Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Influence of cobalt ferrite content on the structure and magnetic properties of $(CoFe_2O_4)_X$ $(SiO_2\text{-}PVA)_{100\text{-}X}$ nanocomposites

Thomas Dippong[a], Oana Cadar[b], Erika Andrea Levei[b], Iosif Grigore Deac[c], Lucian Diamandescu[d], Lucian Barbu-Tudoran[e]

[a] Technical University of Cluj-Napoca, North University Center of Baia Mare, Department of Chemistry and Biology, 76 Victoriei Street, 430122 Baia Mare, Romania
[b] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath Street, 400293 Cluj-Napoca, Romania
[c] Babes-Bolyai University, Faculty of Physics, 1 Kogalniceanu Street, 400084 Cluj-Napoca, Romania
[d] National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania
[e] National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donath Street, 400293 Cluj-Napoca, Romania

ARTICLE INFO

Keywords:
nanocomposite
cobalt ferrite
crystallinity degree
hybrid matrix
Mössbauer effect
magnetic measurements

ABSTRACT

$(CoFe_2O_4)_X(SiO_2\text{-}PVA)_{100\text{-}X}$ (X = 5, 25, 50, 75 and 95%) nanocomposites were prepared via sol-gel route and annealed at 700 and 1100 °C. The influence of $CoFe_2O_4$ content on the structure, morphology and magnetic properties of nanocomposites was studied. X-ray diffraction patterns, Mössbauer and Fourier transform infrared spectra revealed the formation of $CoFe_2O_4$ as unique magnetic phase. The crystallinity degree increases with the $CoFe_2O_4$ content and the annealing temperature. Transmission electron microscopy images revealed the spherical shape of the obtained nanocomposites. Mössbauer spectra exhibit typical magnetic sextets, allowing the calculation of the cations distribution among tetrahedral and octahedral sites and the stoichiometry of $CoFe_2O_4$. A strong correlation between the particle morphology and the magnetic properties of nanocomposites was found. The highest saturation magnetization was identified for $(CoFe_2O_4)_{95}(SiO_2\text{-}PVA)_5$ nanocomposite.

1. Introduction

Ceramic nanocomposites (NCs) with high electromagnetic performance, high magnetocrystalline anisotropy, photocatalytic activity, superparamagnetic features, high coercivity and moderate saturation magnetization, large magnetostrictive coefficient, chemical stability, high mechanical strength, low toxicity, high biocompatibility and low production cost are at high demand. Thus, $CoFe_2O_4$ is widely used in a variety of applications, such as: nanosensors, gas sensors, data and energy storage, magnetic refrigerator and photo-catalyst, magnetic resonance imaging, magnetic storage, super capacitors, microwave absorbers, heat transfer, lithium ion battery, bio-diagnosis, drug delivery, water treatment, and black coloring agents for ceramics [1–10]. Moreover, nanostructured cobalt ferrites as nanorods, nanowires, nanotubes, hollow nanospheres and nanocups have been fabricated [9].

$CoFe_2O_4$ crystallizes into partially inverse spinel structure, with Co^{2+} and Fe^{3+} ions located in both tetrahedral and octahedral sites. The $CoFe_2O_4$ properties depend on the preparation methods, raw materials, annealing time and temperature [3–5]. Sol-gel, co-precipitation, solvo/hydrothermal, thermal decomposition, mechanical alloying, ultrasonic cavitation, hydrolysis, pulsed laser deposition, ball milling, micelle, reverse micelle, micro-emulsion, microwave assisted synthesis, thermal decomposition, microwave combustion and auto-combustion are the most used methods for preparation of pure and doped $CoFe_2O_4$ nanoparticles [3–8,10–13]. The sol-gel approach allows the efficient production of $CoFe_2O_4$ magnetic nanoparticles with controlled morphology and enhanced opto-magnetic and catalytic properties [8,14–16].

Nanoparticles dispersion in hybrid matrices is an effective method to reduce particle agglomeration, less energy demanding and environmentally friendly, uses non-toxic and biocompatible reagents and leads to materials with superior properties [17,18]. Poly(vinyl alcohol) (PVA) is a highly hydrophilic, non-toxic and biocompatible polymer with good water solubility, gas permeability, chemical and thermal resistance. PVA/SiO_2 hybrid matrix obtained by the chemical cross-linking of SiO_2 and PVA, as a result of the interaction between hydroxyl and silanol groups, are important in a variety of fields as they combine the advantages of the inorganic phase (thermal stability, rigidity) and the organic phase (flexibility, ductility, processability) [19–31].

