Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 7, Part 1
ISSN 1313-2539, Published at: http://www.scientific-publications.net

SYNTHESIS ROUTE AND STRUCTURAL PROPERTIES OF NANOFERRITES

Katerina Zaharieva, Zara Cherkezova-Zheleva, Boris Kunev, Maya Shopska, Ivan Mitov
Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St.,
Bl.11, 1113 Sofia, Bulgaria

Abstract

The nanodimensional magnesium ferrite materials $Mg_{0.25}Fe_{2.75}O_4$, $Mg_{0.5}Fe_{2.5}O_4$ and $MgFe_2O_4$ with different stoichiometry were prepared by co-precipitation procedure using $MgCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ and NaOH as precipitant. The physicochemical methods - X-ray diffraction analysis, Moessbauer spectroscopy and FTIR spectroscopy were performed to investigate the structural properties of obtained nanosize magnesium ferrite type samples. The registered experimental data were determined the presence of spinel ferrites and additional precursor phases as iron oxihydroxides and double layered hydroxides in ferrite materials $Mg_xFe_{3-x}O_4$ (x=0.5;1). In the case of magnesium ferrite sample $Mg_xFe_{3-x}O_4$ (x=0.25) the existence of non-stoichiometric spinel ferrite and intermediate phase - iron oxihydroxides were observed only.

Key words: *magnesium ferrites, co-precipitation, physicochemical methods*

1. INTRODUCTION

Spinel ferrites with the general formula AFe_2O_4 (A = Mn, Co, Ni, Mg, or Zn) are very important magnetic materials because of their interesting magnetic and electrical properties combined with chemical and thermal stabilities (S. Maensiri, M. Sangmanee, A. Wiengmoon, 2009, Y.M.Z. Ahmed, E.M.M. Ewais, Z.I. Zaki, 2010). The general formula of magnesium ferrite, $MgFe_2O_4$, could be written as $(Mg_{1-x}Fe_x)[Mg_xFe_{2-x}]O_4$, where parentheses and square brackets denote cation sites of tetrahedral (A) and octahedral [B] coordination, respectively. The subscript letter x represents the so-called degree of inversion (defined as the fraction of the (A) sites occupied by Fe^{3+} cations) (Y.M.Z. Ahmed, E.M.M. Ewais, Z.I. Zaki, 2010). Magnesium ferrite, $MgFe_2O_4$, is a soft magnetic n-type semiconducting material which finds a great number of applications in heterogeneous catalysis, adsorption, sensors, magnetic technologies and components for biomedical applications (M.G. Ferreira da Silva, M.A. Valente, 2012, S.K. Pradhan, S. Bid, M. Gateshki, V. Petkov, 2005). Nanoparticles of $MgFe_2O_4$ have good photoelectrical properties (A. Pradeep, P. Priyadharsini, G. Chandrasekaran, 2008). Magnesium ferrites ($MgFe_2O_4$), having a spinel structure, show a rectangular hysteresis loop, making them highly suitable for use in the area of memory and switching circuits of digital computers, and in low-loss microwave devices in microwave radar system (Jong-Gyu Paik, Man-Jong Lee, Sang-Hoon Hyun, 2005). There are several methods for synthesizing nanosized magnesium spinel ferrite particles, such as ceramic, co-precipitation, microwave hydrothermal method,, sol gel, citrate gel process, combustion method, high energy milling, and mechanical alloying (M. Rashad, 2007). The main direction in current research investigation is the preparation of nanodimensional magnesium ferrite materials by co-precipitation method. The other important aspect of our research study is the physicochemical characterization of obtained magnesium ferrite samples using X-ray diffraction analysis, Moessbauer and FTIR spectroscopy.

2. EXPERIMENTAL

2.1. Synthesis route of magnesium ferrites

The magnesium ferrite type materials **Sample A** - $Mg_{0.25}Fe_{2.75}O_4$, **Sample B** - $Mg_{0.5}Fe_{2.5}O_4$, and **Sample C** - $MgFe_2O_4$ were synthesized using co-precipitation technique. The preparation method was carried out with 0.03 M aqueous solutions of $FeCl_2 \bullet 4H_2O$, $FeCl_3 \bullet 6H_2O$ and $MgCl_2 \bullet 6H_2O$ mixed in a ratio of 3:8:1, 1:4:1, 0:2:1. The precipitant 0.3 M NaOH was added by dropwise into the mixture until pH became 12.5. The co-precipitation method was conducted under constant stirring. After co-precipitation the prepared mixture was stirred for one hour. The obtained brown precipitates were centrifuged and washed with distilled water up to neutral reaction at pH=7. The products were dried at 35 ^oC.

