

Synthesis of nanocrystalline nickel ferrite by thermal decomposition of organic precursors

Marcela Stoia · Paul Barvinschi ·
Lucian Barbu Tudoran · Mirela Barbu ·
Mircea Stefanescu

ICMVT2011 Conference Special Chapter
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract Nickel ferrite powders were synthesized by thermal decomposition of the precursors obtained in the redox reaction between the mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with polyalcohol: 1,4-butanediol, polyvinyl alcohol and also with their mixture. During this reaction the primary C–OH groups were oxidized at –COOH, while secondary C–OH groups at C=O groups. The carboxylic groups formed coordinate to the present Ni(II) and Fe(III) cations leading to carboxylate type compounds, further used as precursors for NiFe_2O_4 . These precursors were characterized by thermal analysis and FT-IR spectrometry. All precursors thermally decomposed up to 350 °C leading to nickel ferrite weakly crystallized. By annealing at higher temperatures, nanocrystalline nickel ferrite powders were obtained, as resulted from XRD. SEM images have evidenced the formation of nanoparticulate powders; these powders present magnetic properties characteristic to the oxidic system formed by magnetic nanoparticles.

Keywords Butanediol · Nickel ferrite · Nanoparticles · Polyvinyl alcohol · SEM

M. Stoia (✉) · M. Barbu · M. Stefanescu
Faculty of Chemistry and Chemical Engineering, University
“Politehnica” Timisoara, P. Victoriei No. 2, 300006 Timisoara,
Romania
e-mail: marcela.stoia@chim.upt.ro

P. Barvinschi
Faculty of Physics, West University of Timisoara, Bv. V. Parvan
No. 4, 300223 Timisoara, Romania

L. B. Tudoran
Electron Microscopy Center, Faculty of Biology & Geology,
Babes-Bolyai University, 5-7 Clinicilor Street, 400006
Cluj-Napoca, Romania

Abbreviations

1,4BG 1,4-butanediol
PVA Polyvinyl alcohol

Introduction

Development of spinel ferrite nanoparticles has been intensively pursued because of their technological and fundamental scientific importance. Ferrites have received great attention as a result of their magnetic and electronic properties. It is well known that the chemical, structural, and magnetic properties of spinel ferrite nanoparticles are strongly influenced by their composition and microstructures, which are sensitive to the preparation methodologies [1]. Many ferrites with the spinel structure, MFe_2O_4 (where M: Ni, Zn, Mn, Co, Cd or their mixtures) are extensively used in a number of electronic devices. This is because of its high permeability at high frequencies, remarkably electrical resistivity, mechanical hardness, chemical stability, and reasonably low cost. Since the last decade, quite new and interesting magnetic properties have been reported for nanocrystalline spinel ferrites [2]. Spinel-type ferrite nanoparticles have gained great interest in the past few years because of their good electromagnetic performance and their applications in information storage, medical diagnosis technology, sensor technology, magnetic warming and cooling technology [3], efficient hyperthermia agents for cancer therapy [4], important catalysts for CO_2 and H_2O decomposition [5], and gas sensors for gases like liquefied petroleum gas, ethanol, CO, and CH_4 [6].

NiFe_2O_4 is one of the most important spinel ferrites which have attractive properties for the application as soft magnets and low loss materials at high frequencies.

NiFe₂O₄ is a typical soft ferromagnetic material, which crystallizes in a completely inverse spinel structure with all nickel ions located in the octahedral sites and iron ions occupying tetrahedral and octahedral sites. Several studies have been devoted to the synthesis and the magnetic properties of NiFe₂O₄ nanoparticles prepared by a variety of chemical routes [7].

Ferrite nanoparticles have been prepared by a variety of methods as coprecipitation reaction [8], sonochemical reaction [9], microwave route [10], reverse and normal micelles [11], chimie douce approach [12], alkalide reduction [13], sol–gel method [14] microemulsion method [15], polymer pyrolysis method [16], and mechanical-milling method [17].

In literature, several polyvinyl alcohol (PVA) based synthesis methods of nanocrystalline mixed oxides powders have been reported. PVA assisted sol–gel processes can result in uniform, monophasic, and even nanosized particles for many multicomponent oxides such as spinels (NiFe₂O₄, LiMn₂O₄, CoFe₂O₄) [18–20].

In our previous studies, we have synthesized several simple and mixed oxides [21–23] starting from metal nitrates and different organic diols. We have established that at temperatures around 100 °C, a redox reaction takes place between the metal nitrates and diol, resulting in its oxidation to dicarboxylate anions that coordinate to the metal cations forming different carboxylate coordination compounds.

In this article, we report the synthesis of nanocrystalline nickel ferrite by the thermal decomposition of some organic precursors obtained in the reaction between Ni(II) and Fe(III) nitrates and two polyols: PVA and 1,4-butanediol (1,4BG), and with a mixture PVA–1,4BG. The ferrite was obtained at low temperature (starting with 300 °C) as nanocrystalline powder, with interesting magnetic properties. The evolution of the crystallinity degree and crystallites diameter was studied by X-ray diffraction. Ferrite nanoparticles size was estimated from SEM and TEM images.

