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Impact of chemical composition on preparation of nanodimensional spinel ferrites

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The nanostructured manganese and zinc ferrite-type materials were synthesized using preparation methods such as co-precipitation or co-precipitation and mechanochemical treatment. The physicochemical techniques – Powder X-ray diffraction analysis (PXRD), Mössbauer and Fourier transform infrared (FTIR) spectroscopy were performed in order to establish the phase composition, structure and magnetic behavior of prepared nanodimensional ferrite-type samples. The PXRD results determined that single non-stoichiometric ferrite phase ($Zn_xFe_{3-x}O_4$, x=0.25) as well as ferrite ($Zn_xFe_{3-x}O_4$, x=0.5;1, $Mn_xFe_{3-x}O_4$, x=0.25;0.5;1) and additional akaganeite phases were obtained by co-precipitation procedure. The presence of ferrite and iron phases and elimination of akaganeite was achieved using high-energy ball milling. The synthesized nanosized manganese and zinc ferrite-type materials possess the mean crystallite size about 7–13 nm and 6–13 nm respectively. The superparamagnetic (SPM) and collective magnetic excitations (CME) behavior of the obtained nanodimensional manganese and zinc ferrite-type samples was confirmed by Mössbauer study. In our investigations was determined the relationship on the chemical composition of obtained manganese and zinc ferrites and used methods – co-precipitation and mechanochemical treatment.

Key words: mechanochemical treatment, nanodimensional manganese and zinc ferrite-type materials.

INTRODUCTION

Presently, many researchers have focused their studies on the preparation of nanomaterials, such as spinel ferrite nanocrystals. These materials are interesting for investigations because of their surface effect (large surface-to-volume ratio) and quantum confinement effects (size-dependent properties). These factors influence their chemical and physical properties [1]. Magnetic mixed oxides with structural formula MFe_2O_4 (M = divalent ion, Co, Mg, Mn, Ni), are distinguished to be technologically important materials, because of their controllable properties such as high corrosion resistance, high thermodynamic stability, low magnetic transition temperature, low melting point, high specific heating and high electrical conductivity [2]. Nanocrystalline spinel ferrites can be broadly used in various fields, such as switching and magnetic devices, magnetic refrigeration, catalyst, permanent magnets, ferrofluids, targeted drug delivery, microwave and biomedical applications and sensor technology [3–8]. The attention is directed to the development and use of new approaches to control the morphologies of nanomaterials in order to find the better solution of environmental and health problems [9]. The controllable production of nanodimensional materials including magnetic nanomaterials is the basis for more detailed study of nanoscience and technology because the size, shape and structure of the materials are of great importance determining their catalytic, optical, mechanic or magnetic properties [10]. The synthesis methods for obtaining of nanoparticles which are more environmentally friendly, faster, and more energy efficient have attracted more attention. In this sense, the precipitation technique in aqueous chemistry could find a solution [11]. Mechanical milling is a simple, effective and energy saving method for preparation of nanostructures [12].

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The aim of the present paper is to investigate the impact of chemical composition on preparation of nanodimensional spinel ferrites. Therefore the series of manganese and zinc ferrite-type samples were obtained by different synthesis methods as co-precipitation or co-precipitation and mechanochemical treatment. The Powder X-ray diffraction analysis, Mössbauer and FTIR spectroscopy were used to study the changes in a chemical composition of ferrite materials.

