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The Influence of chemical composition on magnetic properties and magnetostriction coefficient of cobalt ferrites

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Four series of cobalt ferrites were prepared by conventional ceramic method. Calcined powders were analyzed by X-ray diffraction and Mössbauer spectroscopy to characterize the crystal structure. Green bodies were sinterized at temperatures between 1250°-1300°C, in air, for 5 hours. Chemical composition of samples and sintering parameters have a strong influence on the magnetic and magnetostrictive properties of the sintering bodies.

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1. Introduction

In the last two decades cobalt ferrite was intensely studied thanks to magnetostriction properties useful for applications in the automotive industry, as magnetostrictive sensors [1-4].

The advantages of oxidic magnetic materials employment in magnetostrictive sensors consist in lower costs as compared to metal alloys, and absence of eddy currents caused by the high resistivity of oxides.

The cobalt ferrite displays the structure of a reverse spinel:

$$(Fe)\ [CoFe]\ O_4$$

where the round brackets stand for tetrahedral position ions, and the square brackets stand for the octahedral position ions of the crystalline lattice [5].

Cobalt ferrite, as all the simple spinels, allows the formation of solid solution series. The major advantage of these solutions consists in the continuous variation of their physical properties as a function of their composition. The formation of spinelic solid solutions implies the substitution of the bivalent cation with another bivalent one, or a combination of cations to insure the electrical neutrality of the ensemble. The kind of placement of the substituting ions in tetrahedral or octahedral sites of the spinel lattices is due to causes like: the ionic radius, the charge and electronic configuration of the cation [6].

The present study aims at showing the correlation between chemical composition, microstructural and magnetic properties of cobalt ferrites sintered at different temperatures. Four categories of samples were considered: stoichiometric cobalt ferrite, cobalt ferrite with excess of iron, cobalt ferrite with manganese and cobalt ferrite with silicon substitutions.

2. Experimental

Cobalt ferrite samples with different chemical compositions were synthesized using the high-temperature ceramic method [7].

The starting materials were added in, depending on their active substance contents and chemical formula of the desired ferrites, then wet (distilled water) mixed in a steel ball mill for 8 hours. After oven drying, the mixtures were calcined, as shown in Table 1. The so calcined material was wet milled without any additive in ball mills for 16 hours. The calcination and milling were repeated in the same conditions in order to insure the homogeneity of the ferrite powders.

The ferrites powders were investigated by XRD and Mössbauer spectroscopy. XRD measurements were performed in order to understanding the crystalline phase and to provide the lattice parameters. XRD data were collected with a DRON X-ray diffraction meter linked to a data acquisition card and processing facility. Cu *Kα* radiation ($\lambda = 1.540598$ Å) and a graphite mono-chromator have been used.

The ^{57}Fe Mössbauer spectra were recorded at room temperature using a 15 mCi ^{57}Co-Fe source and a conventional constant-acceleration spectrometer (Promeda type equipment) in transmission geometry. The velocity was calibrated by α-Fe at room temperature. Lorentzian line shapes were used to the fit the Mossbauer spectra recorded. All isomer shifts are given relative to that of α-Fe at room temperature.

Table1. Cobalt ferrites with substitutions prepared by conventional ceramic method

Chemical composition of samples	Starting materials	First calcination	Second calcination
$CoFe_2O_4$	α-Fe_2O_3 Riedel de Haen (>99% Fe_2O_3) Co_3O_4 BDH (>99Co_3O_4)	900°C 5h, air	900°C 5h, air
$Co_{0.8}Fe_{2.2}O_{4+\delta}$	α-Fe_2O_3 Riedel de Haen (>99% Fe_2O_3) Co_3O_4 BDH (>99Co_3O_4)	900°C 5h, air	900°C 5h, air
$CoFe_{1.8}Mn_{0.2}O_4$	α-Fe_2O_3 Riedel de Haen (>99% Fe_2O_3) Co_3O_4 BDH (>99Co_3O_4) $MnCO_3$ Riedel de Haen (54%MnO)	950°C 5h, air	950°C 5h, air
$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	α-Fe_2O_3 Riedel de Haen (>99% Fe_2O_3) Co_3O_4 BDH (>99Co_3O_4) SiO_2 p.a.(>99% SiO_2)	950°C 5h, air	950°C 5h, air