2.2. Physicochemical techniques for investigation of magnesium ferrites

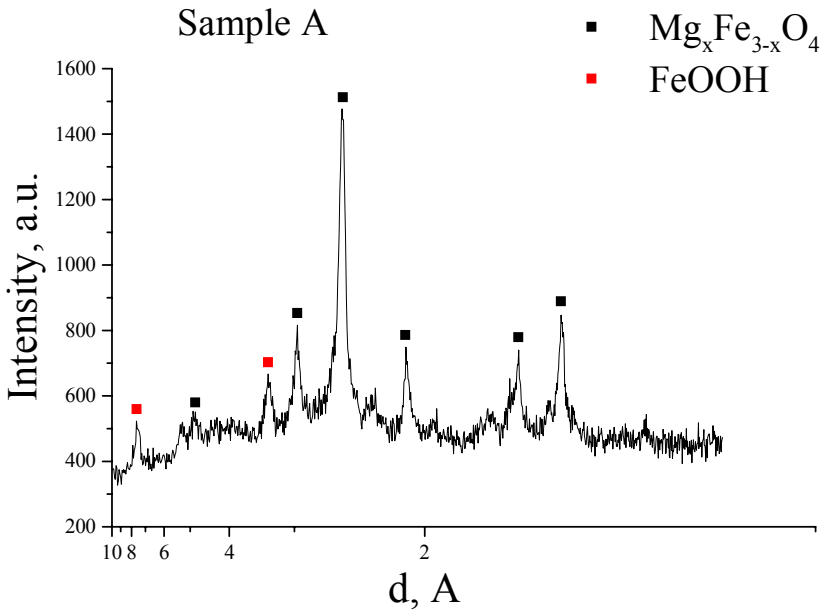
The phase composition of prepared nanosize magnesium ferrite samples was investigated by X-ray diffraction (XRD) analysis carried out with a TUR M62 apparatus with PC management and data accumulation, using HZG-4 goniometer and CoKα radiation. JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used to determine the presence of phases. The magnetic structure and behavior of obtained nanodimensional ferrite materials was established by Moessbauer spectroscopy on the apparatus Wissenschaftliche Elektronik GmbH, working with a constant acceleration mode, $^{57}Co/Cr$ source, α-Fe standard. The computer fitting was used to calculate the parameters of hyperfine interactions of Moessbauer spectral components: isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the site of iron nuclei (H_{eff}), line widths (FW) and component relative weights (G). FTIR measurements were performed with a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) in the middle (400-4000 cm^{-1}) region by KBr pellets technique.

