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The synthesis of doped manganese cobalt ferrites by auto combustion technique

M. N. PALAMARU[a], A.R. IORDAN[a], C. D. ARUXANDEI[a], I. A. GORODEA[a], E. A. PERIANU[a] I. DUMITRU[a]
M. FEDER[b], O. F. CALTUN[a*]
[a]*"Alexandru Ioan Cuza" University, Faculty of Physics, Department of Solid State and Theoretical Physics, 700506, Iasi, Romania*
[b]*National Institute o Material Physics, 077125, Bucharest, Romania*

$CoMn_xFe_{2-x}O_4$ with x = 0; 0.10; 0.25; 0.40; 0.60 and 2.0 were prepared by low temperature combustion method. The samples were investigated using X-ray diffraction analysis at room temperature. All the synthesized samples exhibited XRD patterns specific for cubic spinel phase with a space group Fd3m. Infrared spectroscopic analysis, using KBr pellets in the range 400 - 4000 cm^{-1} was carried out using a FTIR 600Plus Fourier transform infrared spectrometer. The magnetic properties of samples have been characterized at room temperature using a vibrating sample magnetometer, the magnetic properties measurements demonstrate an increase of the saturation magnetization with the increase of Mn content.

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1. Introduction

Spinels of the type $M^{2+}M^{3+}_2O_4$ attract great deal of interest because of their diverse applications [1]. In the case when M^{2+} is Fe, the resulting spinel ferrites having a general chemical composition of MFe_2O_4 (M= Mn, Mg, Zn, Ni, Co) are among the most widely used magnetic materials [2]. The spinel structure is essentially cubic, with the O - ions forming a fcc lattice. The cations (usually metals) occupy 1/8 of the tetrahedral sites and 1/2 of the octahedral sites and there are 32 O-ions in the unit cell.

In a normal spinel the M^{2+} cations occupy tetrahedral sites and Fe^{3+} cations occupy octahedral sites, whereas in an inverse spinel only half of the Fe^{3+} ions occupy tetrahedral sites. Actually, most spinel ferrites adopt a structure somewhere between these two extremes so the structural formula is usually written as: $(M^{2+}_{1-c}Fe^{3+}_c)$ $[M^{2+}_cFe^{3+}_{2-c}]$ $\{O^{2-}\}_4$ where the round and square brackets denote (A) and (B) sites respectively and *c* represents the degree of inversion. The properties of the spinel ferrites materials depends on its microstructure that is sensitive to the preparation method which can play a very important role in defining of the chemical structural and magnetic properties of a spinel ferrite.

Inverse spinel cobalt ferrite $CoFe_2O_4$ has been paid a great deal of attention for its applications such as high-density magnetic and magneto-optic recording media. $CoFe_2O_4$ is known as an inverse spinel exhibiting ferrimagnetism below 793 K [3]. The octahedral Co^{2+} (d^7) ions in $CoFe_2O_4$ are in the high spin state and the tetrahedral in the octahedral Fe^{3+} (d^5) ions are in the high spin state with the spin directions antiparallel to each other.

In the present work the effects of Mn doping on the structural and magnetic properties of $CoFe_2O_4$ have been investigated. Spinel compounds $CoMn_xFe_{2-x}O_4$ (x = 0; 0.10; 0.25; 0.40; 0.60; and 2.0) were prepared by citrate gel process and chracterized by X-ray diffraction (XRD), infrared spectra (IR) and vibrating sample magnetometry (VSM).

2. Experimental procedure

Chemical synthesis routes play a crucial role in preparing the final product and less cumbersome than traditional methods for the production of fine grained mixed oxide powder, having a good physical properties. Chemical processing can minimize three major problems associated with diffusion, impurities and agglomeration.

In the solid state methods the mechanical mixing of oxides or carbonates after calcinations is used, resulting an inferior quality of ceramics due to poor sintering behavior, non-homogeneity, abnormal grain growth and imprecise control of cation. Consequently, the electrical and mechanical properties of the final product are feeble.

Recently, several variants of self-sustaining combustion synthesis was proposed [4]. Unlike the Pekini or amorphous citrate processes, these self-sustaining combustion processes are rapid and may approach the direct conversion from the molecular mixture of the precursor solution to final oxide product, avoiding the formation of crystalline phases that require intercrystallite diffusion, for completion of reaction. The low temperature combustion synthesis technique has been proved to be a novel, extremely facile, time saving and energy-efficient route for the synthesis of ultrafine powders.

In the present study we report the synthesis of $CoMn_xFe_{2-x}O_4$ powders by the low temperature combustion procedure, with citric acid metal nitrates gel precursors.

The stoichiometric quantities of nitrate salts were dissolved in distilled water and required amount of citric acid was added as chelating agent. The mixed solution was kept heated at 368K for 7 h with uniform stirring and evaporated to obtain a highly viscous gel. Thus, obtained gel was placed in a hot plate and maintained at 573K. The powder was milled again and the material was pressed in pellets of 1 cm diameter and 0.3 cm thick by applying a pressure of 50MPa. Pellets were then sintered at 1173K for 10 h in static air atmosphere. The schematic diagram that summarizes the experimental synthesis route is presented in Fig. 1. All the synthesized samples exhibited XRD patterns for the cubic spinel phase with a space group Fd3m. The absence of extra reflections in the diffraction patterns of as-prepared materials ensures the phase purity.