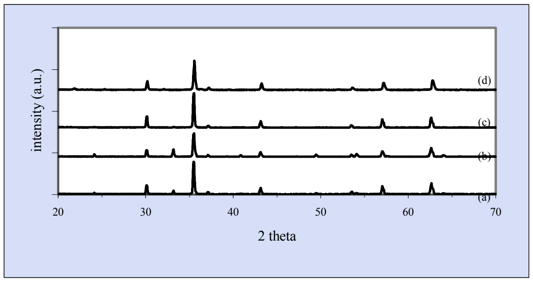


Fig.1. X-ray diffraction spectra of: a) $CoFe_2O_4$; b) $Co_{0.8}Fe_{2.2}O_{4+\delta}$; c) $CoFe_{1.8}Mn_{0.2}O_4$; d) $Co_{1.3}Si_{0.3}Fe_{1.4}O_4$, after the second calcinations and fine-divided.

The fine-divided ferrite powders were pressed into ring core (outer diameter, inner diameter and thickness of 17, 11 and 5mm respectively) and cylindrical (diameter of 11mm and height of 5mm) shapes. The green density of the specimens was 2.8+/-0.2g.cm^{-3}. Successive sets of specimens were sintered in a box furnace, in air, for 5 hours at temperatures between 1250° – 1300°C. The cooling rate was 100°C/h.

Microstructure analysis on fractured surface of sintered samples was performed using a VEGA II Tescan surface electron microscope.

The magnetic properties were measured by means of a home made vibration magnetometer. From the hysteresis loops, recorded in 200 measurement points, was deduced and plotted the maximum magnetization, remanence magnetization and coercitive field values. The measurements were done in perpendicular and parallel directions to the pressing axis.

3. Results and Discussion

3.1. Characterization of calcined ferrite powders

The X-ray diffractograms of the reaction mixtures after pre-sintering treatments are shown in Fig. 1.

Refinement the X-ray diffraction data show that samples are mainly composed of spinel phase (Table 2). Only sample $Co_{1.3}Si_{0.3}Fe_{1.4}O_4$ is mono-phase system, the other samples studied are two-phase system, commonly obtained when using conventional high-temperature technique to get spinel ferrites [8]. Lattice parameters of studied samples are smaller than theoretical value for $CoFe_2O_4$ of 8.38A [6, 8], with the exception of $CoFe_{1.8}Mn_{0.2}O_4$ sample.

Table 2. Data from X-ray diffraction patterns of calcined cobalt ferrites

Sample	H_1					H_2				
	H (KOe)	Δ (mm/s)	IS (mm/s)	W (mm/s)	A %	H (KOe)	Δ (mm/s)	IS (mm/s)	W (mm/s)	A %
$CoFe_2O_4$	503,3	0,042	0,398	0,42	53,6	481,4	0,069	0,305	0.39	46,4
$Co_{0.8}Fe_{2.2}O_{4+\delta}$	502,7	-0,003	0,423	0,41	64,5	483,0	0,128	0,263	0,40	35,4
$CoFe_{1.8}Mn_{0.2}O_4$	504,9	0,096	0,395	0,38	31,6	482,3	0,046	0,35	0,43	68,4
$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	501,4	0,080	0,383	0,35	17,8	474,3	0,068	0,323	0,46	55,7

