The effect of Sr$^{2+}$ on the structure and magnetic properties of nanocrystalline cobalt ferrite

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We report the effect of Sr$^{2+}$ on the structure, morphology and magnetic properties of CoFe$_2$O$_4$ synthesized by microwave-assisted combustion method. Results from X-ray diffraction and Mössbauer spectroscopy at 298 K suggest the formation of a mixed spinel Sr$^{2+}$ substituted CoFe$_2$O$_4$. However, secondary phases like CoO, SrCO$_3$ and SrFeO$_{2.96}$ were also observed. A decrease in the lattice parameter and particle size were observed with the addition of Sr$^{2+}$. The crystallite size of ferrite phase ranged from 53 to 62 nm. Magnetic studies showed a gradual decrease in the saturation magnetization and remanence with the increase of Sr$^{2+}$ content, and an increasing value of the coercive field.

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1. Introduction

CoFe$_2$O$_4$ is magnetic material with high coercivity field ($H_c$), moderate saturation magnetization ($M_s$), excellent chemical stability and mechanical hardness [1–3], which makes it a potential candidate for many technological applications such as magneto-hyperthermia, magnetic drug delivery, information storage among others [4–6]. The unit cell of spinel ferrite consists of cubic closed packed arrangement of oxygen with 64 tetrahedral (A-site) and 32 octahedral (B-site) interstitial sites, being only 8 A-sites and 16 B-sites occupied by the metal cations. This large amount of empty sites allow the migration of cations between interstitial sites during synthesis. Their physical and chemical properties depend strongly on their composition, structure, shape and particle size, which are affected by the processing method and thermal treatment [7]. The magnetic properties of these materials can be modified by replacing ions located at A and/or B sites [8,9]. The substitution with non-magnetic ions is particularly interesting. For example, Kumar and coworkers synthesized a mixed spinel La$^{3+}$ substituted CoFe$_2$O$_4$ nanoparticles by a citrate method [9] and observed that crystallite size, magnetocrystalline anisotropy, $M_s$ and $H_c$ decreased with the increase of La$^{3+}$ concentration. The authors concluded that La$^{3+}$ have preference for B sites and because lanthanum have zero magnetic moment do not participate in the A–B intersite superexchange, therefore, affecting the magnetic properties.

Similar results were found in Ca$^{2+}$ doped CoFe$_2$O$_4$ [10], the authors concluded that the decrease in anisotropy constant is a consequence of decreasing the exchange interaction of Co$^{2+}$ by the addition of nonmagnetic Ca$^{2+}$.

CoFe$_2$O$_4$ nanoparticles have been prepared by several methods including sol–gel [11], thermal decomposition [12], coprecipitation [13], emulsion [14], hydrothermal [15] and combustion [16]. Among these methods, auto combustion reaction has attracted considerable attention due to its convenient processing, simple experimental setup, significant saving in time and energy, and homogeneous products [16].

After reviewing the literature, we noted that there is not any work on Sr$^{2+}$ substituted CoFe$_2$O$_4$ and we believe that it is interesting to study its influence on the structure, morphology and magnetic properties of the CoFe$_2$O$_4$ phase. Thus, we report the synthesis of nanocrystalline CoFe$_2$O$_4$ doped with Sr$^{2+}$ prepared by microwave-assisted combustion method.

2. Experimental

Synthesis of magnetic ferrites: Nanocrystalline Sr$^{2+}$:CoFe$_2$O$_4$ ferrites were prepared using Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O as oxidizing agents and CO(NH$_2$)$_2$ as fuel. Stoichiometric amounts of nitrates and urea were determined based on the total oxidizing and reducing valences of the components, according to the concepts of propellant chemistry [17]. The samples with Sr/Co nominal molar ratio equal to 0, 0.11, 0.42 and 1.0 were named CF,
CF510, CF530 and CF550, respectively. For the synthesis, a small amount of distilled water at 70 °C was used to mix the reagents. In microwave oven, the solution is boiled and its decomposition occurred with copious emission of gases (N₂, NO₂, CO₂). When the ignition temperature was reached, it began to burn and release a great deal of heat producing a brown powder. The time interval for complete combustion process was about 15 min.

Materials characterization: The samples were characterized by X-ray diffraction (XRD) using a Mini Flex RIGAKU diffractometer and Cu Ka radiation. The XRD patterns were refined by the Rietveld method using the program MAUD. The crystallite size was determined by using the Debye–Scherer formula [18]. The morphology of the powders was analyzed on a Philips XL 30 digital scanning microscope. Mössbauer spectra were recorded at room temperature using a spectrometer from Wiessel with a 57Co:Rh source and activity of 25 mCi. Magnetic measurements were performed at 298 K in a homemade vibrating sample magnetometer (VSM).