This paper presents the evolution of magnetic properties with the increase of $CoFe_2O_4$ content embedded in the SiO_2-PVA hybrid matrix and the annealing temperature. The formation of $CoFe_2O_4$ crystalline phase was studied by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy, while the formation of SiO_2-PVA hybrid

E-mail address: dippong.thomas@yahoo.ro (T. Dippong).

https://doi.org/10.1016/j.ceramint.2018.01.226
Received 4 December 2017; Received in revised form 26 January 2018; Accepted 26 January 2018

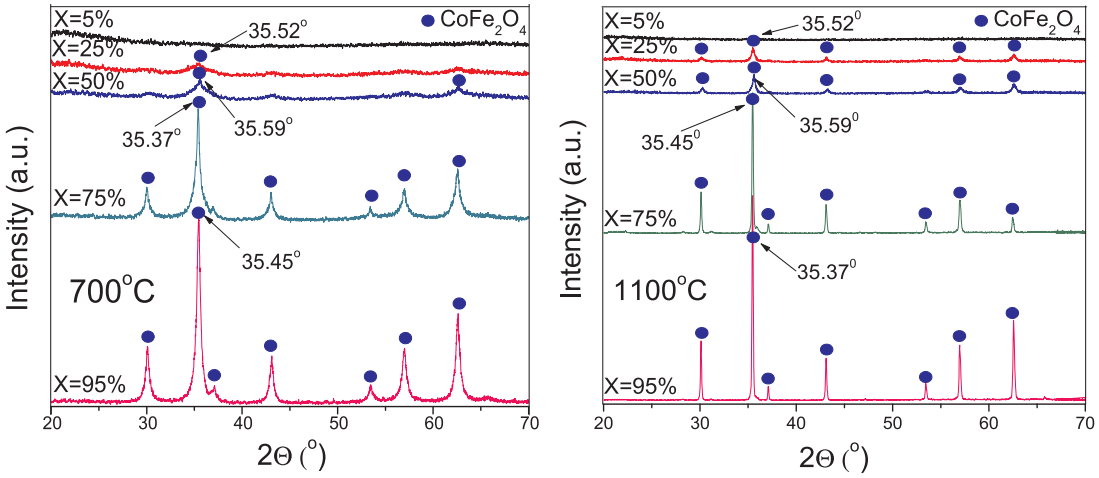

Fig. 1. XRD patterns of $(CoFe_2O_4)_X$ $(SiO_2\text{-}PVA)_{100\text{-}X}$ NCs annealed at 700 and 1100 °C.

matrix was investigated by FT-IR. The Co/Fe/Si ratio in $(CoFe_2O_4)_X$ $(SiO_2\text{-}PVA)_{100\text{-}X}$ (X = 5, 25, 50, 75 and 95%) NCs was confirmed by energy-dispersive X-ray spectroscopy (EDX). The shape, morphology and size of $CoFe_2O_4$ nanoparticles dispersed in SiO_2-PVA matrix were investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The magnetic properties were measured using a vibrating sample magnetometer (VSM). The Mössbauer spectroscopy was used to investigate the cation distribution and to establish the stoichiometry of $CoFe_2O_4$ structure.

2. Materials and methods

2.1. Synthesis

$(CoFe_2O_4)$ $(SiO_2\text{-}PVA)$ NCs were prepared by a modified sol-gel route. $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, 1,4-butanediol (1,4-BD), tetraethyl orthosilicate (TEOS), PVA (145.000 g/mol), ethanol and HNO_3 65% of analytical grade (Merck, Germany) were used without further purification. *Solution 1:* Fe and Co nitrates (1:2 molar ratio) were dissolved in deionized water, at room temperature (RT), followed by the addition of 1,4-BD (NO_3^-:1,4-BD = 1:1 molar ratio), ethanol and 65% HNO_3 until complete dissolution. *Solution 2:* Amounts of TEOS corresponding to 95, 75, 50, 25 and 5% wt. of total nitrates and ethanol (TEOS:ethanol = 1:1 M ratio) were added dropwise under continuous stirring to a PVA solution (PVA:NO_3^- = 0.0003:1 molar ratio), at 70 °C. Solution 1 and 2 were mixed together under continuous stirring for 30 min and kept at RT until gelation (1–4 months). The obtained gels were dried at 40 °C (5 h), preheated at 400 °C (5 h) and annealed at 700 °C (5 h) and 1100 °C (5 h). The obtained NCs were defined as $(CoFe_2O_4)_X$ $(SiO_2\text{-}PVA)_{100\text{-}X}$, where X is the wt.% of $CoFe_2O_4$ corresponding to 5, 25, 50, 75 and 95% of the total nitrates.