Experimental

Materials and preparation methods

Analytically pure PVA, 1,4BG, Fe(NO₃)₂·9H₂O, and Ni(NO₃)₂·6H₂O (supplied by Merck) were used as reagents without further purification.

NiFe₂O₄ ferrite was synthesized by mixing the corresponding quantities of Ni(II) and Fe(III) nitrates (calculated for 3 g of nickel ferrite) with 1,4BG (for molar ratio 1,4BG: NO₃[−] = 0.567:1), or with a corresponding volume of 5% PVA-water solution (for a molar ratio PVA

monomer: NO₃[−] = 0.567:1) and in the third case with the equimolar mixture of 1,4BG and PVA solution (for a molar ratio polyol: NO₃[−] = 0.567:1). The metal nitrates were dissolved in the corresponding volume of 1,4BG, with an addition of 1.0 cm³ water. The obtained solutions were carefully heated on a stove up to 160 °C, when a redox reaction took place between metal nitrates and the polyol, forming fluffy products, further used as precursors for nickel ferrite. The as synthesized precursors have been characterized by thermal analysis and FTIR spectroscopy. By the controlled thermal decomposition of the precursors at 290 °C, a magnetic powder is obtained which was further annealed at different temperatures. The obtained powders have been characterized by X-ray diffractometry, FT-IR spectrometry, specific surface area, and magnetic measurements.

Characterization methodology

Thermal analysis was performed on a 1500D MOM Budapest Derivatograph. The heating was achieved in static air, up to 500 °C, with a heating rate of 5 °C min^{−1}, on Pt plates using α-Al₂O₃ as inert material. The synthesized powders were characterized by FT-IR spectrometry with a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range 400–4000 cm^{−1}. Phase analysis was achieved with D8 Advance-Bruker AXS diffractometer, using the Mo-K_α radiation (λ_{Mo} = 0.7093 Å). SEM images have been recorded on a Quanta 3D FEG (FEI) microscope, while TEM microscopy was performed on a JEOL JEM 1010 microscope. The magnetic investigations on the powders in the as-prepared state were carried out at room temperature under AC (50 Hz) applied magnetic fields of amplitudes up to 160 kA/m. Specific surface area measurements have been performed, based on nitrogen adsorption, on a ASAP-2020 Micromeritics apparatus.

Results and discussions

PVA based synthesis method consists in thermal treatment of the metal nitrates–PVA solution, or in the gelation, followed by calcination. The presence of PVA in the system is favorable for the obtaining of mixed oxide spinel at lower temperatures and for shorter calcination times [18]. It was also reported that the carbonaceous residue that results after PVA thermal decomposition can act as a surfactant for the oxidic particles, preventing the aggregation of oxide nanoparticles. According to Ari et al., PVA acts as a metal chelating agent and thereby inhibits the segregation of metals during heating [19, 20]. According to Saha et al. [18], when the metal nitrates–PVA solution is heated once, the volume of the solution of mixed metal nitrates and PVA

