



Structural and magnetic influence of yttrium-for-iron substitution in cobalt ferrite



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ABSTRACT

Yttrium-substituted cobalt ferrites of nominal composition $\text{CoY}_x\text{Fe}_{1.98-x}\text{O}_4$, $x = 0; 0.1; 0.2; 0.3$, were prepared using the sol-gel combustion method. A slight iron deficiency in the formulation was designed in order to improve yttrium solubility in the spinel structure. The inclusion of Y in the lattice reached 10% cationic substitution. XRD Rietveld analysis and Raman spectra confirm that yttrium enters the lattice in octahedral sites, increasing the inversion parameter of cobalt ferrite. Mössbauer results confirm the cation distribution obtained with Rietveld refinements. Saturation magnetization and Curie temperature decrease with iron substitution, confirming the B site occupancy of Y ions. Yttrium inclusion promotes a cation distribution which modifies the Raman spectra. A model is proposed to explain the observed vibrational modes.

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1. Introduction

Cobalt ferrite (CoFe_2O_4) is a well-known and widely used ferrimagnetic hard material because of its wide range of applications in environmental science, recording media, magnetic sensors and catalytic materials, among others [1]. Its crystal system is face centered cubic while its crystal structure is mixed spinel, whose corresponding space group is O_h^7 (Fd-3m). Its unit cell consists of 56 atoms where 32 of them are oxygen anions and the remaining 24 atoms are metallic cations divided such that 8 of them occupy tetrahedral (A) sites and 16 occupy octahedral (B) sites. The cation distribution is generally represented as $(\text{Co}^{2+\delta} \text{Fe}^{3+1-\delta})_A[\text{Co}^{2+1-\delta} \text{Fe}^{3+1+\delta}]_B\text{O}_4$, where δ is the inversion parameter (which is 1 for a normal spinel and 0 for an inverse spinel structure), and is extremely important because it determines the electromagnetic properties of the material. For most ferrites, δ depends upon the method of preparation, while cation distribution is related to the thermal treatment [2]. Previous studies reported an inversion parameter $\delta \sim 0.2$ – 0.3 for cobalt ferrite [3].

Over the last years, several authors [4–9] have studied the

effects of the substitution of Fe^{3+} by rare earth (RE) cations such as Y^{3+} , Gd^{3+} or La^{3+} in the magnetic and structural properties of cobalt ferrite. Few works have reported the synthesis of single phase RE-substituted spinel ferrites, although relatively low concentrations of the dopants were explored (cationic substitution <7%). The presence of secondary phases is attributed mainly to the large size of the RE cation, which finds it difficult to fit in either tetrahedral or octahedral sites. The electric, magnetic and microwave absorption properties of ferrites can be controlled by substitution with RE ions, and changes in these properties are related to the segregation of secondary phases in grain boundaries, so it is important to control RE solubility in ferrites [10,11].

To our knowledge there is only one study, albeit non exhaustive, of yttrium-substituted cobalt ferrite with a nominal Y cationic substitution of 7% which is reported as single phase [6]. It is therefore of interest to further deepen the study of yttrium solubility in cobalt ferrite.

In earlier works, we achieved an enhancement of Nd solubility in the crystalline structure of Sr hexaferrites, obtaining single phase materials by proposing an iron deficient formulation [12–14]. Taking these previous results into account, in this work we intend to enhance Y substitution up to 10% in Co ferrite, by proposing a slight iron deficiency in the formulation. A thorough structural

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analysis is performed using different characterization techniques.

2. Experimental details

2.1. Samples preparation

All the samples were prepared by the self-combustion method, as described elsewhere [15]. For synthesizing CoFe_2O_4 , different proportions of iron nitrates and cobalt oxalates were weighed according to the required stoichiometric proportion and diluted in water (considering that $[\text{Fe(III)}] + [\text{Co(II)}] = 1 \text{ M}$). A 3 M citric acid solution (50 ml) was added to each metal solution (50 ml) and heated at 40 °C for approximately 30 min with continuous stirring. The final mixture was slowly evaporated until a highly viscous gel was formed. The resulting gel was heated at $T < 200 \text{ °C}$; when it ignited in a self-propagated process. The final residue was calcined at 800 °C for 2 h.

Yttrium nitrates, previously dissolved in 3 M citric acid solutions, were used for the preparation of the Y-doped samples ($\text{CoY}_x\text{Fe}_{1.98-x}\text{O}_4$, $x = 0.1; 0.2; 0.3$). A slight deficiency in iron content was considered (1 at.%) for all the substitutions.

The obtained samples were labeled Y0, Y1, Y2 and Y3, being the number related to the yttrium content, x . The samples labels and nominal compositions are shown in Table 1.

2.2. Characterization methods

In order to determine the actual composition of the prepared powders, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was performed. An Ar plasma Spectro Modula Flame was used. The detection limits for Fe, Co and Y were 0.25 ppm, 1 ppm and 0.25 ppm, respectively.

X-ray diffraction (XRD) powder diffractograms were measured with a Philips PW 3860 diffractometer, in the 2θ range 20–110, with a step size of 0.02, for 8 s per step. A Sigma Zeiss Field Emission scanning electron microscope with an Oxford EDS detector (LAMARX facilities) was used to characterize the morphology and elemental composition of the samples.