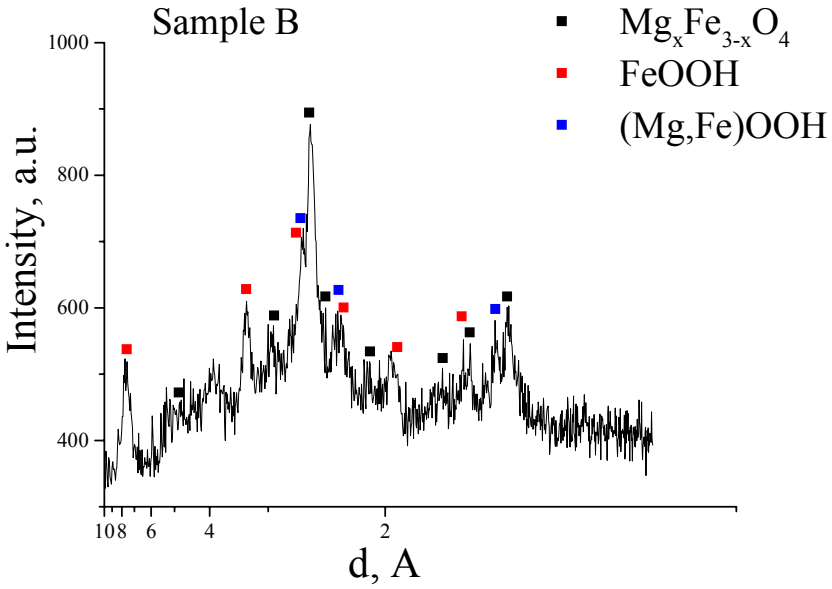
3. RESULTS AND DISCUSSION

X-ray diffraction patterns of synthesized series magnesium ferrite materiaals **Sample A** - $Mg_{0.25}Fe_{2.75}O_4$, **Sample B** - $Mg_{0.5}Fe_{2.5}O_4$, and **Sample C** - $MgFe_2O_4$ are presented on Fig. 1. In the diffractograms of all prepared ferrite samples are detected the diffraction lines corresponding to the spinel ferrite phase $Mg_xFe_{3-x}O_4$ (PDF-88-1943; 75-0449). Also the diffraction peaks reveal to the different content of additional intermediate phases as β-FeOOH (PDF-75-1594) and/or iron-magnesium hydrotalcite (PDF-14-0191) are indexed in the XRD spectra of **Sample A** - $Mg_{0.25}Fe_{2.75}O_4$, **Sample B** - $Mg_{0.5}Fe_{2.5}O_4$, and **Sample C** - $MgFe_2O_4$.

The mean crystallite size, lattice strain and unite cell parameter of spinel ferrite phase estimated by Scherrer equation (U. Schwertmann, R. Cornell, 1991) are shown in Table 1. As can be seen the calculated value of average particle size of magnesium ferrite materials is about 9.1 nm. It was found that magnesium ferrite sample **Sample A** - $Mg_{0.25}Fe_{2.75}O_4$ containing low quantity magnesium ions in ferrite structure possess the biggest average particle size (11,7 nm) compared with **Sample B** - $Mg_{0.5}Fe_{2.5}O_4$, and **Sample C** - $MgFe_2O_4$ (7.8 nm).

ISSN 1313-2539, Published at: http://www.scientific-publications.net





ISSN 1313-2539, Published at: http://www.scientific-publications.net

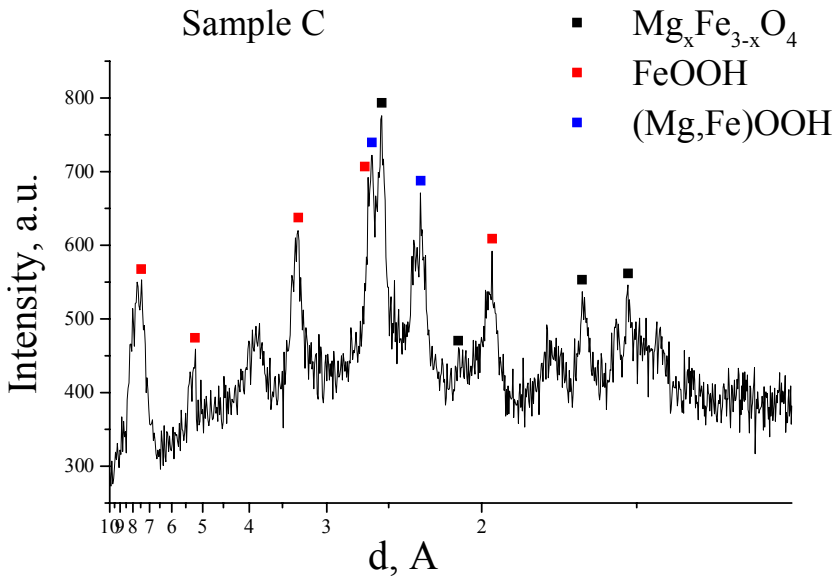


Fig. 1. XRD patterns of obtained samples.

Table 1. Mean crystallite size (D), lattice strain (e) and unite cell parameter (a) of spinel ferrite phase.

