UDK 541.124-16

Formation of Magnetic Microstructure of the Nanosized NiFe$_2$O$_4$ Synthesized Via Solid-State Reaction

T. Žák[1], V. Ćosović[2*)], A. Ćosović[3], B. David[1], N. Talijan[2], D. Živković[4]

[1] Institute of Physics of Materials AS CR, v.v.i., Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia
[3] Institute for Technology of Nuclear and Other Mineral Raw Materials, Franse d' Eperea 86, 11000 Belgrade, Serbia
[4] Technical Faculty in Bor, University of Belgrade, Vojske Jugoslavije 12, 19210 Bor, Serbia

Abstract:

Magnetic NiFe$_2$O$_4$ structure formation was studied through structural, compositional and magnetic characterization of obtained reaction products of a simple, high yielding and low-cost solid-state reaction. Initial annealing of the starting oxides mixture at 700°C did not allow us to observe formation of the desired magnetic phase. In contrast, subsequent thermomagnetic measurements up to 800°C indicated the considerable increase of the magnetic moment, which can be reasonably assigned to the changes in phase composition and formation of magnetic NiFe$_2$O$_4$ structure during the heating cycle of measurements. Nanosized NiFe$_2$O$_4$ phase formation has been confirmed by the following XRD and MS phase analyses and its nanocrystalline structure by XRD and SEM/TEM techniques. The obtained hysteresis loop taken after TM measurements suggest the increased volume of magnetically active material and thus additionally support the previous findings.
Keywords: NiFe$_2$O$_4$ nanoparticles, Solid-state reaction, Phase composition, Magnetic properties

1. Introduction

The soft or low coercivity ferrites are the most widely used group of magnetic materials utilized by electrical, electronic, information and home appliance industry, thus representing very important basic functional materials. Essentially, they are non-conductive ceramic materials based on iron oxides as well as nickel, zinc, and/or manganese compounds [1]. Due to low coercivity, their magnetization can be easily reversed without significant dissipation of energy. At the same time, their high electrical resistivity facilitates fairly low energy losses at high frequencies. Hence, they are extensively used in such applications where reduction of the different losses accompanying high-frequencies is more important than the static magnetic properties [2].

Although, majority of these materials have spinel structure, large number of magnetic

_____

*)** Corresponding author**: vlada@tmf.bg.ac.rs

ferrites like nickel ferrite ($NiFe_2O_4$), a well-known ferrimagnetic material, have in fact an inverse spinel structure. This structure is represented by the formula $(Fe^{+3})_A(Ni^{+2}Fe^{+3})_BO_4$ in which half the atoms of iron occupy the tetrahedral (A) sites and the other half together with magnetic atoms occupy the octahedral (B) sites [3,4]. Mixed spinel structure with the certain degree of inversion is common as well.

The synthesis of nanosized $NiFe_2O_4$ has been studied by many investigators [5-8]. Accordingly, there are various, both wet and solid-state, synthesis techniques available e.g. co-precipitation, sono-chemical precipitation, hydrothermal synthesis, spray drying, freeze-drying, pulsed wire discharge and high energy ball milling, to name a few [7-10]. As each of them is being characterized by different disadvantages ranging from low yield, impurity formation, extensive agglomeration to complicated synthesis schemes, investigation of alternative processing routes is still burning topic [8,11,12].

It is widely recognized that the properties of nanocrystalline ferrites are size dependent and known to be very sensitive to the applied synthesis route [13-15]. Previous studies found in literature [16,17] point to difference between metal oxides obtained by grinding of solid metallic salts with sodium hydroxide and those obtained via hydroxides in solution. It is suggested that during solid-state reaction hydroxides decompose by a strong heat of reaction to produce oxides. However, the usual drawback of the conventional solid-state reactions for the preparation of Ni-ferrites is that at high temperatures, formation of a polycrystalline ferrite compound with a large crystallite size is favored. Consequently, this leads to loss of their peculiar structural and magnetic properties [7]. Nevertheless, the undesired grain growth during the solid-state reaction can be suppressed by addition of different inhibitors such as sodium chloride [16,18].

