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COBALT FERRITIC NANOPARTICLES OBTAINED BY CHEMICAL COPRECIPITATION AND HYDROTHERMAL METHODS

M. Bradiceanu[1], P. Vlazan[1], S. Novaconi[1], I. Grozescu[1], P. Barvinschi[2]

[1]*National Research & Development Institute for Electrochemistry and Condensed Matter, Timisoara , Romania.*

[2]*West University of Timisoara, Faculty of Physics, nr.4, V. Parvan Blvd., Timisoara, Romania*

Abstract
Cobalt ferrite ($Co_xFe_{3-x}O_4$) is a cubic ferrite with inverse spinel nanodimensional structure, particles being very special ones due their magnetically interesting properties. Cobalt ferrite nanopowders were produced using the chemical coprecipitation, an economical synthesis way for ultrafine $Co_xFe_{3-x}O_4$ of different compositions (where X = 0.25, 0.5, 0.8, 1.0) and sizes (4-10nm) and hydrothermal method. The powders were characterized by XRD measurements. The main advantage of these two synthesis methods consist in dimensional control of the particle dimensions and form according to the desired magnetic properties. Beside the hydrothermal way provides a higher degree of crystallinity, larger particles and most pronounced magnetic properties.
Keywords: cobalt ferrite, chemical coprecipitation, hydrothermal.

1. Introduction

The best permanent magnets contain a substantial quantity of cobalt. Such permanent magnets are represented by cobalt ferrites. Cobalt ferrites are spinels and have the formula $M_xFe_{3-x}O_4$ where M is (Co^{2+}) divalent cation cobalt. The oxygen anions, O^{2-} adopt a close packed cubic crystal structure and the metal cations occupy the interstices in an unusual two lattice arrangement. In each unit cell, containing 32 oxygen anions, 8 cations are coordinated by 4 oxygens (tetrahedral sites), and 16 cations are coordinated by 6 oxygen (octahedral sites). The incorporation of cobalt ions results in an increase in saturation magnetization and in coercivity. Cobalt ferrites have high permeability and saturation magnetization, a high anisotropy and electrically insulating [1].

The methods widely used for the synthesis of magnetic cobalt ferrite are: coprecipitation, hydrothermal, reverse micelles, freeze-drying, spray roasting, and sol-gel processing [2]. In the present paper we describe the synthesis of cobalt ferrites by chemical coprecipitation and hydrothermal methods. The powders obtained are characterized by XRD diffraction, the hydrothermal synthesis pattern providing cobalt ferrite nanoparticles with better characteristics.

2. Method and samples

Chemical coprecipitation

The coprecipitation method was widely used to synthesize iron oxides. To obtain cobalt-ferrite nanoparticles $Co_xFe_{3-x}O_4$ of different compositions (where X = 0.25, 0.5, 0.8, 1.0), the next precursors were used: aqueous solutions of Fe $(NO_3)_6 \cdot 9H_2O$ and Co $(NO_3)_2 \cdot 6H_2O$, mixed in stoichiometric proportion. Sodium Dodecile Sulfate was added then to obtain the micelle solution. The obtaining mixture was heated between 50 - 80°C by a magnetic stirring provided with heating. The mixture pH was brought at values between 9.5 and 11 with NaOH 10% solution, the synthesis temperature being maintained at 70-95°C for 4-5 hours under vigorous magnetic agitation. The separation of particles was performed by decantation and filtration, then were washed with acetone on filter (paper) by 5-6 times and dried in an air oven at 60°C for 2 hours.

Hydrothermal synthesis

Cobalt ferrite has been synthesized too using hydrothermal method that provides different classes of nanostructurated anorganic materials from aquaeous solutions, by means of small Teflon autoclaves. The synthesis conditions of $Co_xFe_{3-x}O_4$ nanoparticles are: the temperature up to 200°C and the pressure up to 100bars. These pressure - temperature conditions facilitate the use of autoclaveas with a simple structure that favours uniform particle obtaining. The synthesis precursors are: Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), Cobalt nitrate($Co(NO_3)_2 \cdot 6H_2O$) and Dodecile Sulfate ($C_{12}H_{25}SO_4Na$) – 0.3 moles; for the Co concentration (X) in the $Co_xFe_{3-x}O_4$ sample we choosed various values: X = 0.25, 0.5, 0.8, 1.0. The reactants concentration is the same in hydrothermal and chemical coprecipitation methods. The experimental procedure consists in obtaining of precursor solutions with eligible concentration and mixing them under continuous agitation in order to obtain then a homogeneous solution that will be introduced in an autoclave. The autoclavation process takes place at 140-200^{0}C for 4-5 hours. After that the precipitate was separated by filtration and dried in oven at 80^{0}C, obtaining a powder characterized by X ray diffraction.