EXPERIMENTAL

The co-precipitation procedure was carried out for preparation of manganese and zinc [13] ferrite-type materials *Sample A* – $Mn_{0.25}Fe_{2.75}O_4$, *Sample B* – $Mn_{0.5}Fe_{2.5}O_4$, *Sample C* – $MnFe_2O_4$, *Sample D* – $Zn_{0.25}Fe_{2.75}O_4$, *Sample E* – $Zn_{0.5}Fe_{2.5}O_4$ and *Sample F* – $ZnFe_2O_4$. The starting 0.03 M aqueous solutions of $FeCl_2{\bullet}4H_2O$, $FeCl_3{\bullet}6H_2O$ and $MnCl_2.4H_2O$ or $ZnCl_2$ were prepared and mixed in a ratio of 3:8:1, 1:4:1, 0:2:1. The pH values of mixtures were reached 12.5 and 13 by dropping a precipitant 0.3 M NaOH at continuous stirring. After co-precipitation procedure the mixtures was stirred for one hour. The prepared brown precipitates were centrifuged and washed with distilled water up to neutral reaction (pH=7). The products were dried at 35 °C. The co-precipitated *Sample A, Sample B*, *Sample C*, *Sample E* and *Sample F* were mechanochemically treated in order to obtain *Sample G* – $Mn_{0.25}Fe_{2.75}O_4$, *Sample H* – $Mn_{0.5}Fe_{2.5}O_4$, *Sample I* – $MnFe_2O_4$, *Sample J* – $Zn_{0.5}Fe_{2.5}O_4$ and *Sample K* – $ZnFe_2O_4$. The milling process was performed in argon (*Sample A* and *Sample B*), helium (*Sample E*) or air (*Sample C* and *Sample F*) atmosphere for 1 (*Sample F*) or 2 (*Sample A*, *Sample B*, *Sample C* and *Sample E*) hours and rotation speed 500 rpm. The weight ratio between sample and balls was 1:30. The Highenergy planetary ball mill type PM 100, Retsch, Germany and stainless steel grinding jar of 50 ml volume was used for mechanochemical treatment. The phase composition and magnetic behavior of obtained manganese and zinc ferrite-type materials were physicochemically characterized by Powder X-ray diffraction analysis, Mössbauer and FTIR spectroscopy. The PXRD spectra of manganese and zinc ferrite-type samples during the preparation were recorded on a TUR M62 apparatus with computer management and data collection, working with HZG-4 goniometer and CoKα radiation. The JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used to establish the phases. The average crystallite size, lattice microstrain parameter and unit cell parameter of the ferrite materials were estimated by Williamson-Hall diagram [14].

Mössbauer investigations were performed with apparatus Wissenschaftliche Elektronik GmbH, working with a constant acceleration mode, $^{57}Co/Rh$ source (activity ≈50 mCi) and α-Fe standard. The mössbauer parameters of hyperfine interactions of spectral components: isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the site of iron nuclei (H_{eff}), line widths (FWHM) and component relative weights (G) were determined by computer fitting. FTIR measurements were collected with a Fourier infrared spectrometers: Bruker-Vector 22 and IRAffinity-1 “Shimadzu”.

RESULTS AND DISCUSSION

On the Figures 1 and 2 are presented PXRD spectra of obtained nanostructured manganese and zinc ferrite-type materials. The co-precipitated *Samples A*, *B* and *C* contain manganese ferrite (PDF-73-1964) and additional akaganeite (PDF-34-1266) phases (Fig. 1). Powder X-ray diffractograms of zinc ferrite-type samples registered the presence of single non-stoichiometric zinc ferrite phase $Zn_xFe_{3-x}O_4$ (PDF-01-1109; 75-0449) for *Sample D*. The ferrite $Zn_xFe_{3-x}O_4$ (PDF-01-1109) and different amount of intermediate akaganeite (PDF-34-1266) phases are determined in co-precipitated *Samples E* and *F* (Fig. 2) [13]. The mechanochemical treatment of co-precipitated manganese and zinc ferrite-type materials after one or two hours in inert media (argon, helium) or air initiate the formation of spinel ferrite $Zn_xFe_{3-x}O_4$ or $Mn_xFe_{3-x}O_4$ and iron (Fe) (PDF-87-0721) phases in *Samples G*, *H*, *I*, *J* and K. The presence of iron phase in samples is due to contamination during the milling process. The additional akaganeite phase disappeared during the high-energy ball milling process. The calculated average crystallite size, lattice microstrain parameter and unit cell parameter of studied spinel ferrite phases are illustrated in Table 1. The determined values correspond to the prepared nanodimensional manganese and zinc ferrite materials with mean crystallite size about 7–13 nm and 6–13 nm.