Given that the magnetic properties of $NiFe_2O_4$ ferrite magnetic materials are directly related to their structure and phase composition, formation of magnetic microstructure of the nanosized nickel ferrite synthesized via solid-state reaction was analyzed and discussed through structural, compositional and magnetic characterization of obtained reaction products.

2. Experimental

The investigated nickel ferrite material was prepared by a simple high yielding and low-cost solid-state reaction route, using analytical grade $NiSO_4 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, NaOH and NaCl as precursors. Adopted synthesis route is modified molten sodium chloride route proposed by S. L. Darshane et al. [16] where sodium chloride is used as grain growth inhibitor. Solid precursors are mixed in the molar ratio of 1:2:8:10, respectively and ground together in an agate mortar for about 60 min. During the mixing process, exothermal reaction takes place yielding in mixture of nickel and ferrite oxides. In order to synthesize $NiFe_2O_4$ this mixture is subjected to calcination at 700^oC for 4 h. Pure polycrystalline $NiFe_2O_4$ nanoparticles are obtained with subsequent crushing and washing of produced powder, with deionized water, to remove present sodium chloride.

Additional advantage of the adopted synthesis route is that the grain growth during the solid-state reaction is inhibited by the sodium chloride, given that it facilitates formation of the coating around the nanoparticles that prevents the aggregation of nuclei to large particles [18].

The powder samples of the obtained ferrite magnetic material were characterized using diverse experimental techniques. Phase composition was determined by the X-Ray diffractometry (XRD) and by [57]Fe Mössbauer spectroscopic phase analysis (MS). All XRD measurements were done with powder samples at ambient temperature. For a quantitative analysis and determination of crystallite size HighScore plus with Rietweld structural models based on the ICSD database were used. Mössbauer spectra were taken in the standard transmission geometry using a [57]Co(Rh) source at room temperature. The calibration was

done against an α-iron foil. For the spectra fitting and decomposition, the "CONFIT" software package was used [19]. The thermomagnetic curves were measured on the EG&G vibrating sample magnetometer in the field of 4 kAm^{-1} in vacuum. The heating and cooling rate was 4 °Cmin^{-1} with 30 min. delay at maximum of 800°C. Method of interpretation of comparable thermomagnetic measurement (TM) could be found in previous investigations [20]. Morphology and structure of the obtained powder samples were analyzed by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Magnetic properties were measured on the temperature of the ambient on Vibrating sample magnetometer (VSM) with magnetic field strength of 800 kAm^{-1}.

3. Results and Discussion

In line with the mechanism of $NiFe_2O_4$ formation proposed by Darshane et al. [16] the mixture of nickel and ferrite oxides was firstly annealed at 700°C. The subsequent XRD analysis has revealed only presence of the oxides from the starting mixture confirming that nickel ferrite phase has not been formed (Fig.1). It could be that some of the processing conditions were not met and/or that the annealing time used in this study does not allow us to observe the formation of the desired magnetic phase.
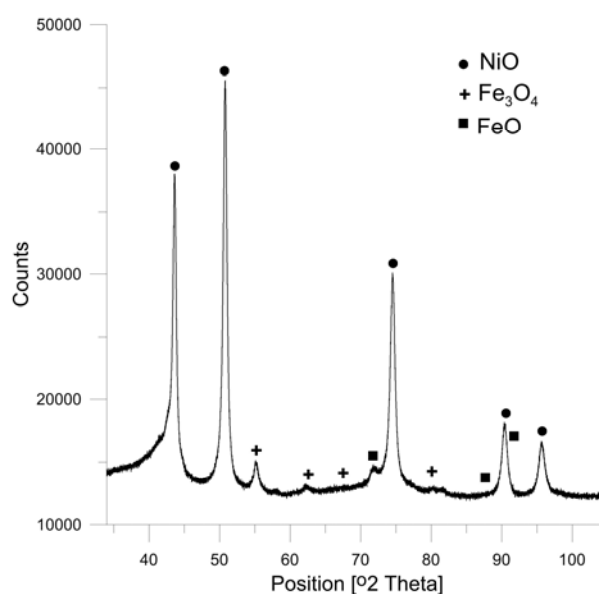