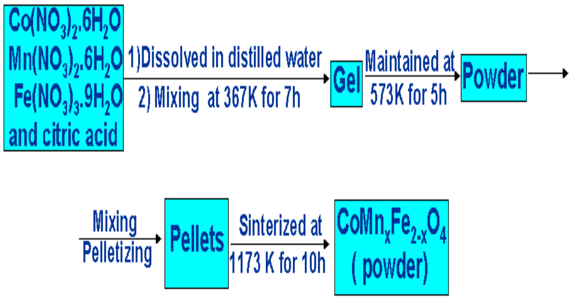


Fig. 1 Schematic diagram of experimental procedure for synthesis of $CoMn_xFe_{2-x}O_4$ powders by citrate gel process

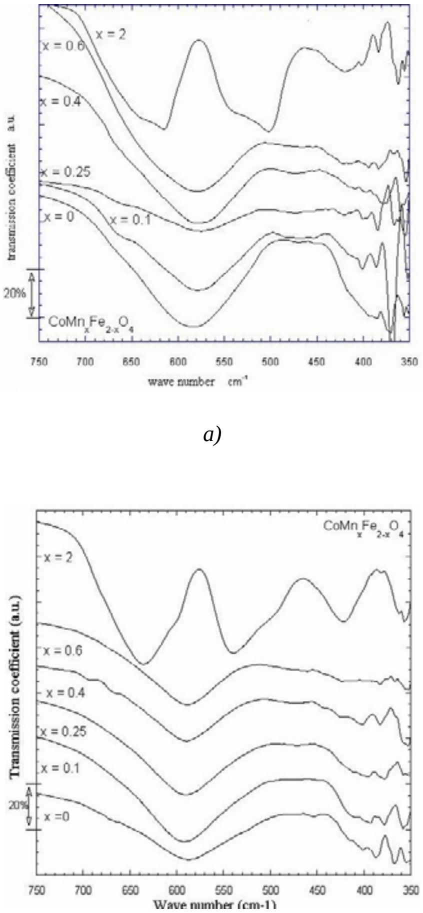
3. Results and discussions

Fourier transform infrared spectra (FT-IR) were recorded in the range 4000 to 400 cm^{-1} with 2 cm^{-1} resolution on a Bruker Vector –22 Fourier transform spectrometer using the KBr pellet technique.

The FT-IR spectra for the $CoMn_xFe_{2-x}O_4$ with x = 0; 0.10; 0.25; 0.40; 0.60 and 2.0 calcinated at 923 K and 1123K are show in Fig. 2, a and b.

Analyzing the IR absorption spectra it is observed that the spinel phase in not the only one phase in this system. The peak from 672 cm^{-1} is attributed to the tetrahedral Co and the maximum of the absorption in the range of 450-550cm^{-1} is attributed to octahedral Mn [5,6].

The presence of Co in tetrahedral centers is proved by the occurrence of the absorption maximum at 660 cm^{-1} due to the vibration of CoO_4. It can be seen that absorption band of 388cm^{-1} corresponding to vibration Fe-O and the band of 379 cm^{-1} is for vibration Mn-O. One observed that the absorption band of 388 cm^{-1} shift to high frequency with the increasing of Mn content, x.



a)

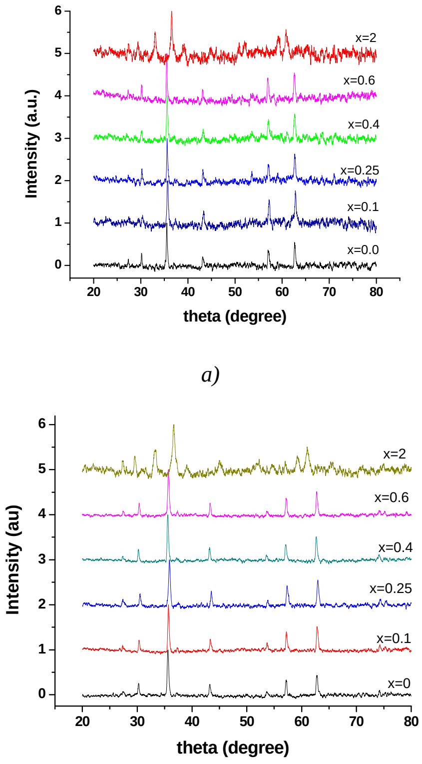
b)

Fig. 2. The IR spectra for samples of CoMnxFe2-xO4 sintered at: a) 930K and b)1123K

The bands at 672cm^{-1}, 450-550cm^{-1} and 300cm^{-1} of the calcinated powders indicate the formation of metal oxide, confirmed by XRD as the single spinel.