3. Results and discussion

XRD spectra proper to $Co_xFe_{3-x}O_4$ particles, where X= 0.25, 0.50, 0.80 and 1.00 represents the Co concentration in the above mentioned sample, obtained by chemical coprecipitation method provide data regarding the degree of crystallinity and particle size (Figure 1). The peaks are not very high and broad, fact that implies a lower degree of

crystallinity and small size of the cobalt ferrite nanoparticles (4-10nm) respectively. Increasing the value of cobalt concentration in the sample, the peaks are higher and tighter. The best result is obtained for the sample number 4, when the cobalt concentration is X =1. Higher peaks indicate a better degree of crystallization, and a narrow, tight peak indicates particles with a larger size.

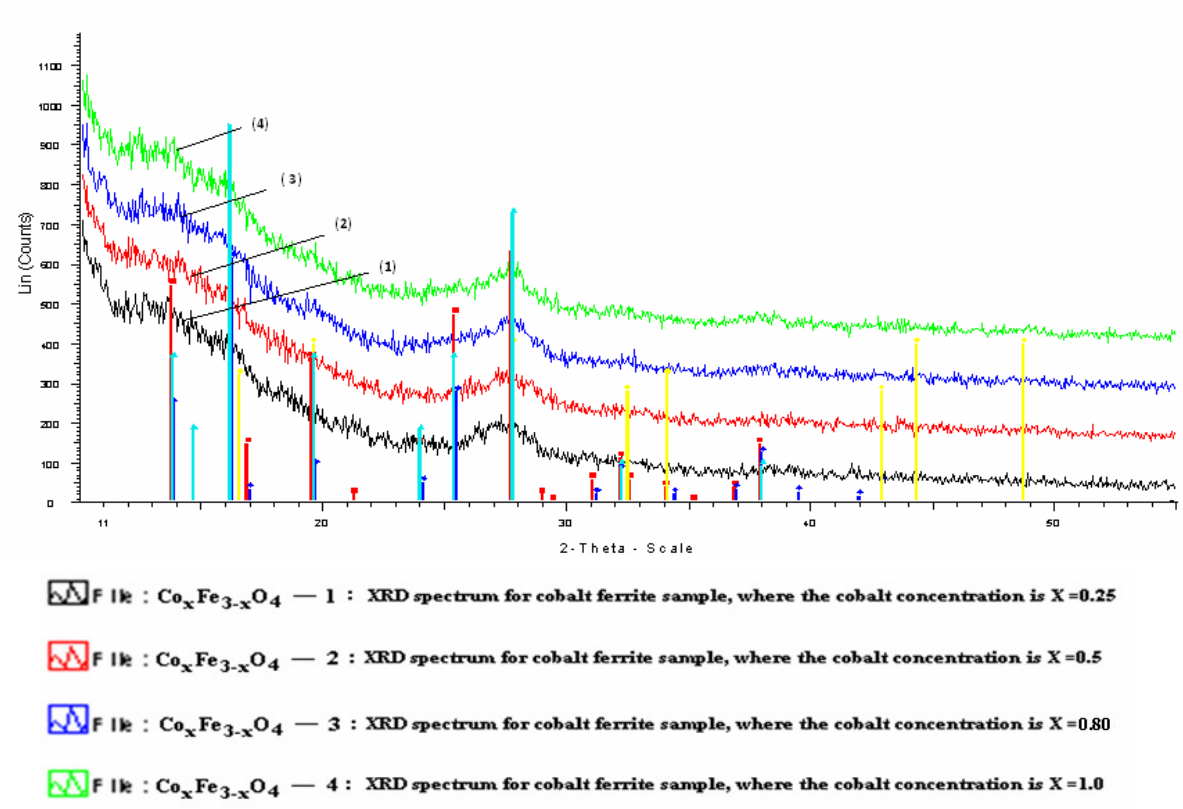

Figure 1: X-ray diffraction patterns of cobalt ferrite $Co_xFe_{3-x}O_4$ with various concentrations of Co (X=0.25, 0.50, 0.80, 1.00) prepared by chemical coprecipitation method.

The peaks in diffraction pattern indicate the cobalt ferrite crystallization plans. Although the synthesis temperature is low, up to 200°C, by chemical coprecipitation it is possible to obtain nanoparticles of $Co_xFe_{3-x}O_4$ with desirable form and size.

Particle's size represents the substance performance critical factor in monodisperse nanoparticles magnetic activity.

Figure 2 provides the XRD spectra of cobalt ferrite powder obtained by hydrothermal method. The four spectra are plotted for the four values X=0.25, 0.50, 0.80 and 1.00 of Co concentrations in $Co_xFe_{3-x}O_4$ sample. We can observe better results, namely a higher degree of crystallinity due higher diffraction peaks than coprecipitation specific ones, larger particles and also much pronounced magnetic properties.