Fig. 1. X-ray diffractogram of the sample annealed at 700°C

Further analysis of the phase composition using Mössbauer spectroscopy supported findings of the XRD analysis. Nevertheless, confirmation of the phase composition using MS is not so straight forward. Considering that the main characteristic of the ^{57}Fe Mössbauer spectroscopy is that it can only "see" iron containing phases there was no possibility to gain any information about nickel oxide and metallic nickel in the analyzed sample. Consequently, the obtained MS spectrum (Fig. 2) contains only information regarding iron containing phases.

The most of the sample volume is represented by a pair of doublets and there is only about 16 % of the ferromagnetic iron. However, the phase is so weak, that it is not possible to assign the spectrum component to any specific structure. According to related literature Goya et al. [21], determined values of the hyperfine parameters at room temperature (quadrupolar splitting QS = 0.52(4) mm/s and isomer shift IS = 0.30(2) mm/s for the first doublet (D1) in

the spectrum are typical of Fe_3O_4 nanoparticles in the superparamagnetic state. Hence, the doublet probably originated in the fast relaxation of the particle magnetic moment in the superparamagnetic state.
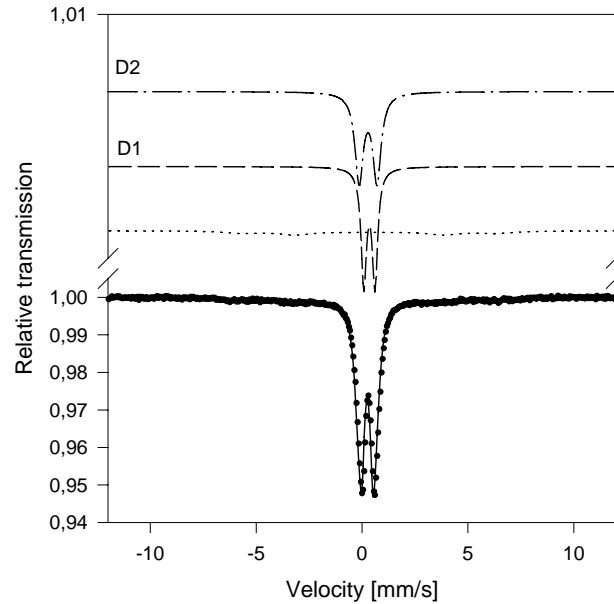

Fig. 2. Mössbauer spectra of the powder sample annealed at $700^{o}C$

Furthermore, a quadrupole splitting QS = 0.84(2) mm/s and isomer shift IS = 0.29(1) mm/s for the second doublet (D2) in the spectrum are consistent with the parameters found in study of Saeed Kamali-M et al. [22] for superparamagnetic iron oxide nanoparticles. It is further stated that this doublet emanates from ferric iron in a non-spherical local surrounding, possibly coming from the rim of the iron oxide core.
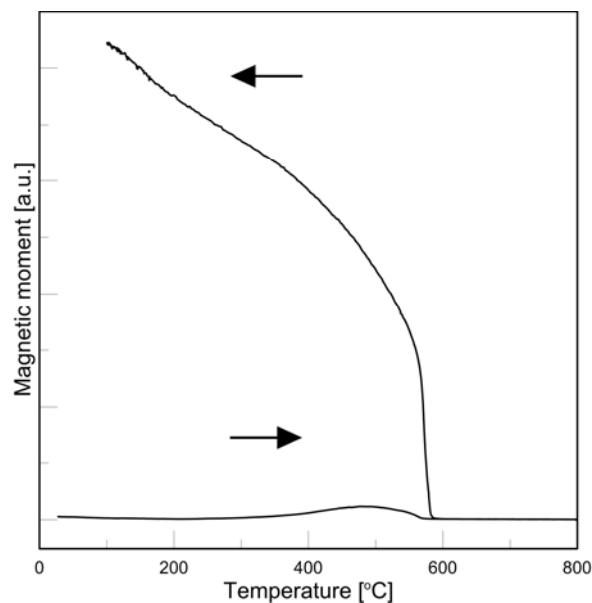