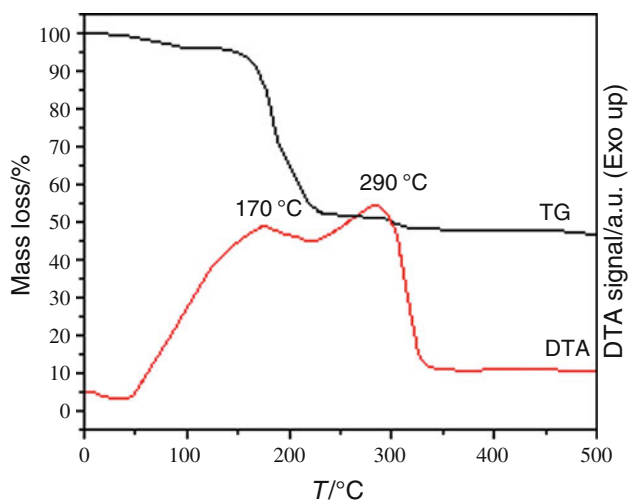


Fig. 1 TG and DTA curves of the precursor FeNiBG

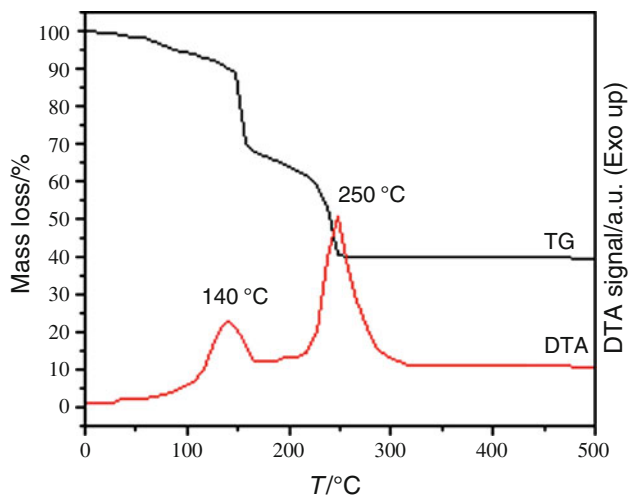


Fig. 2 TG and DTA curves of the precursor FeNiPVA

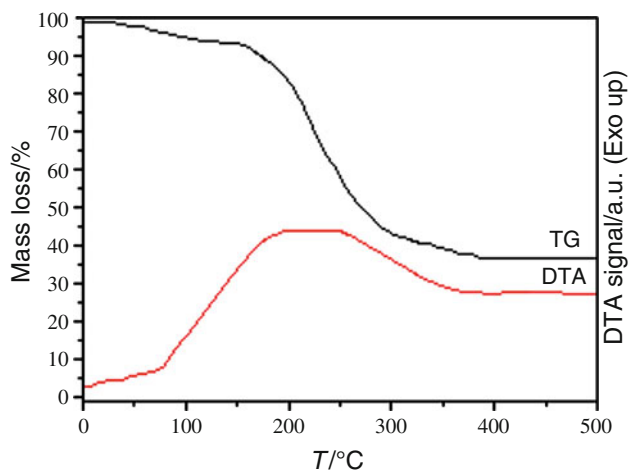


Fig. 3 TG and DTA curves of the precursor FeNiPVABG

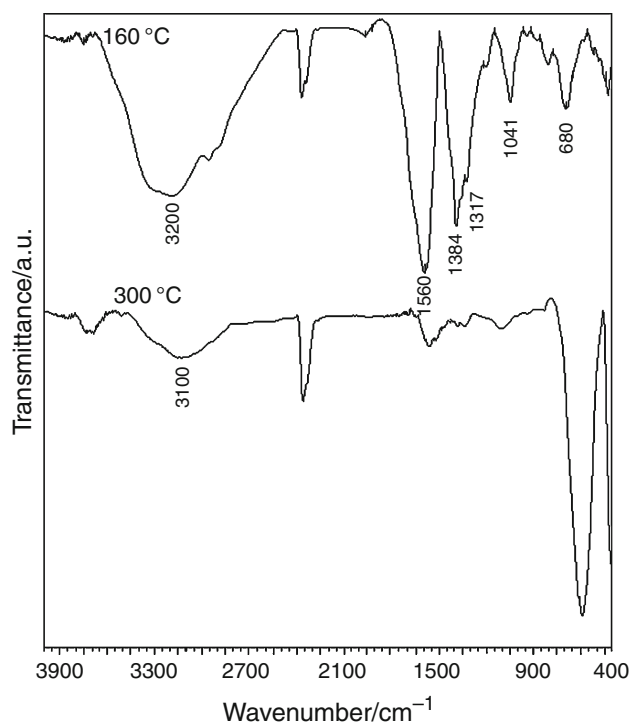


Fig. 4 FTIR spectra of the precursor FeNiBG as synthesized at 160 °C and annealed at 300 °C

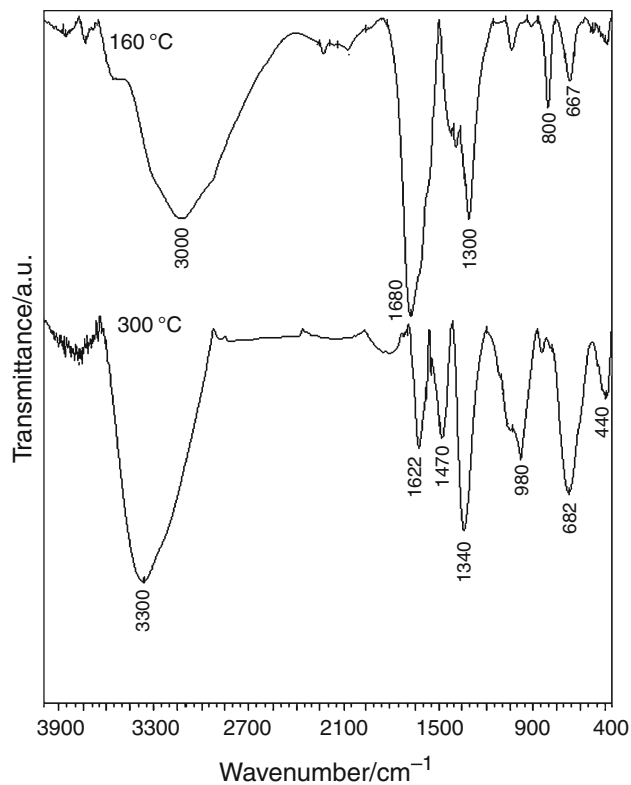


Fig. 5 FTIR spectra of the precursor FeNiPVA as synthesized at 160 °C and annealed at 300 °C

is reduced, the nitrate ions provide an in situ oxidizing environment for the decomposition of PVA.