The Mössbauer spectra at room temperature of obtained nanostructured manganese and zinc ferrite-type samples are shown on Figures 3 and 4. The spectra of *Samples A*, *B*, *D*, *G*, *I*, *J* and *K* are superposition of sextet and doublet components. The doublet lines only are registered in Mössbauer spectra of the other three co-precipitated *Samples C*, *E* and *F*. The calculated Mössbauer parameters after the best computer fitting of spectra with respective components are presented in Table 2. The calculated hyperfine parameters of sextet components can

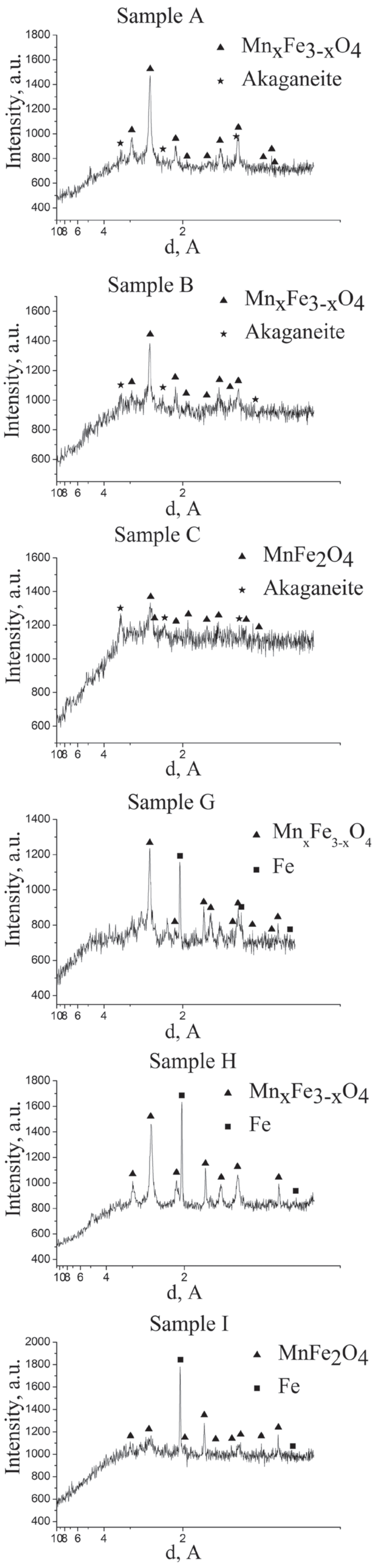

Fig. 1. PXRD patterns of synthesized nanosized manganese ferrite-type samples

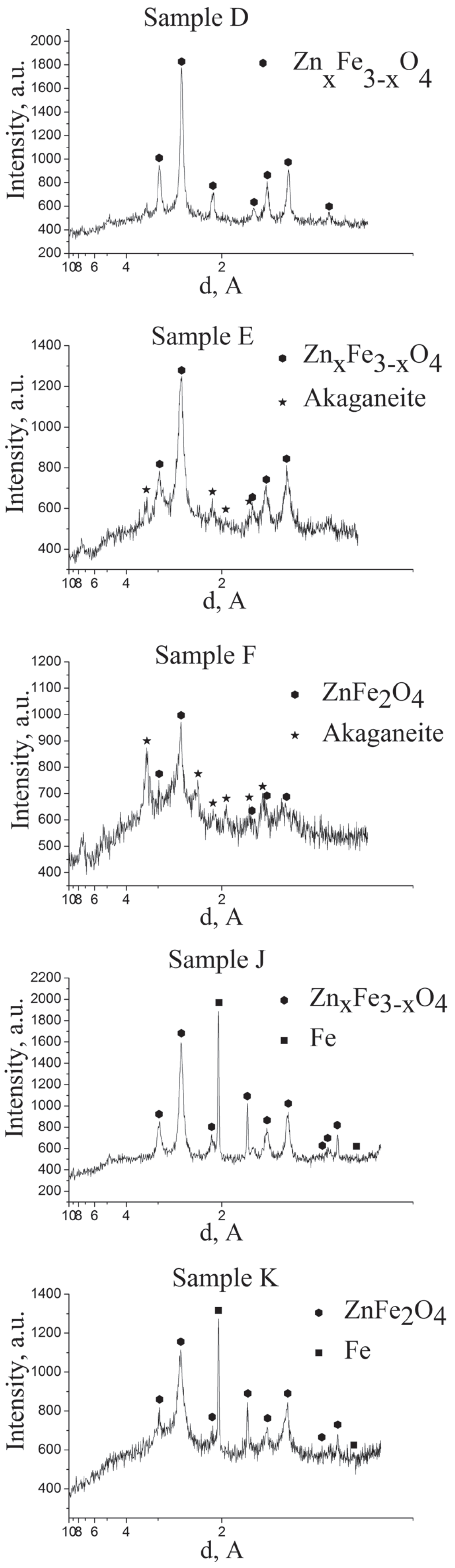

Fig. 2. PXRD patterns of synthesized nanosized zinc ferrite-type samples

Table 1. Calculated values of mean crystallite size (D), lattice strain (**ε**) and unit cell parameter (a) of ferrite phases

Sample	D, nm	ε, a.u	a, Å
Sample A	9.5	4.2.10^{-3}	8.485
Sample B	9.3	3.7.10^{-3}	8.489
Sample C	7.8	4.1.10^{-3}	8.497
Sample D	12.8	5.9.10^{-3}	8.412
Sample E	6.8	4.2.10^{-3}	8.421
Sample F	6.9	4.2.10^{-3}	8.447
Sample G	12.5	4.3.10^{-3}	8.415
Sample H	9.5	4.3.10^{-3}	8,486
Sample I	7.8	4.1.10^{-3}	8.496
Sample J	7.8	4.1.10^{-3}	8.383
Sample K	7.8	4.1.10^{-3}	8.382