Fig. 3. Thermomagnetic curves of the studied powder sample

Generally speaking, it is clear that the role of surface atoms or atoms on some irregular position rises with diminishing size of particles. The influence of surface (or interface) atoms on Mössbauer spectra is very known as well [23]. The broad wings in the spectrum suggest that there is some superposition of weak sextets near blocking temperature where both superparamagnetic and ferromagnetic interaction are present.

Taking into consideration reaction conditions used in similar solid state reaction [8] that suggests formation of $NiFe_2O_4$ phase at slightly higher annealing temperature, themomagnetic measurements up to 800°C were utilized to observe desired phase formation. The temperature dependence of the total magnetic moment of the investigated powder sample at an applied field of 4 kAm^{-1} is presented on Fig. 3.

In regard to the determined phase composition of the studied starting material and that it is essentially nonmagnetized, during heating in the temperature range ambient temperature to 800 ^{o}C, no significant decrease of total magnetic moment can be observed. In contrast, cooling curve displays rapid and considerable increase of total magnetic moment with a decrease of temperature. This behaviour can be reasonably considered as a result of the formation of the optimal phase composition and formation of magnetic microstructure during heating cycle which essentially represents thermal treatment. Additionally, the observed increase of total magnetic moment during the subsequent cooling cycle can be attributed to "field cooling process" as well as overall decrease in thermal energy. Given that, starting from the magnetically disordered state, during cooling, magnetic moments tend to minimize energy against the external magnetic field and the final state results in an anisotropic moment distribution, appearing outside as an enlargement of a bulk magnetic moment.

In order to gain insight into newly formed phase composition of the studied sample after TM, XRD analysis was used. The obtained X-ray diffractogram is given in Fig.4.
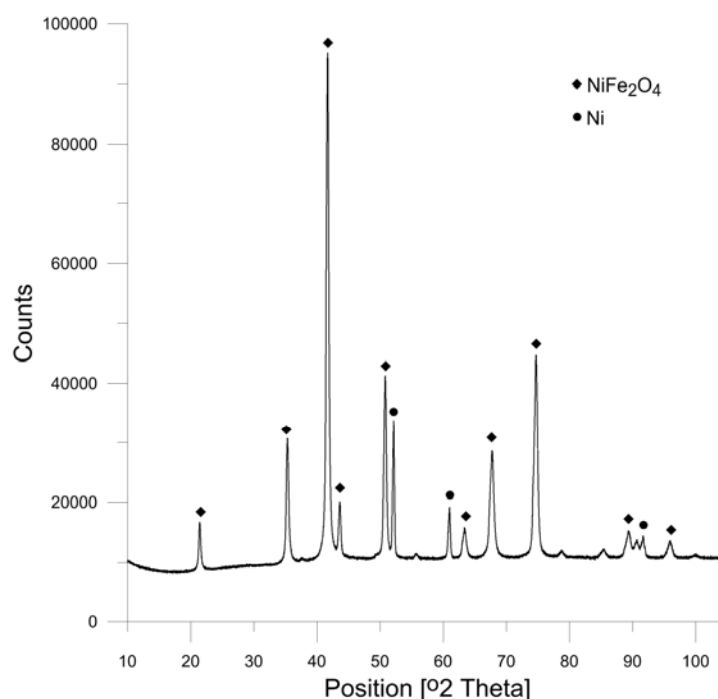