Sample	D, nm	e, a.u	a, A
$Mg_{0.25}Fe_{2.75}O_4$	11,7	$3,8.10^{-3}$	8.3798
$Mg_{0.5}Fe_{2.5}O_4$	7,8	$4,2.10^{-3}$	8.3742
$MgFe_2O_4$	7,8	$4,2.10^{-3}$	8.4144

The Moessbauer spectra at room temperature of synthesized nanosize magnesium contained ferrite samples are displayed on Fig. 2. The best fitting of the spectra is made by using CONFIT program. The spectrum of **Sample A** is superposition of sextet and doublet lines. The presence of two doublet components only are registered in the cases of others two samples – **Sample B** and **Sample C**. The calculated Moessbauer parameters are presented in Table 2. The calculated hyperfine parameter values of doublet components could be due to the presence of iron ions in ultradisperse ferrite particles with superparamagnetic (SPM) behaviour and size bellow 10 nm (U. Schwertmann, R. Cornell, 1991, F.Nakagomi et al., 2009, Q. Xu et al., 2009). On the other hand the doublet components partially include also the existence of some iron ions in intermediate phase (oxihydroxide or hydrotalcite phase) (U. Schwertmann, R. Cornell, 1991, M. R. Schütz, A. E. Schedl, F. E. Wagner, J. Breu, 2011). The calculated values of hyperfine parameters belong to the sextet components could be associated with the presence of highly disperse ferrite phase with size bellow 20 nm demonstrating collective magnetic excitations (CME) behaviour (U. Schwertmann, R. Cornell, 1991, F.Nakagomi et al., 2009, Q. Xu et al., 2009). The tetrahedrally and octahedrally coordinated iron ions in a spinel phase are differentiated only in the Moessbauer spectrum of **Sample A**.

ISSN 1313-2539, Published at: http://www.scientific-publications.net

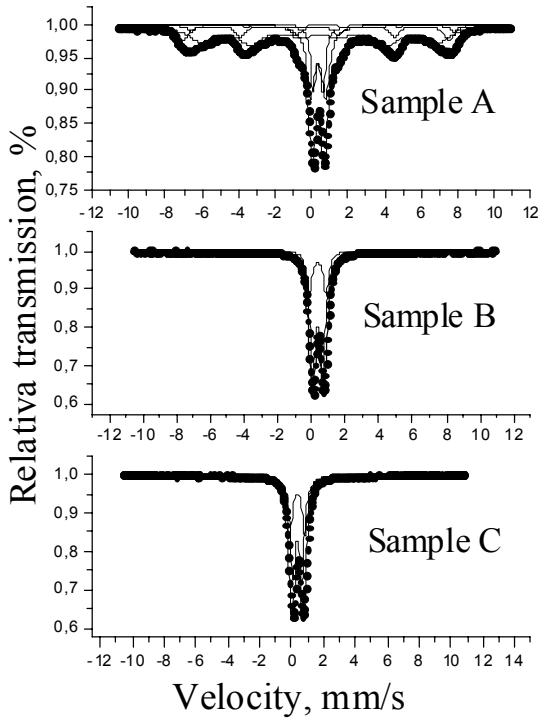


Fig. 2. Moessbauer spectra of synthesized samples.

Table 2. Moessbauer parameters of samples.

Sample	Components	IS, mm/s	QS, mm/s	H_{eff}, T	FMHW, mm/s	G, %
Sample A	Sxt. 1	0.28	0.06	45.2	0.64	14
	Sxt. 2	0.62	0.05	44.7	0. 47	8
	Sxt. 3	0.43	0.02	39.6	1.64	42
	Dbl. 1	0.36	0.57	-	0.36	20
	Dbl. 2	0.36	0.92	-	0.44	16
Sample B	Dbl. 1	0.36	0.58	-	0.42	58
	Dbl. 2	0.36	0.98	-	0.45	42
Sample C	Dbl. 1	0.36	0.59	-	0.40	61
	Dbl. 2	0.36	0.97	-	0.42	39