We have previously studied the obtaining of spinel ferrites, by the redox reactions between metal nitrates and different diols [21–23]. We have observed in our studies that with the increase of the length of the organic chain of the diol, the nanoparticles are smaller in size and the temperature of spinel formation is lower, leading to a better crystallinity for the same temperature. Thus, we have decided to introduce in the system PVA beside the diol in order to obtain smaller, less agglomerated ferrite nanoparticles. We have studied comparatively the evolution of three systems: $\text{Ni}(\text{NO}_3)_2\text{-Fe}(\text{NO}_3)_3\text{-1,4BG}$ (sample FeNiBG), $\text{Ni}(\text{NO}_3)_2\text{-Fe}(\text{NO}_3)_3\text{-PVA}$ (sample FeNiPVA), and $\text{Ni}(\text{NO}_3)_2\text{-Fe}(\text{NO}_3)_3\text{-PVA-1,4BG}$ (sample FeNiPVABG), in order to establish the best solution for the obtaining of fine, less agglomerated nickel ferrite nanoparticles. After thermal treatment at 160 °C, we have obtained powders containing the corresponding nickel ferrite precursors: FeNiBG, FeNiPVA, and FeNiPVABG. The thermal behavior of these precursors is shown in Figs. 1, 2, and 3, and it is quite different.

The precursor FeNiBG (Fig. 1) thermally decomposes in two overlapped exothermic steps, with maxima on DTA

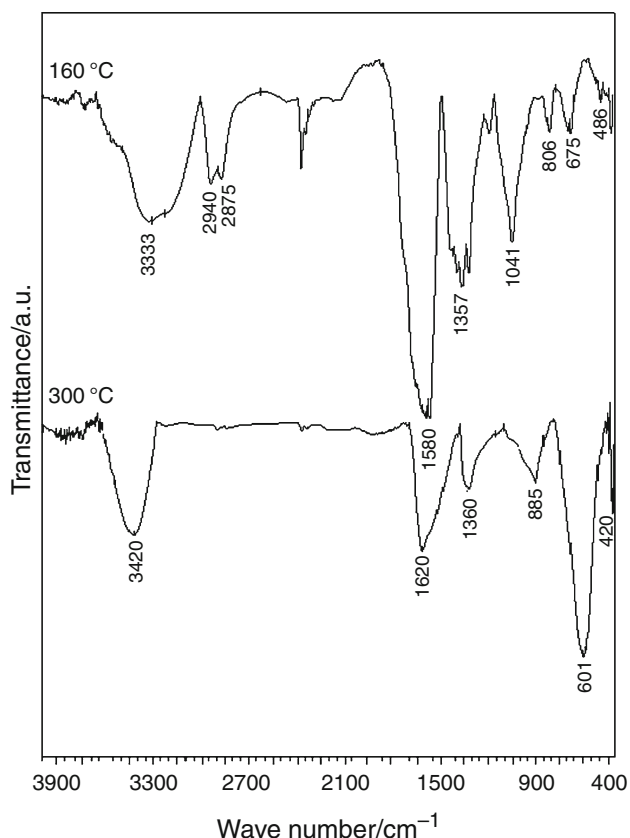


Fig. 6 FTIR spectra of the precursor FeNiPVABG as synthesized at 160 °C and annealed at 300 °C

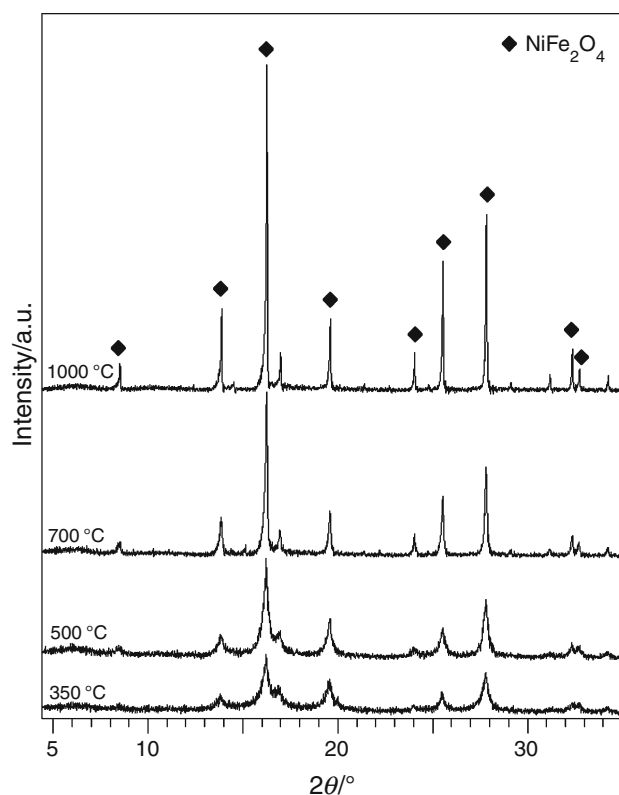


Fig. 7 XRD patterns of the powders obtained at 350, 500, 700, and 1000 °C from FeNiBG precursor

curve located at 170 and 290 °C. The thermal decomposition finishes up to 350 °C, with formation of the corresponding oxidic system, presenting magnetic properties.