Fig. 4. X-ray diffractogram of the investigated Ni-ferrite powder after TM

According to obtained XRD results for the sample after TM measurements, it consists of 89 wt% $NiFe_2O_4$ phase and 11 wt% Ni, with their crystallite sizes being estimated to 25 and 45 nm, respectively. The presence of the Fe_3O_4 phase in the nickel ferrite sample was considered as well, given that most of its peaks overlap those of $NiFe_2O_4$. However, peaks

that are specific only for Fe_3O_4 phase are in positions where only very weak signal or almost none was measured. Hence, the presence of the Fe_3O_4 phase, if any, is practically negligible.

Phase composition of the obtained Ni-ferrite powder after TM was further analyzed using Mössbauer spectroscopy and the corresponding spectrum is presented in Fig.5. The obtained results indicate that about 60% of the iron atoms belong to the complete regular nickel ferrite structure. The rest is either on some "redundant" tetrahedral position or on position that is the not the full-value octahedral one as such atoms do not have the supposed number of nearest iron neighbors. Such result can be explained by taking into account the results of XRD analysis i.e. determined phase composition and corresponding crystallite sizes.
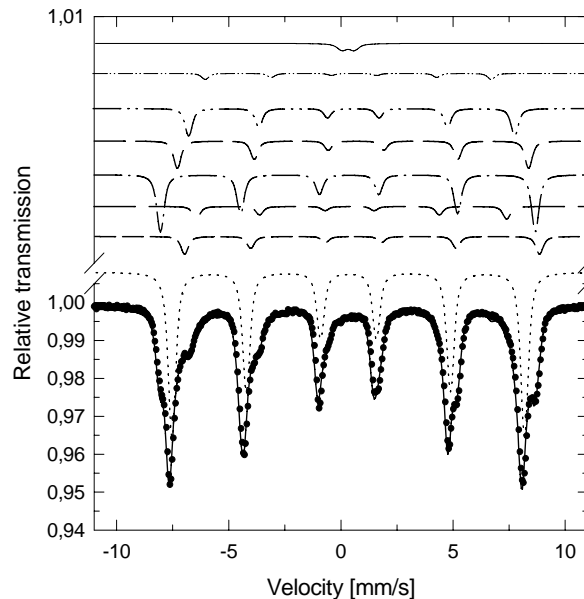

Fig. 5. Mössbauer spectra of the investigated Ni-ferrite magnetic material after TM

Studies found in literature suggest that the ratio of the tetrahedral (A) and octahedral (B) sites in the ultrafine samples may be somewhat different from that in the bulk materials [7]. It was found that the small particle size promotes a mixed spinel structure whereas bulk form is an inverse spinel [8]. Furthermore, in a similar study by Morrish and Hanada [24] of ultrafine $NiFe_2O_4$ particles with a crystallite size of ca. 25 nm, authors also pointed out the possibility that the sample was either non-stoichiometric or not completely inverse, which can also be the case with the studied sample, given that presence of metallic nickel was determined by XRD. Limited Ni^{2+} substitution for Fe^{2+} as an outcome of the used solid-state reaction should be considered as well [7]. In line with the XRD results, MS phase analysis did not find presence of Fe_3O_4 phase.