be related to tetrahedrally coordinated Fe^{3+} ions in a spinel phase – Sxt1 and octahedrally coordinated $Fe^{2.5+}$ ions in a spinel phase – Sxt2 for *Sample D* [13]. The sextet component Sxt1 corresponds to iron ions show collective magnetic excitations (CME) behavior in RT spectra of *Samples A* and *B*. The calculated hyperfine parameters of doublet components in Mössbauer spectrum of *Sample D* could be attributed to the presence of ferrite particles with superparamagnetic (SPM) behaviour [13]. On the other hand the doublet components partially include also the existence of some iron ions in intermediate akaganeite phase (*Samples A*, *B*, *C*, *E* and *F*). The characteristic components for nanosized metal iron phase are registered in the spectra of mechanochemically treated manganese and zinc ferrite-type materials as doublet (Dbl), singlet (Sng) or sextet (Sxt) components belonging to iron rich and Mn or Zn rich regions [15]. In the Mössbauer spectra of *Samples G*, *I*, *J* and *K* after mechanochemical process are observed two superparamagnetic doublets attributed to the presence of ferrite particles with superparamagnetic (SPM) behavior. The determined hyperfine parameters of three (Sxt1, Sxt2 and Sxt3) or two (Sxt1 and Sxt2) sextet components can be attributed to iron ions show collective magnetic excitations (CME) behavior for *Samples G* and *H*. The presence of spinel phase presented by two sextet components – Sxt 1 due to tetrahedrally coordinated