In case of FeNiPVA (Fig. 2) precursor, two separate exothermic effect associated with two mass losses are registered: one at 140 °C, corresponding to the unfinished redox reaction between NO_3^- ions and PVA; the other one at 250 °C, corresponds to the thermal decomposition of the formed precursor. The thermal decomposition completes up to 280 °C, leading to a magnetic powder (probably nickel ferrite). In case of the precursor FeNiPVABG (Fig. 3), the thermal decomposition takes place in a large interval: 150–350 °C, leading at 350 °C to a magnetic powder.

The as synthesized precursors and their decomposition products obtained at 300 °C were analyzed by FT-IR spectrometry. The obtained spectra are shown in Figs. 4, 5, and 6.

In the spectra of the precursor FeNiBG (Fig. 4) synthesized at 160 °C, a strong band characteristic to the NO_3^- ions that appears at 1384 cm^{-1} which means that the redox reaction was not complete in this case. The strong bands at ~ 1590 and $\sim 1320\text{ cm}^{-1}$ are characteristic to the symmetric and antisymmetric stretching vibrations of COO^- groups [24], formed as oxidation products of the

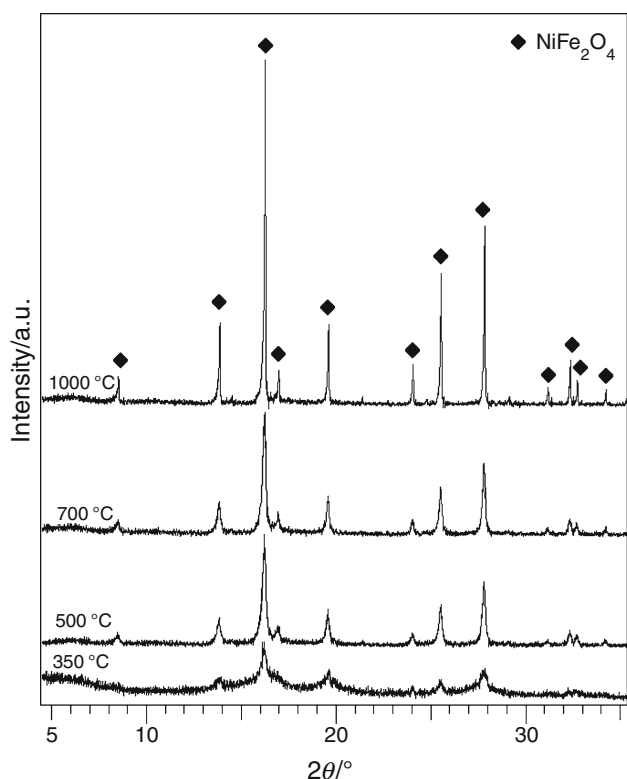


Fig. 8 XRD patterns of the powders obtained at 350, 500, 700, and 1000 °C from FeNiPVA precursor

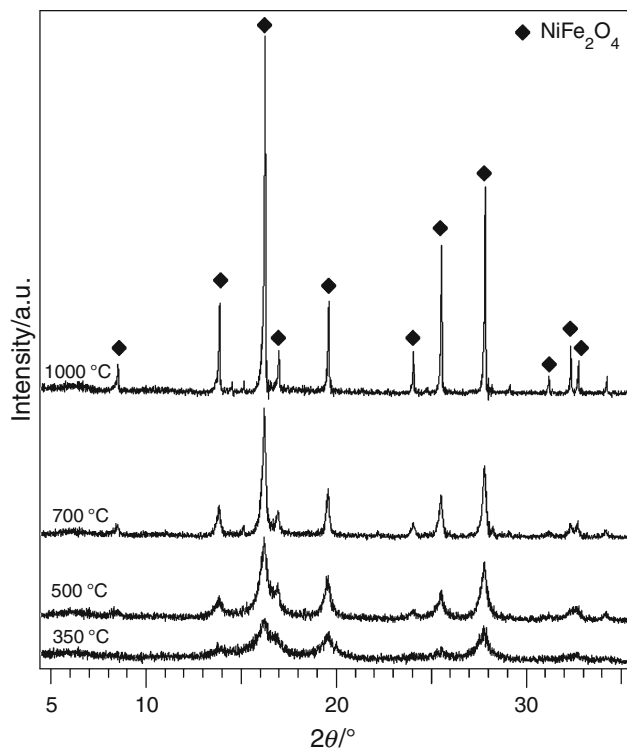


Fig. 9 XRD patterns of the powders obtained at 350, 500, 700, and 1000 °C from FeNiPVABG precursor

C–OH groups and coordinated to the metal ions. This band characteristic to NO_3^- is not visible in the spectra of the precursors FeNiPVA (Fig. 5) and FeNiPVABG (Fig. 6) obtained at 160 °C, which suggest that in these cases the redox reaction $\text{NO}_3^- + \text{OH}-\text{C}\equiv$ took place quantitatively.