Morphology and structure of the Ni-ferrite powder obtained after TM measurements up to 800°C was initially studied using SEM. The presented SEM image (Fig.6) illustrates presence of nanoscale $NiFe_2O_4$ particles that form much larger agglomerates which effectively obscure the true morphology of the obtained powder.
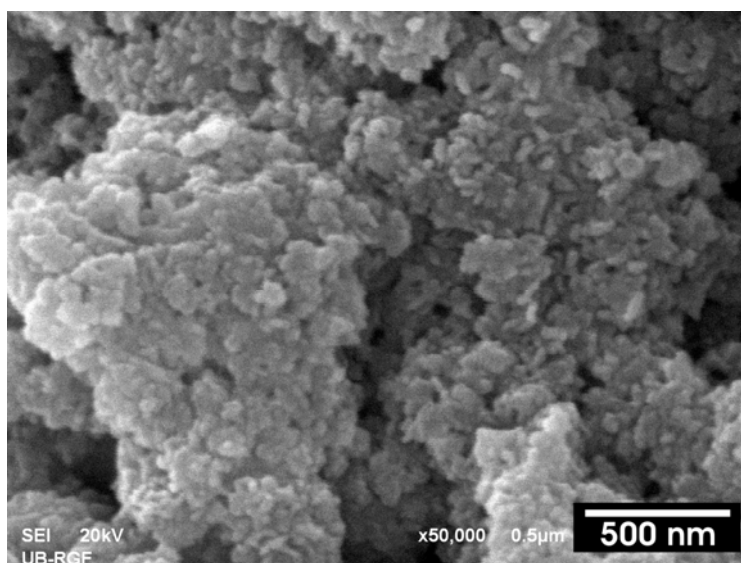
Fig. 6. SEM image of the obtained Ni-ferrite powder after TM

In order to gain better insight into the morphology, TEM analysis was utilized. TEM micrograph of the investigated magnetic powder (Fig.7) clearly shows individual nanoparticles of the nanocrystalline $NiFe_2O_4$. Moreover, the average particle size estimated from the TEM image is consistent with the crystallite size determined by XRD.
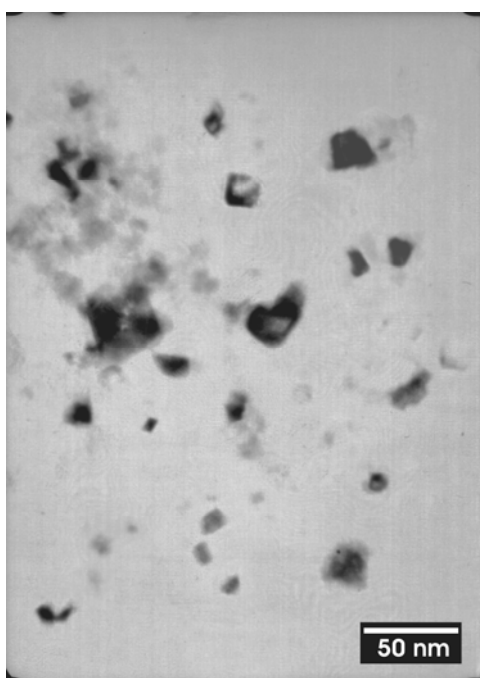