Table 3 Data from Mössbauer spectra patterns of cobalt ferrites samples

Sample	Unit cell lengths a_o (Å)	d_{RX} (g/cm^3)	Phase determined (%)
$CoFe_2O_4$	8.3742	5.30	86.90 spinel, 13.10 hematite
$Co_{0.8}Fe_{2.2}O_{4+\delta}$	8.3786	5.32	67.10 spinel, 32.90 hematite
$CoFe_{1.8}Mn_{0.2}O_4$	8.3820	5.29	97.90 spinel, 2.10 hematite
$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	8.3533	5.18	100.00 spinel

Note: H is hyperfine magnetic field at Fe nucleus; H_1 corresponds to Fe atoms in octhahedral positions in the spinel structure; H_2 corresponds to Fe atoms in tetrahedral positions in spinel structure; Δ is the quadripole splitting, and shows the presence of the electric field gradient to Fe nucleus; IS is the isomer shift, function of changes in electron density at the nucleus; W is the half-width of the resonance absorption line; A is the relative area of a sub-spectrum.

Table 4. Physical and magnetic properties of samples sintered in various conditions

Sintering Parameters	Sample	d (g/cm^3)	P (%)	M_{max} (emu/g)	M_r (emu/g)	H_c (Oe)	H (Oe)	$d\lambda_{II}/dH$ (x10^{-3} Oe^{-1})
1250°C 5h air	$CoFe_2O_4$	3.98	24.90	59.8	13	918	6120	57
	$Co_{0.8}Fe_{2.2}O_{4+\delta}$	4.20	21.05	37.4	9.86	773	6415	26
	$CoFe_{1.8}Mn_{0.2}O_4$	4.54	14.77	65.9	9.45	442	3760	41
	$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	4.68	9.65	70	7.08	200		
1275°C 5h air	$CoFe_2O_4$	4.20	20.75	59.4	12.1	767	5907	51
	$Co_{0.8}Fe_{2.2}O_{4+\delta}$	4.32	18.79	44.8	12.8	625	6570	16
	$CoFe_{1.8}Mn_{0.2}O_4$	4.60	13.05	65.6	8.39	378	4410	57
	$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	4.71	9.07	69.9	5.42	161	1165	39
1300°C 5h	$CoFe_2O_4$	4.29	19.05	57	12.7	774	5340	51
	$Co_{0.8}Fe_{2.2}O_{4+\delta}$	4.20	19.36	42	11.6	625	7122	18
	$CoFe_{1.8}Mn_{0.2}O_4$	4.61	12.85	63	8.3	374	4085	64
	$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	4,78	7.72	60	4.2	160	856	38

The X-ray densities, d_{RX}, were calculated by relationship:

$$d_{RX} = 8M / N\, a_o^3$$

where M is molecular mass and N is Avogadro number [9].

The Mössbauer spectra of the fine-divided ferrite powders were done on samples having the thickness ~7 mg Fe/cm^2. The experimental data was fitted and the corresponding hyperfine parameters are shown in Table 3.

The data obtained from the analysis of the Mössbauer spectra lead to the conclusion that iron is present in the Fe^{3+} oxidation state, according to the isomer shift values. The iron excess in sample $Co_{0.8}Fe_{2.2}O_{4+\delta}$ is preferentially found in the octahedral positions of the spinel lattice.

The decrease of the magnetic sub-lattices magnetic fields due to the substitution of iron by manganese in the $CoFe_{1.8}Mn_{0.2}O_4$ sample is lower than reported in the literature [10,11]. The Manganese ions preferentially substitute iron in the octahedral positions because Fe^{3+} has the higher preference for the tetrahedral positions, as compared to the Co^{2+} and Mn^{3+} cations.

Silicon employment as a substitute in sample $Co_{1.3}Si_{0.3}Fe_{1.4}O_4$ caused the weakening of the magnetic field corresponding to the tetrahedral position iron, and the occurrence of a new sub-lattice having the following parameters: H= 456,8; Δ=-0,68; IS= 0,482; W=0,51. The silicon ions preferentially substitute Fe^{3+} from the octahedral positions.

3.2. Characterization of the sintered body ferrites

The physical properties (density, d and porosity, P) and magnetic and magnetostriction coefficient as a function of sintering parameters of sintered bodies are given in Table 4.