2.2. Characterization

The formation of $CoFe_2O_4$ phase was investigated using a Bruker D8 Advance diffractometer, operating at 40 kV and 40 mA, with CuK_α radiation (λ = 1.54178 Å) at RT, while the formation of SiO_2-PVA hybrid matrix and Co-O and Fe-O bonds from $CoFe_2O_4$ was confirmed using a Perkin Elmer Spectrum BX II FT-IR spectrometer. Mössbauer measurements were performed at RT with a WissEL-ICE Oxford Mössbauer cryomagnetic system. The γ-rays were provided by a ^{57}Co source in a Rh matrix. To avoid the additional contributions to the line widths the thickness of the samples was calculated at ~ 5 mg Fe/cm^2. The isomer shift is given relative to α-Fe at RT. The size, shape and clustering of $CoFe_2O_4$ nanoparticles embedded in the hybrid matrix were studied using a Hitachi HD2700 scanning transmission electron microscope, while the particle size distribution was determined using the UTHSCSA ImageTool Software. The morphology and dispersion of the obtained NCs were studied using a Hitachi SU8230 ultra-high resolution scanning electron microscope, on sputter-coated samples (with 5 nm Au), coupled with an Oxford Instruments X-Max 1160 EDX detector. The magnetic measurements were performed with a Cryogenic VSM. The hysteresis loops were recorded in magnetic fields from −1 to 1 T, at RT. Magnetization (M) vs. magnetic field (H) measurements were performed to find the saturation magnetization M_S. The powder samples were embedded in an epoxy resin to prevent any nanoparticles movement [22]. For the samples that didn't show saturation of magnetization in magnetic fields up to 5 T, saturation magnetization (M_S) value was obtained by fitting the M(H) curve using Eq. (1).

$$M(H) = M_S\left(1+\frac{a}{\mu_0 H} + \frac{b}{(\mu_0 H)^2}\right) \quad (1)$$

where M is the magnetization, Ms is the saturation magnetization, a and b are the parameters determined by the fitting procedure, μ_o is the permeability of the free space and H is the magnetic field.

3. Results and discussion

The XRD diffractograms of $(CoFe_2O_4)_X$ $(SiO_2\text{-}PVA)_{100\text{-}X}$ (X = 5, 25, 50, 75 and 95%) NCs annealed at 700 and 1100 °C (Fig. 1) show a single phase $CoFe_2O_4$ with cubic spinel structure (JCPDS file No.22-1086) [32]. As expected, no peaks for SiO_2-PVA matrix were observed [32]. The most intense peak described by 311 Miller indices (2θ° = 36.45) was attributed to the ideal orientation of the planes in ferrites, while the peak described by Miller indices 440 (2θ° = 44.32) and 220 (2θ° = 62.53) corresponds to octahedral and tetrahedral sites, respectively [32–34]. For the NCs with low matrix content (X = 75 and 95%), the formation of well-crystalized single phase $CoFe_2O_4$ is clearly observed; for X = 25 and 50%, $CoFe_2O_4$ crystallinity decreases, while for NCs with high matrix content (X = 5%), no crystalline phase was identified. However, for X = 5%, VSM measurements revealed a magnetic phase, while FT-IR and Mössbauer analysis identified this phase as $CoFe_2O_4$, suggesting a very poor crystallization (if any) of the ferrite.

High annealing temperature and $CoFe_2O_4$ content lead to an increase of the diffraction lines intensity, as a result of better crystallization. For NCs with X = 25 and 50%, annealed at 700 °C, the presence of crystalline $CoFe_2O_4$ is barely noticeable, while at 1100 °C, the $CoFe_2O_4$ lines appear clearly. Moreover, the narrow diffraction peaks at 1100 °C indicates the increase of the crystallites size (CS) [35]. For NCs annealed at 700 and 1000 °C, there is a slight shift of the 311 peak towards lower angles, attributed to migration of Co^{2+} ions from octahedral to tetrahedral sites and to opposite transfer of equivalent number