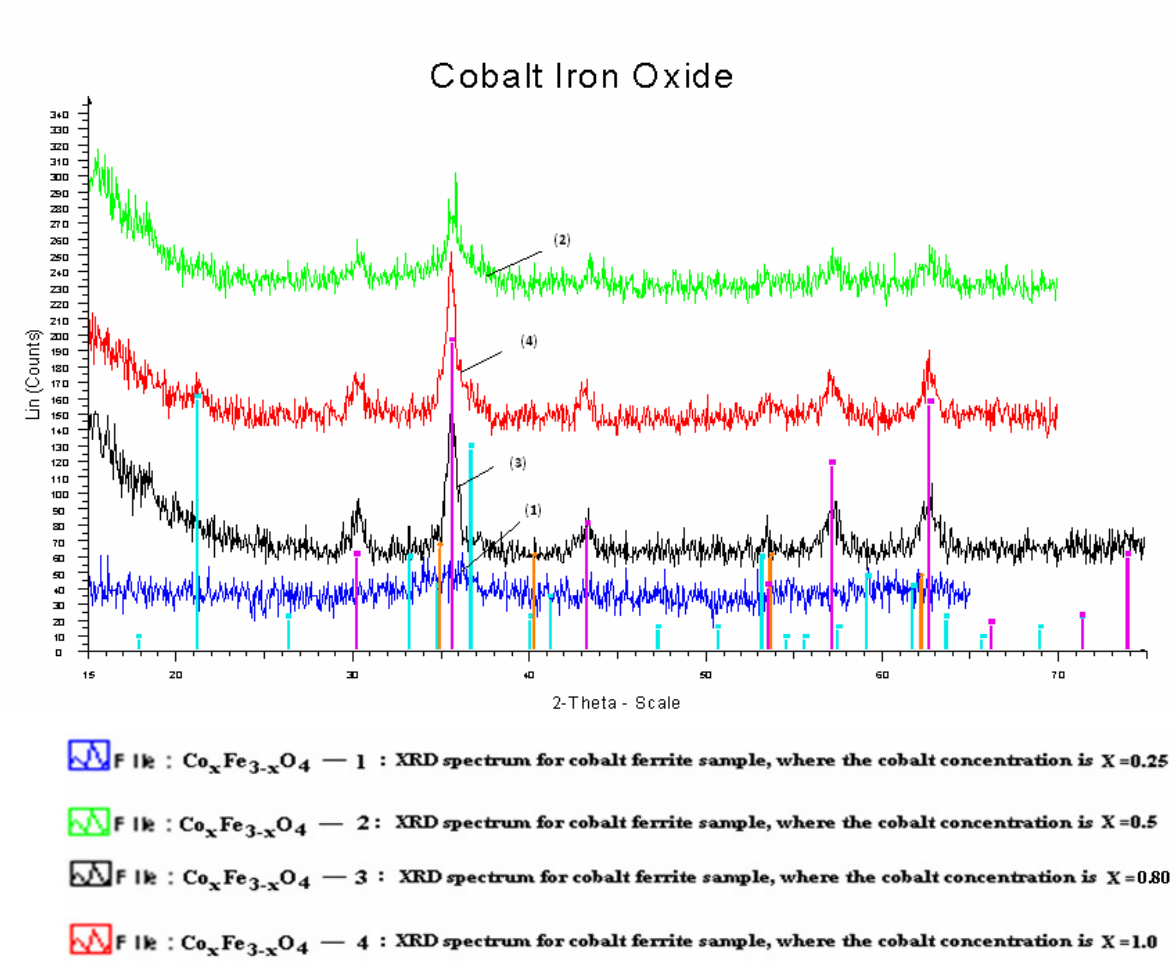

Figure 2: X-ray diffraction patterns of cobalt ferrite $Co_xFe_{3-x}O_4$ with various concentrations of Co (X=0.25, 0.50, 0.80, 1.00) prepared by hydrothermal method.

The peaks are narrow, suggesting larger nanoparticles (40-50nm) of $Co_xFe_{3-x}O_4$ sample. Increasing the Co concentration we obtain higher and tighter peaks, indicating a higher crystallinity and larger particles. Thus the best result is acquired for X=1. The most important attribute of hydrothermal synthesis consists in reduction of particle agglomeration attended to narrow size distribution. In conclusion the hydrothermal method has benefits such as: a clean product with high degree of crystallinity at a relative low reaction temperature (up to 200ºC), form and dimension size controll and also monodispersed particles.

4. Conclusions

We synthetized cobalt ferrite nanopowders by chemical coprecipitation and hydrothermal methods, using in both cases the same reactant concentrations. Obtaining of a single phase asks for an adequate selection of pH value, reaction medium, synthesis time and

crystallization temperature. The height and the width of XRD peaks indicate the degree of crystallization and particle size specific to $Co_xFe_{3-x}O_4$ sample respectively.

By chemical coprecipitation synthesis method, the obtained powder is not very well crystallized (not very high diffraction peaks in diffraction pattern), with small particle sizes.

Instead, using the same precursors, pH and temperature values, by hydrothermal method we obtained cobalt ferrite nanoparticles with a higher degree of crystallinity as result from XRD patterns, larger particles and much pronounced magnetic properties.

Acknowledgement

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