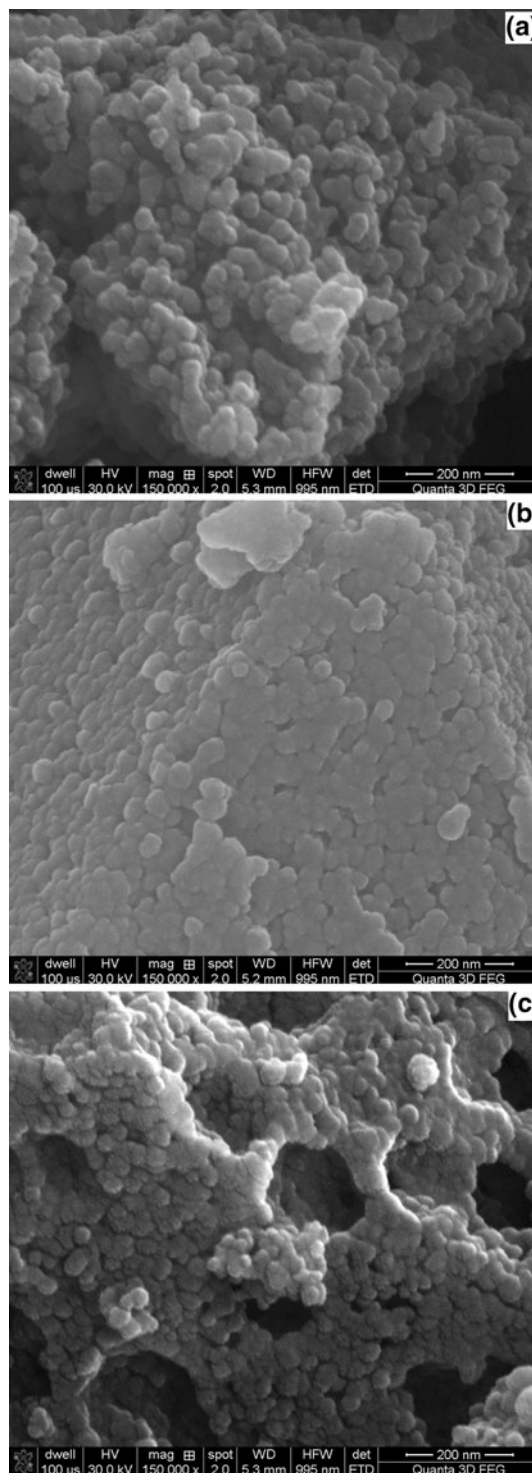


Fig. 10 SEM images of NiFe_2O_4 powders obtained at 700 °C from **a** FeNiBG, **b** FeNiPVA, and **c** FeNiPVABG

In case of the precursor FeNiPVA, two strong bands appear at 1680 and 1300 cm^{-1} , and can be assigned to the C=O bonds formed by the oxidation of the C–OH groups from PVA. In this case, the formation of a metal carboxylate is not evident.

The spectrum of the precursor FeNiPVABG (Fig. 6) clearly evidenced the formation of the metal carboxylates, through the bands located at 1360 and 1580 cm^{-1} and there is no band at 1380 cm^{-1} (no residual NO_3^- ions). By thermal treatment at 300 °C, only FeNiBG (Fig. 4) and FeNiPVABG (Fig. 6) thermally decompose completely leading to the formation of nickel ferrite (two bands at 680 and 400 cm^{-1}) at this low temperature. FeNiPVA precursor (Fig. 5) is not completely decomposed at 300 °C; there are some residual bands (1340 and 1620 cm^{-1}) but also a band at 680 cm^{-1} , characteristic to the nickel ferrite.

In order to obtain the nanocrystalline nickel ferrite powders, the precursors have been first decomposed at 350 °C (when all three precursors are completely decompose), then annealed at higher temperatures. By annealing the decomposition products for 3 h at 500, 700, and 1000 °C, crystallized nickel ferrite powders were obtained with characteristic magnetic properties.

XRD patterns of the powders annealed at different temperatures, obtained from the three precursors are shown in Figs. 7, 8, and 9. All XRD patterns evidence the presence of nickel ferrite spinel (JCPDS no. 86-2267 [25]) as sole crystalline phase. The crystallization degree is low at 350 °C, but significantly increases with the annealing temperature.

The evolution of the powders obtained by annealing the FeNiPVABG precursor (Fig. 9) is intermediary, between those of the former discussed precursors.