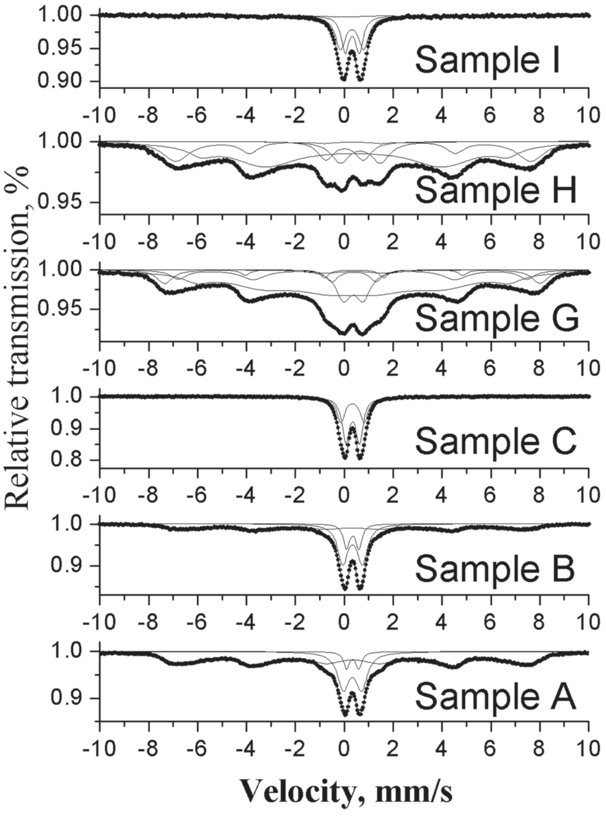

Fig. 3. Mössbauer spectra at room temperature of obtained nanodimensional manganese ferrite-type materials

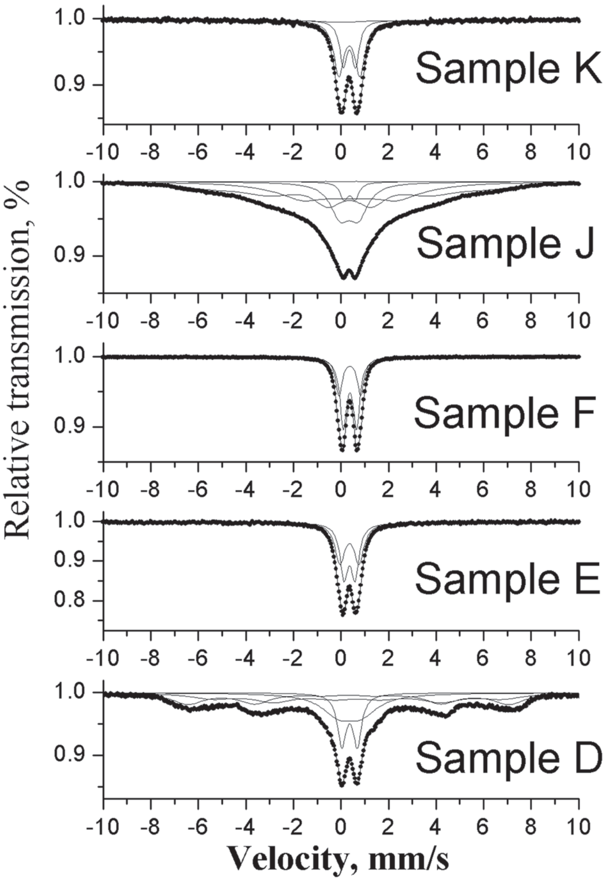

Fig. 4. Mössbauer spectra at room temperature of obtained nanodimensional zinc ferrite-type materials

Table 2. Mössbauer parameters of nanostructured manganese and zinc ferrite-type samples at RT

