiles of XRD patterns for the other compositions are typical spinel structure even so in literature such materials may have additional phases according to the studies of Sichu et al. [8] and Ajroudi et al. [9]. At this stage, one cannot judge neither their presence nor their absence because of the lack resolution of the XRD patterns and because additional phases can get the same symmetry with very weak difference of lattice parameters. Moreover, recently Kim and his co-workers [19] confirmed the difficulties to discriminate the maghemite from the magnetite using only the XRD tool.

The cobalt content dependence of the cell parameter estimated from the XRD data after Rietveld refinement calculations (using FullProf software), is illustrated in Fig. 1. It slightly increases with increasing cobalt content. This behavior which has been observed in several solid substitutions [18,20] fairly follows the Vegard's law and might be thus related to the difference in the cationic radii of Co^{2+} and Fe^{3+} [21].

Fig. 2 displays the conventional and high resolution transmission electron microscopy (CTEM and HRTEM) for$Co_xFe_{3-x}O_4$ with x = 0, 0.2, 0.4 and 0.8 as well as the selected area diffraction patterns (SAED) for x = 0 and size distributions (insert) established form more than 200 nanoparticles for x = 0, 0.2 and 0.4.

Three shapes of nanoparticles can be easily identified: spheroidal, rectangular and elongated ones. For x = 0, two kinds of SAED were found. The first shows the existence of the magnetite and hematite reticular planes done on the both kinds of nanoparticles (small~50 nm and large~250 nm). The largest particles (SAED done on a large nanoparticle) are indexed in the spinel structure. Here, one can assign the large nanoparticles to magnetite and the small ones to hematite. For the other samples (x > 0), we see a clear difference between the two kinds of shape, whereas it was not possible to undergo any symmetry difference neither by XRD nor

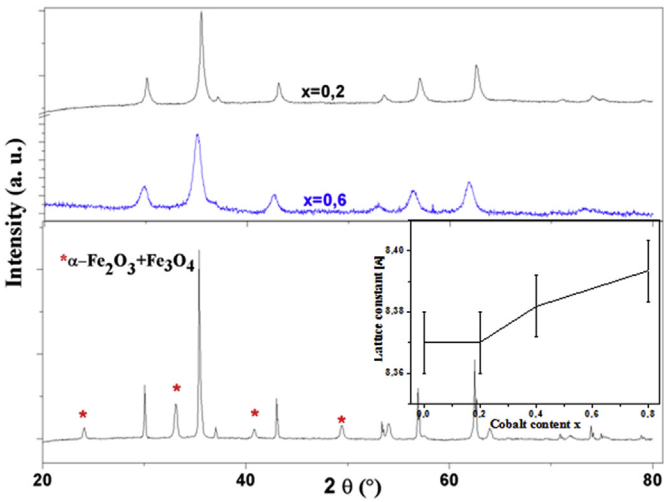

Figure 1. XRD patterns of $Co_xFe_{3-x}O_4$ with x = 0, 0.2 and 0.6 (inset: lattice constant).