Fig. 7. TEM micrograph of the obtained Ni-ferrite powder after TM

Apart from the phase composition and structural characterization, magnetic properties of the samples annealed at 700°C and after TM up to 800°C were investigated as well. The obtained magnetization vs. magnetic field plots i.e. corresponding hysteresis loops are given in Fig. 8.
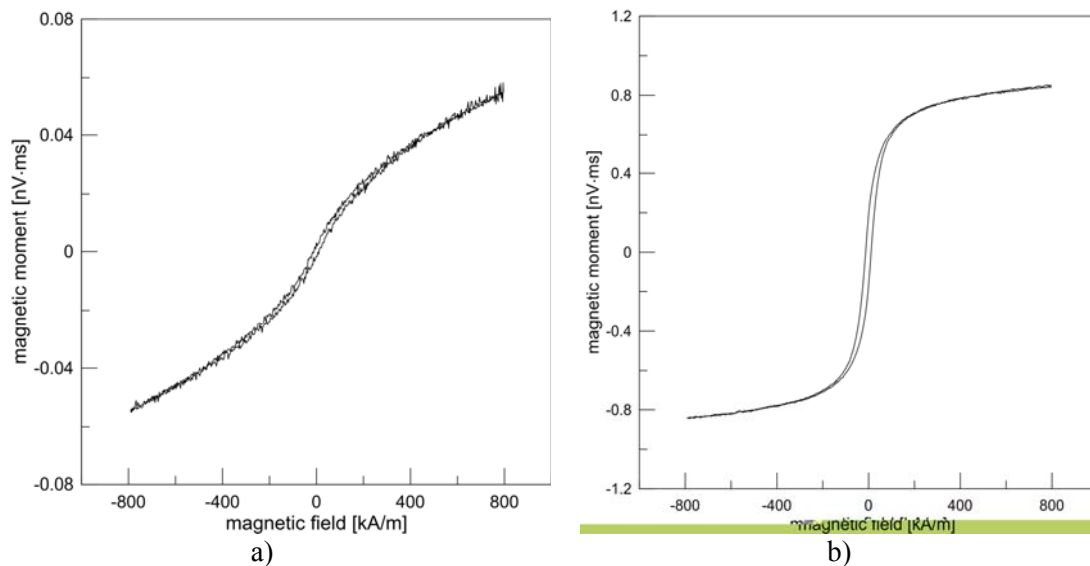
Fig. 8. Hysteresis loops of the investigated powder samples a) annealed at $700^{\circ}C$ and b) after thermomagnetic measurements up to $800^{\circ}C$

The presented hysteresis loops (Fig. 8) demonstrate substantial difference in the magnetic quality. As revealed by the structural analyses, the sample annealed at $700^{\circ}C$ (Fig. 8a) shows superparamagnetic behavior with considerably small magnetization and no coercivity. Seeing that during the TM the structure changes into $NiFe_2O_4$, which is ferrimagnetic, net magnetization and overall magnetic quality increase significantly (Fig. 8b) due to the increased volume of magnetically active material.

4. Conclusions

Nanosized $NiFe_2O_4$ magnetic material was prepared by a simple high yielding and low-cost solid-state reaction route. Formation of magnetic microstructure was studied and discussed through structural, compositional and magnetic characterization of obtained reaction products. Initial annealing of the starting oxides mixture at $700^{\circ}C$ did not allow us to observe formation of the desired magnetic phase. This could probably be because some of the processing conditions were not met and/or that the annealing time used in this study was not adequate. In contrast, the considerable increase of the magnetic moment with a decrease of temperature was observed on the obtained thermomagetic curve. It can be reasonably assigned to the changes in phase composition and formation of magnetic $NiFe_2O_4$ structure during the heating cycle of measurements up to $800^{\circ}C$ as well as to "field cooling process" and overall decrease in thermal energy during the following cooling cycle. $NiFe_2O_4$ phase formation has been confirmed by the subsequent XRD and MS phase analyses and its nanocrystalline structure by XRD and SEM/TEM techniques. Increase of the net magnetization and overall magnetic quality illustrated by the obtained hysteresis loop taken after TM measurements suggest the increased volume of magnetically active material and thus additionally support the previous findings.