Sample	Components	IS, mm/s	QS, mm/s	H_{eff}, T	FWHM, mm/s	G, %
Sample A	Sxt 1 – Fe - spinel, CME	0.35	0	43.2	1.72	70
	Dbl 1 –SPM, core/Akaganeite	0.35	0.50	–	0.28	6
	Dbl 2 – SPM, shell/Akaganeite	0.34	0.75	–	0.57	24
Sample B	Sxt 1 – Fe – spinel, CME	0.35	0.03	42.6	1.85	52
	Dbl 1 –SPM, core/Akaganeite	0.35	0.51	–	0.30	13
	Dbl 2 – SPM, shell/Akaganeite	0.34	0.80	–	0.50	35
Sample C	Dbl 1 –SPM, core/Akaganeite	0.34	0.56	–	0.35	61
	Dbl 2 – SPM, shell/Akaganeite	0.34	0.95	–	0.39	39
Sample D	Sxt 1 – Fe^{3+}-tetra, spinel	0.29	0.01	42.0	1.61	29
	Sxt 2 – $Fe^{2.5+}$-octa, spinel	0.69	0	37.8	2.02	58
	Dbl 1 – SPM, core	0.36	0.66	–	0.44	21
	Dbl 2 – SPM, shell	0.36	0.97	–	1.62	22
Sample E	Dbl 1 –SPM, core/Akaganeite	0.36	0.47	–	0.39	51
	Dbl 2 – SPM, shell/Akaganeite	0.36	0.81	–	0.49	49
Sample F	Dbl 1 – SPM, core/Akaganeite	0.37	0.56	–	0.34	64
	Dbl 2 – SPM, shell/Akaganeite	0.37	0.92	–	0.33	36
Sample G	Sxt 1 – Fe – spinel, CME	0.36	–0.08	47.7	0.81	10
	Sxt 2 – Fe – spinel, CME	0.37	–0.06	44.3	0.82	13
	Sxt 3 – Fe – spinel, CME	0.35	0	39.7	1.34	61
	Dbl 1 – SPM, shell	0.37	0.80	–	0.74	12
	Dbl 2 – SPM, core	0.39	1.80	–	0.63	4
Sample H	Sxt 1 – Fe – spinel, CME	0.35	0.03	45.1	1.35	23
	Sxt 2 – Fe – spinel, CME	0.39	0.02	39.1	1.26	57
	Dbl – Fe – metal phase	0.01	1.53	–	0.81	19
	Sng – Fe – metal phase	–0.01	–	–	0.34	1
Sample I	Sxt - Fe – metal phase	0	–	10,2	6.1	14
	Dbl 1 –SPM, core	0.32	0.95	–	0.50	47
	Dbl 2 – SPM, shell	0.33	0.58	–	0.38	39
Sample J	Sxt – Fe – metal phase	0	0	24.8	0.57	1
	Sxt 1 – Fe^{3+} – tetra, spinel	0.36	–0.01	35.8	0.11	42
	Sxt 2 – Fe^{3+} – octa, spinel	0.38		21.3	3.04	33
	Dbl 1 – SPM, core	0.36	0.46	–	0.40	4
	Dbl 2 – SPM, shell	0.35	0.77	–	0.99	20
Sample K	Sxt – Fe – metal phase	0	0	10.6	5.04	12
	Dbl 1 – SPM, core	0.36	0.51	–	0.37	33
	Dbl 2 – SPM, shell	0.35	0.89	–	0.51	55

Fe^{3+} ions and Sxt 2 due to octahedrally coordinated Fe^{3+} ions are registered in the Mössbauer spectrum at RT of *Sample J*. The obtained Mössbauer results confirm the powder X-ray diffraction investigations about registered phases in synthesized ferrite samples. The FTIR spectra of co-precipitated and mechanochemically treated nanosized ferrite-type materials are displayed on Figure 5. The vibrations observed in the region 423–563 cm^{-1} are characteristic of the metal-oxygen bonds in the tetrahedral and octahedral sites of the spinel manganese and zinc ferrites [1, 4, 16]. The registered absorption bands at about 3423–3426 cm^{-1} and 1630–1637 cm^{-1} correspond to the stretching and bending vibrations of the OH groups [10]. The absorption bands at about 1195 cm^{-1} could be attributed to the stretching vibrations of Fe^{3+}–O^{2-} [17]. The FTIR spectra of co-precipitated nanostructured zinc ferrite-type samples are discussed in our previous study [13] in full. The FTIR investigations are in very good agreement with presented Powder X-ray diffraction and Mössbauer data.