IR spectra of the synthesized samples are shown in Fig. 3. The absorption band at about 570 cm^{-1} can be attributed to metal-oxygen vibration in the spinel ferrite structure. This band is characteristic for Fe-O bond at tetrahedral site (S. Maensiri, M. Sangmanee, A. Wiengmoon, 2009, A. Pradeep, P. Priyadharsini, G. Chandrasekaran, 2008, P.P. Hankare et al., 2009, Y. Huang, Y. Tang, J. Wang, Q. Chen, 2006). IR bands/shoulders positioned at about 430, 670 and 840 cm^{-1} are assigned to vibration Mg-O (H. Dhaouadi, H. Chaabane, F. Touati, 2011). The bands of low intensity positioned at about 1074 cm^{-1}, 1375 cm^{-1}, 1495 cm^{-1} and the band at 1551 cm^{-1} show presence of CO_3^{2-} groups and hydrocarbon groups HCO_3^- (J.T. Kloprogge, R.L. Frost, L. Hickey, 2004, William B. White, 1971). Bands characteristic for the presence of physically adsorbed on the surface water molecules, OH groups bound with hydrogen bond and isolated on the surface OH groups are available at about 1631, 3430 and 3740 cm^{-1}, respectively (L. Little, 1966). The literature data presented that such vibrations are characteristic for the brucite-like layer ascribed to layered doubled hydroxides, interlayer water and incorporated carbonate groups in such structures (Kok-Hui Goh, Teik-Thye Lim, Zhili Dong, 2008). Collected infrared spectra show also weak bands at about 2850 and 2925 cm^{-1} can be assigned to the C-H vibrations characteristic for hydrocarbons (L. Little, 1966). Their presence is due to contaminations of used during measurement KBr.

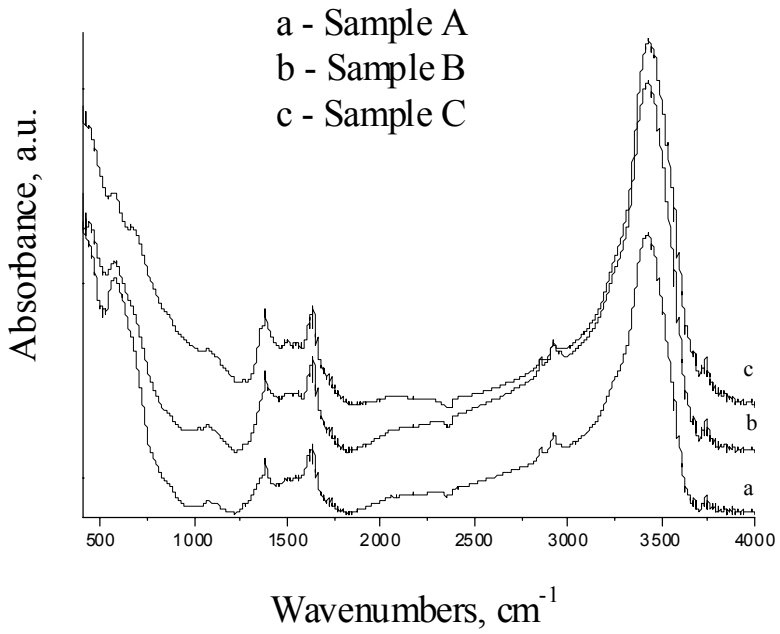


Fig. 3. FTIR spectra of prepared samples.

4. CONCLUSIONS

The nanosize magnesium ferrite type materials $Mg_xFe_{3-x}O_4$, $0 \leq x \leq 1$ with different content of magnesium were produced by direct co-precipitation method using chloride compounds as starting reagents. The used physicochemical methods XRD, FTIR and Moessbauer spectroscopy in our research study established the presence of spinel ferrites and different quantity of additional phases - double layered hydroxide and/or oxihydroxide in synthesized nanoferrite powders $Mg_xFe_{3-x}O_4$

(x=0.25;0.5;1). The obtained results confirmed that prepared magnesium ferrite samples possess high dispersity and average crystallite size bellow 20 nm. The obtained magnesium ferrite materials possess superparamagnetic and collective magnetic excitations behaviour and therefore they could be find potential application as magnetic materials.

ACKNOWLEDGEMENTS

Financial support by the European Social Fund within the framework of Operating Program "Development of Human Resources" (BG051PO001-3.3.06-0050) for covering the expenses for participation in Materials, Methods & Technologies, 15th International Symposium, Sunny Beach, Bulgaria-2013 is gratefully acknowledged.

The present research work was sponsored by the Bulgarian National Science Fund under Project DFNI-E 01/7/2012.

REFERENCES

Ahmed, Y.M.Z., Ewais, E.M.M., Zaki, Z.I. (2010) In situ synthesis of high density magnetic ferrite spinel ($MgFe_2O_4$) compacts using a mixture of conventional raw materials and waste iron oxide. Journal of Alloys and Compounds, vol. 489, pp. 269–274.