The fine nature of the ferrite nanoparticles is evident from the SEM image. In case of the powders obtained at 700 °C (Fig. 10a–c), all samples consists in micrometric aggregates of fine spherical homogenous nanoparticles with similar size, around 50 nm, slightly bigger for the powders obtained from FeNiPVA precursor (Fig. 10b); a sign of early sinterization is visible in this case. It is notable

Table 1 Magnetic properties of nickel ferrite powders

Precursor	Temperature/°C	Ms/emu/g	Hc/Oe
FeNiBG	700	38	340
FeNiPVA	700	35	320
FeNiPVABG	700	31	400
FeNiPVABG	500	17	240
FeNiPVABG	1000	47	180

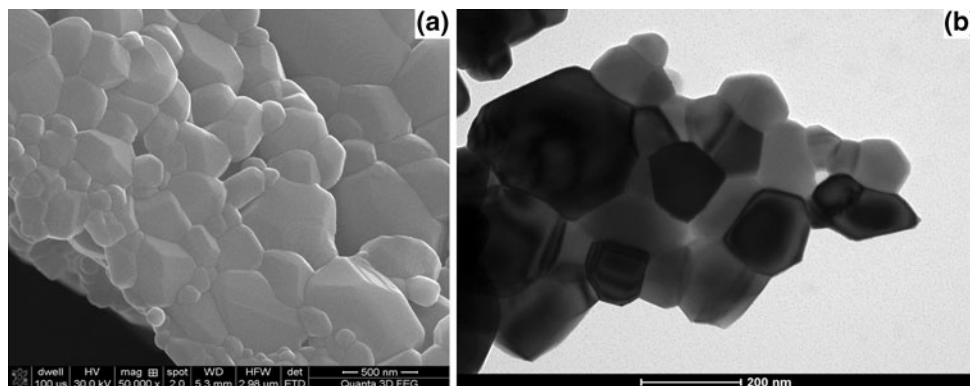
that in case of the powder obtained from FeNiPVABG precursor (Fig. 10c), porous micro-aggregates of nickel ferrite nanoparticles are present, suggesting a higher surface area.

BET specific surface area measurements have been performed on the powders obtained by annealing the precursors at 500 °C. The resulted values have confirmed a higher specific surface area in case of the powder obtained from FeNiPVABG precursor ($S_{\text{BET}} = 42.0 \pm 0.3 \text{ m}^2/\text{g}$) compared with the powder obtained from FeNiPVA precursor ($S_{\text{BET}} = 26.1 \pm 0.2 \text{ m}^2/\text{g}$).

In case of the powders annealed at 1000 °C, the one obtained from FeNiPVA showed an advanced sintering, as evidenced also by SEM (Fig. 11a) and TEM images (Fig. 11b).

The magnetic properties (saturation magnetizations and coercive field) of the synthesized powders are listed in Table 1. It results from the presented data that the value of saturation magnetization slightly decreases with the increasing of the organic content in the precursor, due to the smaller particle size. The values of saturation magnetization significantly increase with the annealing temperature (as results from the data obtained for FeNiPVABG originated sample). The coercive field increases significantly with the increase of annealing temperature from 500 to 700 °C, probably due to the increase in the nanoparticle size. When the annealing temperature increase at 1000 °C, the saturation magnetization increase to 47 emu/g, approaching the value characteristic to the bulk material (55 emu/g).

Fig. 11 SEM (a) and TEM (b) images of NiFe_2O_4 powder obtained at 1000 °C from FeNiPVA



According to the literature [26], the Ms value increases and Hc value decreases with the enhancement of crystallinity of nickel ferrite; thus, the higher saturation magnetization and lower coercivity of the synthesized NiFe₂O₄ sample at 1000 °C are due to the higher crystallinity.

Conclusions

Nanocrystalline nickel ferrite was successfully synthesized by thermal decomposition of organic precursors obtained by the redox reaction of polyalcohols and the mixture of metal nitrates. Two polyalcohols were used: PVA, and for the first time in nickel ferrite synthesis 1,4BG; the mixture of 1,4BG with PVA was used in the third case. All precursors decomposed up to 350 °C leading to weakly crystallized nickel ferrite. By thermal treatment at higher temperatures, the ferrite was obtained as well-crystallized powders, formed by spherical nanoparticles of about 50 nm at 700 °C. The use of the mixture of 1,4BG and PVA, led to a finer powder, with higher specific surface area. In case of the nickel ferrite powder obtained from PVA sintering took place at 1000 °C, visible even at 700 °C. The magnetic properties of the nickel ferrite powders obtained at 700 °C depend on the precursor nature, due to the difference in powder morphology.

Acknowledgements This study was partially supported by the strategic grant POSDRU/21/1.5/G/13798 inside POSDRU Romania 2007–2013, co-financed by the European Social Fund – Investing in People and by the strategic grant POSDRU/88/1.5/S/50783, Project ID 50783 (2009), co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007–2013.