References

1. C.B.Carter, M.G Norton, Ceramic materials: science and engineering, Springer, New York, 2007.
2. K.H.J. Buschow, F.R. de Boer, Physics of magnetism and magnetic materials, Kluwer Academic/Plenum Press, New York, 2003.
3. G.A. Sawatzky, F. van der Woude, A.H. Morrish, J. Appl. Phys., 39 (1968) 1204.
4. D. Kedem, T. Rothem, Phys. Rev. Lett., 18 (1967) 165.
5. S. Komarneni, E. Fregeau, E. Breval, R. Roy, J. Am. Ceram. Soc., 71(1) (1988) C26.
6. T. Pannaprayil, R. Marande, S. Komarneni, S.G. Sankar, J. Appl. Phys., 64 (1988) 5641.
7. T. Kodama, Y. Wada, T. Yamamoto, M. Tsuji, Y. Tamamura, J. Mater. Chem., 5(9) (1995) 1413.
8. .A. Ceylan, S. Ozcan, C. Ni, S.I. Shah, J. Magn. Magn. Mater., 320 (2008) 857.
9. K.V.P.M. Shafi, Y. Koltypin, A. Gedanken, R. Prozorov, J. Balogh, J. Lendvai, I. Felner, J. Phys. Chem. B, 101 (1997) 6409.
10. Y. Kinemuchi, K. Ishizaka, H. Suematsu, W. Jing, K. Yatsui, Thin Solid Films, 407 (2002) 109.
11. .A.S. Albuquerque, J.D. Ardisson, W.A.A. Macedo, J.L. López, R. Paniago, A.I.C. Persiano, J. Magn. Magn. Mater. 226-230 (2001) 1379.
12. V. Sepelak, D. Baabe, D. Mienert, D. Schultze, F. Krumeich, F.J. Litterstb, K.D. Becker, J. Magn. Magn. Mater. 257 (2003) 377.
13. S.N. Dolia, R. Sharma, M.P. Sharma, N.S. Saxena, Indian J. Pure Ap. Phy., 44 (2006) 774.
14. .A. Verma, T.C. Goel, R.C. Mediratta, Mater. Sci. Technol. 16 (2000) 712.
15. R.K. Tiwary, S.P. Narayan, O.P. Pandey, J. Min. Metall. B, 44B (2008) 91.
16. S.L. Darshane, S.S. Suryavanshi, I.S. Mulla, Ceramics International, 35 (2009) 1793.
17. X.R. Ye, D.Z. Jia, J.Q. Yu, X.Q. Xin, Z.L. Xue, Adv. Mater., 11 (1999) 941.
18. J.B.Wiley, R.B. Kaner, Science 255 (1992) 1093.
19. T. Žák, Y. Jirásková, Surf. Interface Anal., 38 (2006) 710.
20. N. Talijan, V. Ćosović, T. Žák, A. Grujić, J. Stajić-Trošić, J. Min. Metall. B,45B (1) (2009) 111.
21. G.F. Goya, Solid State Communications, 130 (2004) 783.
22. S. Kamali-M, T. Ericsson, R. Wäppling, Thin Solid Films, 515 (2006) 721.
23. J.-M. Grenèche and M. Miglierini, in Mössbauer Spectroscopy in Materials Science, edited by M. Miglierini and D. Petridis, Kluwer, Dordrecht, 1999.
24. .A.H. Morrish, K. Hanada, J. Appl. Phys., 52 (1981) 2496.

Садржај: *Испитивано је формирање магнетне $NiFe_2O_4$ структуре преко микоструктурне анализе, анализе фазног састава и мерења магнетних својстава. Испитивани материјал синтетисан је реакцијом у чврстој фази. Првобитном термичком обрадом полазне смеше оксида на 700^oC није постигнуто формирање жељене магнетне фазе. Накнадна термомагнетна мерења до 800^oC су показала значајан пораст укупног магнетног момента испитиваног материјала што је указало*

на промену фазног састава и формирање магнетне микроструктуре у току загревања. Формирање магнетне нанокристалне NiFe$_2$O$_4$ фазе је потврђено рендгенско-дифрактометријском анализом (XRD) и ^{57}Fe Mössbauer спектроскопском фазном анализом (MS). Морфологија и наночестична структура NiFe$_2$O$_4$ фазе је утврђена применом XRD, SEM и TEM анализа. Хистерезиси добијени магнетним мерењима јасно указују на промену магнетних својстава као последице промена у структури и фазном саставу, односно повећања удела магнетне NiFe$_2$O$_4$ фазе након термомагнетних мерења.

Кључне речи: *NiFe$_2$O$_4$ наночестице, реакција у чврстој фази, фазни састав, магнетна својства*