CONCLUSIONS

The nanodimensional manganese and zinc ferrite-type materials were successfully obtained by co-precipitation or co-precipitation and mechanochemical treatment. The prepared ferrite-type samples have a high dispersity and average crystallite size between 7–13 nm and 6–13 nm. The relation

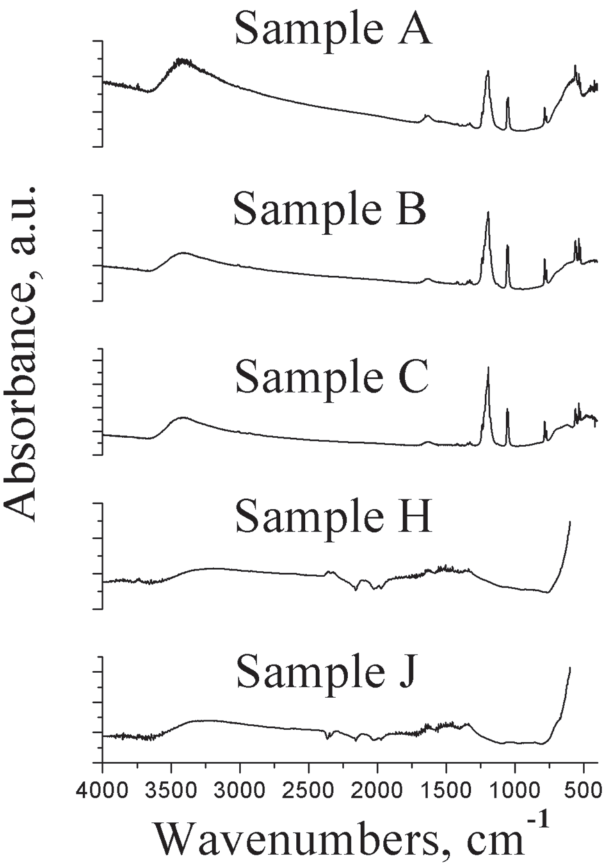

Fig. 5. FTIR spectra of prepared manganese ferrite-type and zinc ferrite-type nanopowders

between chemical composition of obtained manganese and zinc ferrite-type materials and different synthesis methods as co-precipitation and mechanochemical treatment was found. The presence of pure spinel ferrite phase is established in the case of an obtained nanosized $Zn_xFe_{3-x}O_4$, x=0.25 by chemical co-precipitation method. The additional intermediate phase as akaganeite is observed in other co-precipitated manganese and zinc containing ferrite samples. The removal of additional akaganeite phase in manganese and zinc ferrite-type materials was realized by the mechanochemical treatment. The formation of spinel ferrite and iron phases is observed during the milling process. The Mössbauer studies at room temperature established that synthesized manganese and zinc containing ferrite materials possess superparamagnetic (SPM) and collective magnetic excitations (CME) behavior.