Porosity was calculated by relationship:

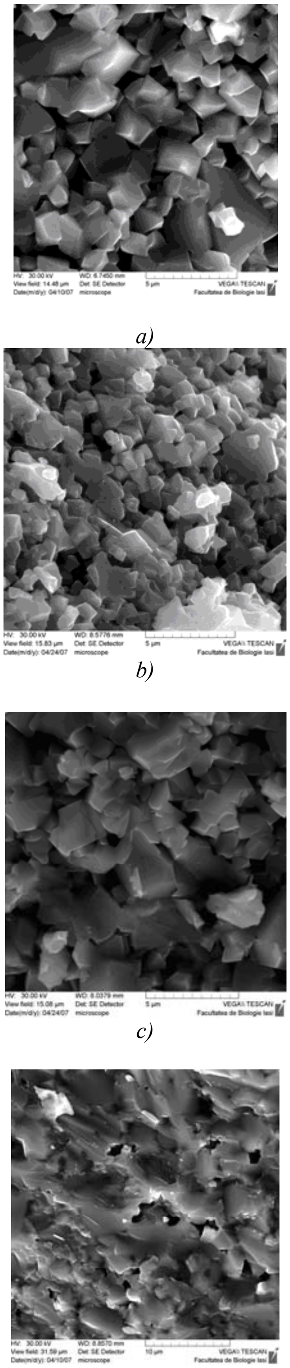
$$P = 100\,[1-(d_{\text{sintered core}} / d_{RX})]\ (\%)$$

Comparatively with $CoFe_2O_4$ sample, silicon substituted cobalt ferrite show a very good densification, highest specific magnetization, lowest coercive field, but a low magnetostriction coefficient. Substitution with manganese, kept high values of specific magnetization and high value of the magnetostriction coefficient, at the same time the coercive field considerably drops.

Rich iron cobalt ferrite show smallest value of magnetostriction. The slope of the magnetostriction curve in the low field region was increased by small amount of manganese ions.

Based on analysis of experimental results from Table 4 it can be concluded that the samples with compositions $CoFe_2O_4$ and $CoFe_{1.8}Mn_{0.2}O_4$ show adequate magnetic and magnetostrictive properties enable to preferred application.

The properties of the ferrite cores are determined essentially by their microstructure, as shown in Fig. 2.



a)

b)

c)

d)

Fig.2 SEM microphotographs of bodies sintered for 5 hours at 1275^{o}C, in air: a) $CoFe_2\ O_4$ sample; b) $Co_{0.8}Fe_{2.2}O_{4+\delta}$ sample; c) $CoFe_{1.8}Mn_{0.2}O_4$ sample d) $Co_{1.3}Si_{0.3}Fe_{1.4}O_4$ sample.

The sample $CoFe_2O_4$ displays a microstructure with relatively uniform grains, with open porosity. The sample $Co_{0.8}Fe_{2.2}O_{4+\delta}$ displays a microstructure with relatively fine grains and a narrow dispersion of sizes. The microstructure of $CoFe_{1.8}Mn_{0.2}O_4$ sample is similar with the microstructure of $CoFe_2O_4$ sample. The sample $Co_{1.3}Si_{0.3}Fe_{1.4}O_4$ displays a abnormal grain growth type microstructure including both giant and very small grains, with a few pores located inside the grains. This behavior can be explain by forming of a eutectic between FeO, (developed at sintering temperatures) and SiO_2. The compound Fe_2SiO_4 have melting point at <1200^{o}C [12].

4. Conclusions

Cobalt ferrites studied in this paper demonstrate the sensitivity of magnetic and magnetostriction properties on the chemical composition and the parameters of sintering process. Samples with compositions $CoFe_2\ O_4$ and $CoFe_{1.8}Mn_{0.2}O_4$ have the best ensemble of magnetic and magnetostrictive properties, useful for applications as sensors.

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