Dhaouadi, H., Chaabane, H., Touati, F. (2011) $Mg(OH)_2$ Nanorods synthesized by a facile hydrothermal method in the presence of CTAB. Nano-Micro Lett., vol. 3, number 3, pp. 153-159.

Ferreira da Silva, M.G., Valente, M.A. (2012) Magnesium ferrite nanoparticles inserted in a glass matrix—Microstructure and magnetic properties. Materials Chemistry and Physics, vol. 132, pp. 264–272.

Goh, Kok-Hui., Lim, Teik-Thye., Dong, Zhili. (2008) Application of layered double hydroxides for removal of oxyanions: A review. Water Research**,** vol. 42, pp. 1343 – 1368.

Hankare, P.P., Vader, V.T., Patil, N.M., Jadhav, S.D., Sankpal, U.B., Kadam, M.R., Chougule, B.K., Gajbhiye, N.S. (2009) Synthesis, characterization and studies on magnetic and electrical properties of Mg ferrite with Cr substitution. Materials Chemistry and Physics, vol. 113, pp. 233–238.

Huang, Y., Tang, Y., Wang, J., Chen, Q. (2006) Synthesis of $MgFe_2O_4$ nanocrystallites under mild conditions, Materials Chemistry and Physics, vol. 97, pp. 394–397.

Kloprogge, J.T., Frost, R.L., Hickey, L. (2004) FT-Raman and FT-IR spectroscopic study of the local structure of synthetic Mg/Zn/Al-hydrotalcites. Journal of Raman Spectroscopy, vol. 35, pp. 967-974.

Little, L. (1966) Infrared spectra of adsorbed species. Academic press Inc., London, New York.

Maensiri, S., Sangmanee, M., Wiengmoon, A. (2009) Magnesium ferrite ($MgFe_2O_4$) nanostructures fabricated by electrospinning. Nanoscale Res Lett., vol. 4, pp. 221–228.

Nakagomi, F., da Silva, S.W., Garg, V.K., Oliveira, A.C., Morais, P.C., Franco Jr, A. (2009) Influence of the Mg-content on the cation distribution in cubic $Mg_xFe_{3-x}O_4$ nanoparticles. Journal of Solid State Chemistry, vol. 182, pp. 2423–2429.

Paik, Jong-Gyu., Lee, Man-Jong., Hyun, Sang-Hoon. (2005) Reaction kinetics and formation mechanism of magnesium ferrites", Thermochimica Acta, vol. 425, pp. 131–136.

Pradeep, A., Priyadharsini, P., Chandrasekaran, G. (2008) Sol– gel route of synthesis of nanoparticles of $MgFe_2O_4$ and XRD, FTIR and VSM study. Journal of Magnetism and Magnetic Materials, vol. 320, pp. 2774– 2779.

Pradhan, S.K., Bid, S., Gateshki, M., Petkov, V. (2005) Microstructure characterization and cation distribution of nanocrystalline magnesium ferrite prepared by ball milling. Materials Chemistry and Physics, vol. 93, pp. 224–230.

Rashad, M. (2007) Magnetic properties of nanocrystalline magnesium ferrite by co-precipitation assisted with ultrasound irradiation. J Mater Sci., vol. 42, pp. 5248–5255.

Schütz, M. R.,. Schedl, A. E.,. Wagner, F. E., Breu J. (2011) Complexing agent assisted synthesis of high aspect ratio Fe^{3+}/Mg^{2+} layered double hydroxides. Applied Clay Science, vol. 54, pp. 281–286.

Schwertmann, U., Cornell, R. (1991) Iron Oxides in the Laboratory. Weinheim, New York-Basel-Cambridge.

William B. White. (1971) Infrared Characterization of water and hydroxyl ion in the basic magnesium carbonate minerals. The American Mineralogist, vol. 56, pp. 46-53.

Xu, Q., Wei Y., Liu Y., Ji, X., Yang, L., Gu, M. (2009) Preparation of Mg/Fe spinel ferrite nanoparticles from Mg/Fe-LDH microcrystallites under mild conditions. Solid State Sciences, vol. 11, pp. 472–478.