3. Results and discussion

The XRD patterns of Sr²⁺:CoFe₂O₄ samples are shown in Fig. 1. Characteristics reflections of CoFe₂O₄ spinel structure (98553-ICSD) was observed. We noticed also the presence of cobalt monoxide (CoO, 9865-ICSD), strontium carbonate (SrCO₃, 166088-ICSD) and strontium ferrite (SrFeO₂.96, 172016-ICSD) phases which are paramagnetic at 298 K [19,20]. The Sr related secondary phases increased with the dopant concentration. The crystallite sizes of the pure cobalt ferrite (CF) was 62 nm and for Sr doped CoFe₂O₄ samples were: 53 nm (CF510), 58 nm (CF530) and 55 nm (CF550). Their lattice parameters were 8.3816 Å (CF), 8.3812 Å (CF510), 8.3787 Å (CF530) and 8.3776 Å (CF550). The decrease in lattice parameter is due to the transfer of Co²⁺ from octahedral sites to tetrahedral sites because of the increased concentration of the Sr²⁺ in octahedral sites. Excess of Sr accumulates at the grain boundaries as secondary phases, these phases may suppress the grain growth [21]. Kumar and coworkers have reported that when some Fe³⁺ are substituted by La³⁺ in CoFe₂O₄, the lattice parameters may increase or decrease depending upon two effects, the large size of La³⁺ tries to increase the lattice parameter and the strain produced by its substitution in the cell, tries to decrease it [10].

Fig. 2 shows the morphology of the CF550 sample. The picture reveals agglomerates of particles and its surface shows large pores formed by the escaping gases during the combustion reaction. The particles in the agglomerates are smaller than 100 nm corroborating the results from the XRD data.

Mössbauer spectra (MS) are shown in Fig. 3a, each spectrum exhibit four subspectra. Two sextets related to Fe³⁺ in the octahedral (site 1) and tetrahedral (site 2) sites of the CoFe₂O₄ phase and two paramagnetic components assigned to SrFeO₂.96 phase [22]. The doublet (site 4) and singlet (site 3) are related to Fe³⁺ and Fe⁴⁺ occupying octahedral sites in perovskite phase, respectively. Table 1 shows the hyperfine parameters obtained from the fits. The ratio of the relative absorption area (RAA) between site 1 and site 2 reveals values of 3.8 (CF510), 5.5 (CF530) and 5.5 (CF550). These results indicate that doping with Sr favors the Fe octahedral occupancy. In CoFe₂O₄, most of Co²⁺ reside on octahedral sites and a small fraction of these ions goes to tetrahedral sites. When Sr²⁺ are introduced into octahedral sites, the Co²⁺ migrate to tetrahedral sites. These Co²⁺ force equal amount of Fe³⁺ migrate to octahedral sites, therefore, decreasing the RAA in site 2. The SrFeO₂.96 phase showed similar total RAA of ~29% for samples CF530 and CF550, being this value larger than the one for sample CF510. From the XRD and MS analysis we may conclude that excess of Sr allows the formation of the SrCO₃ and SrFeO₂.96 phases.

The hysteresis loops for all samples (Fig. 3b) exhibited ferromagnetic behavior. Their magnetic parameters are shown in Table 1. The hysteresis loops for samples CF530 and CF550 have remanence ratio (Mr/Mrₘ) of 0.47 which is very close to the value of 0.5 predicted for uniaxial randomly oriented noninteracting single-domain particles [23]. Sample CF510 has Mr/Mrₘ = 0.38 which can be attributed to an interacting magnetic system [23]. These results seem to indicate that for Sr concentrations above 10%, the paramagnetic secondary phases promote an array of magnetically isolated ferrite nanoparticles. It is observed an increase of Hc with the Sr concentration, followed by a decrease in Mr and Ms. MS showed that the concentration of the SrFeO₂.96 phase increased, reaching a maximum value for samples CF530 and CF550. Thus, we can conclude that the smaller Mr value for samples CF530 and CF550 is related to the mass of the secondary phases, and to spin disorder at the surfaces of nanoparticles. In

![Fig. 1. XRD patterns of Sr²⁺:CoFe₂O₄ ferrites.](image1)

![Fig. 2. SEM image of CF50 sample.](image2)
Hhf is the hyperfine magnetic field. Δ is the quadrupole shift; δ is the isomer shift.

CoFe₂O₄, the particle size to form a multidomain system is about 70 nm [24]. CoFe₂O₄ crystallites exceeding this size will have very reduced \( H_c \) values. Recent studies have reported coercivity field values up to 1.2 kOe for CoFe₂O₄ particles with sizes ranging from 25 to 30 nm, and very small values above 45 nm [25]. In our samples, the \( H_c \) values are about 1.7 kOe. The high \( H_c \) value may be related to pinning of the magnetic moments at the interfaces. In fact, similar results were found in an ensemble of 40 nm size CoFe₂O₄ nanoparticles, the results indicated that even at this size scale, single domain magnetic structures are not achieved possibly due to the existence of dominant pinning sites [26].

4. Conclusions

In summary, we have prepared nanocrystalline \( \text{Sr}^{2+} \cdot \text{CoFe}_2\text{O}_4 \) ferrites by microwave-assisted combustion method, and the structure, morphology and magnetic properties were examined using different techniques. The XRD analysis showed the formation of a \( \text{Sr}^{2+} \)-substituted \( \text{CoFe}_{2}\text{O}_4 \) phase, where the lattice parameter decreased with increasing the strontium concentration. Mossbauer spectra revealed that for the cobalt ferrite phase, \( \text{Sr}^{2+} \) goes mainly to octahedral sites. However, the excess of \( \text{Sr}^{2+} \) favors the production of \( \text{SrCO}_3 \) and \( \text{SrFeO}_{2.96} \) paramagnetic phases. The magnetic measurements showed that when the strontium concentration is increased, the \( M_r \) and \( M_i \) decreases followed by an increase of \( H_c \). All samples in this study showed secondary phases, these results seem to indicate that strontium has low solubility in the \( \text{CoFe}_2\text{O}_4 \) phase.

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