References

- Liu XM, Yang G, Fu SY. Mass synthesis of nanocrystalline spinel ferrites by a polymer-pyrolysis route. *Mat Sci Eng C*. 2007;27:750–5.
- Bucko MM, Haberko K. Hydrothermal synthesis of nickel ferrite powders, their properties and sintering. *J Eur Ceram Soc*. 2007;27:723–7.
- Wang L, Ren J, Wang Y, Liu X, Wang Y. Controlled synthesis of magnetic spinel-type nickel ferrite nanoparticles by the interface reaction and hydrothermal crystallization. *J Alloy Compd*. 2010;490:656–60.
- Zhao DL, Zeng XW, Xia QS, Tang JT. Preparation and coercivity and saturation magnetization dependence of inductive heating property of Fe₃O₄ nanoparticles in an alternating current magnetic field for localized hyperthermia. *J. Alloys Compd*. 2009;469:215–8.
- Gill CS, Long W, Jones CW. Magnetic nanoparticle polymer brush catalysts: alternative hybrid organic/inorganic structures to obtain high, local catalyst loadings for use in organic transformations. *Catal Lett*. 2009;131:425–31.
- Gadkari AB, Shinde TJ, Vasambekar PN. Ferrite gas sensors. (*IEEE*) *Sens J*. 2011;11:849–61.
- Boonchom B, Maensiri S. Non-isothermal decomposition kinetics of NiFe₂O₄ nanoparticles synthesized using egg white solution route. *J Therm Anal Calorim*. 2009;97:879–84.
- Popescu SA, Vlazan P, Notingher PV, Novaconi S, Grozescu I, Bucur A, Sfirloaga P. Synthesis of Ni ferrite powders by coprecipitation and hydrothermal methods. *J Optoelectron Adv Mater*. 2011;13:260–2.
- Shafi KVPM, Ulman A, Yan X, Yang NL, Estourne C, White H, Rafailovich M. Sonochemical synthesis of functionalized amorphous iron oxide nanoparticles. *Langmuir*. 2001;17:5093–7.
- Bensebaa F, Zavaliche F, L'Ecuyer P, Cochrane RW, Veres TJ. Microwave synthesis and characterization of co-ferrite nanoparticles. *J Colloid Interface Sci*. 2004;277:104.
- Lee Y, Lee J, Bae CJ, Park JG, Noh HJ, Park JH, Hyeon T. Large-scale synthesis of uniform and crystalline magnetite nanoparticles using reverse micelles as nanoreactors under reflux conditions. *Adv Funct Mater*. 2005;15:503.
- Gingasu D, Mindru I, Patron L, Stoleriu S. Synthesis of lithium ferrites from polymeric carboxylates. *J Serb Chem Soc*. 2008;73:979–88.
- Mooney KE, Nelson JA, Wagner MJ. Superparamagnetic cobalt ferrite nanocrystals synthesized by alkaline reduction. *Chem Mater*. 2004;16:3155.
- Liu XM, Fu SY, Huang J. Synthesis and magnetic characterization of novel CoFe₂O₄-BiFeO₃ nanocomposites. *Mater Sci Eng B*. 2005;121:255–60.
- Misra RDK, Kale A, Kooi BJ, Hosson JTM. Some aspects of nanocrystalline nickel and zinc ferrites processed using microemulsion technique. *Mater Sci Technol*. 2003;19:1617–21.
- Liu Xian-Ming, Fu SY, Xiao HM, Huang CJ. Synthesis of nanocrystalline spinel CoFe₂O₄ via a polymer-pyrolysis route. *Phys B*. 2005;370:14–21.
- Manova E, Tsoncheva T, Paneva D, Rehspringer JL, Tenchev K, Mitov I, Petrov L. Synthesis characterization and catalytic properties of nanodimensional nickel ferrite/silica composites. *Appl Catal A: General*. 2007;317:34–42.
- Saha SK, Pathak A, Pramanik P. Low temperature preparation of fine particles of mixed oxides. *J Mater Sci Lett*. 1995;14:35–7.
- Ari M, Miller KJ, Marinkovic BA, Jardim PM, Avillez R, Rizzo F, White MA. Rapid synthesis of the low thermal expansion phase of Al₂Mo₃O₁₂ via a sol-gel method using polyvinyl alcohol. *J Sol-Gel Sci Technol*. doi:10.1007/s10971-010-2364-9.
- Sen A, Pramanik P. Preparation of nano-sized calcium, magnesium and zinc chromite powder through metallo-organic precursor solution. *J Mater Synth Process*. 2002;10:107–11.
- Ștefănescu M, Stoia M, Ștefănescu O, Barvinschi P. Obtaining of Ni_{0.65}Zn_{0.35}Fe₂O₄ nanoparticles at low temperature starting from metallic nitrates and polyols. *J Therm Anal Calorim*. 2010;99:459–64.
- Ștefănescu M, Stoia M, Dippong T, Ștefănescu O, Barvinschi P. Preparation of Co_xFe_{3-x}O₄ oxydic system starting from metal nitrates and propanediol. *Acta Chim Slov*. 2009;56:379–85.
- Ștefănescu M, Ștefănescu O, Stoia M, Lazau C. Thermal decomposition of some metal-organic precursors Fe₂O₃ nanoparticles. *J Therm Anal Calorim*. 2007;881:27–32.
- Gonsalves LR, Mojumdar SC, Verenkar VMS. Synthesis of cobalt nickel ferrite nanoparticles via autocatalytic decomposition of the precursor. *J Therm Anal Calorim*. 2010;100:789–92.
- Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data. Swarthmore, 1993.
- Huo J, Wei M. Characterization and magnetic properties of nanocrystalline nickel ferrite synthesized by hydrothermal method. *Mater Lett*. 2009;63:1183–4.