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REFERENCES

1. M. Goodarz Naseri, E. Bin Saion, H. Abbastabar Ahangar, M. Hashim, A.H. Shaari, *Journal of Magnetism and Magnetic Materials*, **323**, 1745 (2011).
2. D. Gherca, N. Cornei, O. Mentré, H. Kabbour, S. Daviero-Minaud, A. Pui, *Applied Surface Science*, **287**, 490 (2013).
3. D. Chen, H.-Y. Liu, L. Li, *Materials Chemistry and Physics*, **134**, 921 (2012).
4. S. Mohapatra, S. R. Rout, A. B. Panda, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **384**, 453 (2011).
5. Z. Ž. Lazarević, Č. Jovalekić, A. Recnik, V. N. Ivanovski, M. Mitrić, M. J. Romčević, N. Paunović, B.P. Cekić, N. Ž. Romčević, *Journal of Alloys and Compounds*, **509**, 9977 (2011).
6. D. Gherca, A. Pui, V. Nica, O. Caltun, N. Cornei, *Ceramics International*, **40**, 9599 (2014).
7. N. M. Deraz, S. Shaban, *J. Anal. Appl. Pyrolysis*, **86**, 173 (2009).
8. D. Chen, Y. Zhang, Z. Kang, *Chemical Engineering Journal*, **215–216**, 235 (2013).
9. H. Chen, P. K. Chu, J. He, T. Hu, M. Yang, *Journal of Colloid and Interface Science*, **359**, 68 (2011).
10. P. Guo, G. Zhang, J. Yu, H. Li, X. S. Zhao, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **395**, 168 (2012).
11. F. Giovannelli, C. Autret-Lambert, C. Mathieu, T. Chartier, F. Delorme, A. Seron, *Journal of Solid State Chemistry*, **192**, 109 (2012).
12. T. Şimşek, S. Akansel, Ş. Özcan, A. Ceylan, *Ceramics International*, **40**, 7953 (2014).
13. K. Zaharieva, Z. Cherkezova-Zheleva, B. Kunev, M. Shopska, V. Petkova, J. Krstić, I. Mitov, *Nanoscience and Nanotechnology* **14** (Eds. E. Balabanova, E. Mileva), (2014), 39-42.
14. G. K. Williamson, W. H. Hall, *Acta Metallurgica*, **1** (1), 22 (1953).
15. O. G. Sokhalov, A. V. Katsov, G. V. Karpenko, Superplasticity and corrosion strength of two phase Fe-Mn alloy, Naukova Dumka, Kiev, 1977.
16. G. Fan, Z. Gu, L. Yang, F. Li, *Chemical Engineering Journal*, **155**, 534 (2009).
17. K. Ahalya, N. Suriyanarayanan, V. Ranjithkumar, *Journal of Magnetism and Magnetic Materials*, **372**, 208 (2014).

ВЛИЯНИЕ НА ХИМИЧНИЯ СЪСТАВ ВЪРХУ ПОЛУЧАВАНЕТО НА НАНОРАЗМЕРНИ ШПИНЕЛНИ ФЕРИТИ

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(Резюме)

Наноструктурирани манганови и цинкови феритен тип материали бяха синтезирани чрез използване на методи като съутаяване или съутаяване и механохимична обработка. Бяха използвани физикохимични техники – рентгенофазов анализ, мьосбауерова и инфрачервена спектроскопия с фурие трансформация с цел да бъде установен фазовия състав, структура и магнитното поведение на получените наноразмерни феритен тип проби. Резултатите от рентгенофазовия анализ показаха, че еднофазен нестехиометричен ферит ($Zn_xFe_{3-x}O_4$, x=0,25), а също така ферит ($Zn_xFe_{3-x}O_4$, x=0,5; 1, $Mn_xFe_{3-x}O_4$, x=0,25; 0,5; 1) и допълнителна фаза акагенит бяха получени чрез процедура на съутаяване. Присъствието на феритна и желязна фаза и премахването на акаганеита беше постигнато чрез използване на високоенергийно мелене. Синтезираните наноразмерни манганови и цинкови феритен тип материали имат съответно среден размер на кристалита 7–13 nm и 6–13 nm. Суперпарамагнитното поведение и колективното магнитно възбуждане на получените наноразмерни манганови и цинкови феритен тип проби беше потвърдено от Мьосбауеровите изследвания. В нашите изследвания беше намерена връзка между химичния състав на получените манганови и цинкови ферити и използваните методи – съутаяване и механохимична обработка.