The XRD patterns of the powder were recorded using a DRON-2 powder diffractometer (Cu k_α radiation, λ = 1,54051Å). The XRD patterns of the as synthesized powders $CoMn_xFe_{2-x}O_4$ at 930 K (Fig. 4, a) suggested that the phase transformation was not accomplished in the combustion reaction. After annealing process done in air for 7 hours an improving of the phase content was observed but the phase transformation was not finalized. Post process thermal treatment is necessary for total phase transformation.

The XRD powder patterns of $CoMn_xFe_{2-x}O_4$ samples anealled at 923 K (Fig. 4, a) and 1123K (Fig. 4, b) demonstrate the increasing of the spinel phase content.



a)

b)

Fig. 3 X-ray powder diffraction patterns of CoMn$_x$Fe$_{2-x}$O$_4$ samples annealed at: a) 930K and b) 1123K

The lattice parameters obtained from XRD pattern for powders, a = 8,3802 Å are in agreement with the corresponding values reported for CoMnFe$_2$O$_4$ phase in literature [6]. On the other hand it is seen that the lattice constants of the Mn-doped powders are larger than that of the CoFe$_2$O$_4$ powders (see Table 1). The variation of the lattice constant of CoMn$_x$Fe$_{2-x}$O$_4$ can be understood by comparing the ionic radius of high-spin Mn^{2+}(0.97 Å) and Mn^{3+}(0.785 Å) ions with that of Fe^{3+}(0.785 Å) ion in the octahedral site. Thus in order to explain the increase of the lattice constant, some form of ionic migration such a Co^{2+} from octahedral to tetrahedral sites it is likely to happen CoMn$_x$Fe$_{2-x}$O$_4$ [7].

4. Magnetic Properties

The magnetic properties of samples have been characterized at room temperature using a vibrating sample magnetometer.

Figs. 5 and 6 present the results of VSM measurement on the CoMn$_x$Fe$_{2-x}$O$_4$ at 930 K and 1123 K, at room temperature. An increase in saturation magnetization (M$_s$) was observed proportional to *x*. On the other hand along with increasing the annealing temperature from 930 K to 1123K it is noticed also an increasing value of saturation magnetization. According to the result we can estimate that the spinel phase improves when the temperature is increase [7, 8].

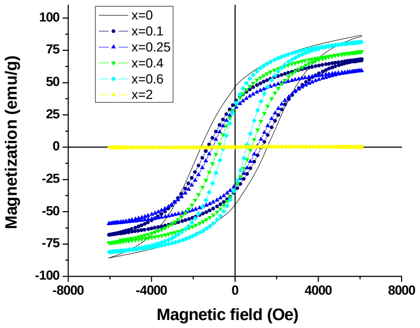


Fig. 5 The hysteresis loops for CoMn$_x$Fe$_{2-x}$O$_4$ annealed at 923K; (x = 0, 0.10, 0.25, 0.40, 0.60)

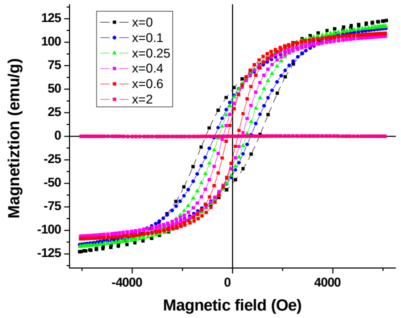


Fig. 6 The hysteresis loops for CoMn$_x$Fe$_{2-x}$O$_4$ (x = 0, 0.10, 0.25, 0.40, 0.60) annealed at 1123K

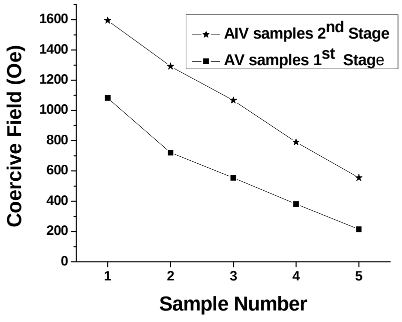


Fig. 7. The coercive field of the CoMn$_x$Fe$_{1-x}$O$_4$ (x1 = 0; x2=0.10; x3=0.25; x4=0.40; x5=0.60)

The decrease of the coercive field (Fig. 7) could be correlated with the phase transformation. Annealing the powders the content of the residual phases decrease and the crystallization process continued but was not accomplished.

5. Conclusions

The magnetic particles of $CoMnxFe_{2-x}O_4$, with x ranging from 0 to 0.6, have been synthesized by combustion reaction method using $Co(NO_3)_2.6H_2O$,$Mn(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ and citric acid as chelating agent.

All the synthesized samples exhibited XRD patterns for the cubic spinel phase with a space group Fd3m. The absence of extra reflections in the diffraction patterns of as-prepared materials ensures the phase purity.

The magnetic properties measurements demonstrate an increase on the saturation magnetization with the increase of Mn content. The thermal treatment induces a decrease of the coercive field, and an increase of the magnetization.

The combustion reaction method produces powders, without intermediate decomposition or further calcinations steps, with magnetic properties, comparable to those of similar powders synthesized by different methods.

Acknowledgements

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*Corresponding author: caltun@uaic.ro