A ^{57}Co source (Rh matrix) was used to record Mössbauer spectra in constant acceleration mode, at room temperature. Powder samples (65 mg) were measured in a round acrylic sample holder of 20 mm diameter. The measured isomer shifts (IS) are referred to $\alpha\text{-Fe}$. The Normos/site Program was used for fitting the measured spectra.

Raman spectra were measured at room temperature with a laser Raman spectrophotometer (Confocal Horiba Jobin-Yvon LabRam HR). The excitation wavelength and laser power were 632.8 nm and $2.8 \pm 0.2 \text{ mW}$, respectively. Spectra were acquired by averaging from three different spots in each sample in order to improve statistical uncertainties.

The magnetic properties were measured with a Lakeshore 7300 vibrating sample magnetometer, at room temperature, with a maximum applied field of 14.5 kOe. The Curie temperature T_C was determined using a differential calorimeter SDT Q600 (TA Instruments) in N_2 atmosphere and under magnetic field, with a heating rate of 10 °C/min. TG curves of weight vs temperature were

used to determine T_C as the maximum of the derivative $d(\text{weight})/dT$.

3. Results and discussion

3.1. Composition and crystalline structure

The actual composition of the samples, determined by ICP, is listed in Table 1. It is interesting to remark that ICP are very close to nominal compositions. In this work, all the structural analyses will be performed considering the ICP values.

Fig. 1 shows the diffractograms of all the prepared samples where the main spinel reflections are indexed.

All the samples have the cubic spinel structure, matching the JCPDS-PDF 22-1086 standard. The XRD peaks indicate the presence of a single phase up to Y3, where the evidence of a very small amount of a secondary phase, indexed as yttrium orthoferrite YFeO_3 , can be noticed as a shoulder near the (311) reflection peak (Fig. 1).

All the XRD patterns were refined using the Rietveld method [16] with the aid of the Fullprof Suite software, based on a refinement using the Fd-3m space group. The Pseudo-Voigt function was used to define the peak profile and a nine-coefficient polynomial was used to fit the background. The initial model and atomic coordinates were taken from the literature. A typical X-ray diffraction pattern, along with Rietveld refined data for sample Y2 have been depicted in Fig. 2. For all the samples, the profiles of observed and calculated data perfectly match to each other and all the experimental peaks are allowed Bragg 2θ positions for the Fd-3m space group. Oxygen positions and other atomic fractional positions were taken as fixed parameters, while lattice constants, isothermal parameters, cation occupancies, scale factors and shape parameters were set as free parameters for the fitting.

The relevant parameters from the refinements, together with the reliability factors (R_{exp} , R_{wp}) and the goodness of fit (GOF) are listed in Table 2. The GOF values obtained for all the refinements (close to 1) indicate the fits are quite reliable.

The cation vacancy in B sites and the inversion parameter δ were calculated using the cationic distribution obtained with the Rietveld refinements, and are listed in Table 2, together with the cell parameters. The inversion parameter δ which is ~ 0.2 for Y0,

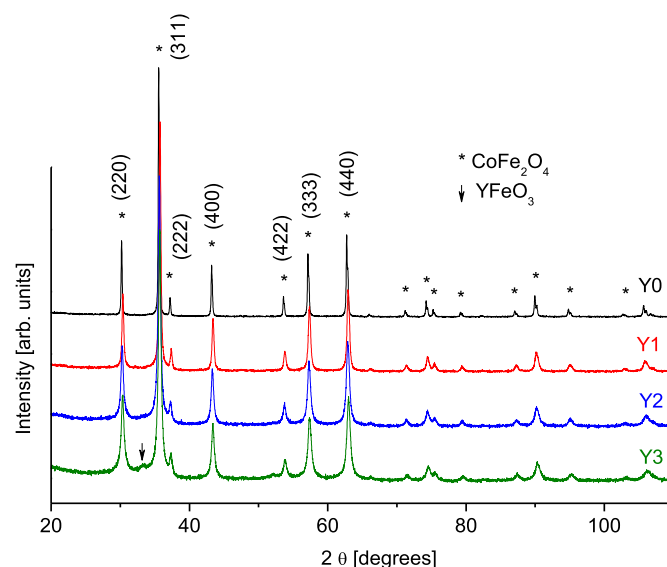


Fig. 1. X ray diffractograms of samples Y0 to Y3.

Table 1
Nominal and ICP compositions of the prepared samples.

Sample label	Y content	Nominal composition	ICP composition
Y0	0	CoFe_2O_4	CoFe_2O_4
Y1	0.1	$\text{CoFe}_{1.88}\text{Y}_{0.10}\text{O}_4$	$\text{CoFe}_{1.79}\text{Y}_{0.08}\text{O}_4$
Y2	0.2	$\text{CoFe}_{1.78}\text{Y}_{0.20}\text{O}_4$	$\text{CoFe}_{1.70}\text{Y}_{0.18}\text{O}_4$
Y3	0.3	$\text{CoFe}_{1.68}\text{Y}_{0.30}\text{O}_4$	$\text{CoFe}_{1.69}\text{Y}_{0.27}\text{O}_4$

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