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LOW-TEMPERATURE SYNTHESIS OF SUPERPARAMAGNETIC $Zn_{0.8}Ni_{0.2}Fe_2O_4$ FERRITE NANOPARTICLES

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Abstract. The crystalline nanoparticles of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ ferrite were synthesized by chemical co-precipitation with precursor concentration of 0.1 M, then modified by 0.25 M solution of oleic acid in 1-pentanol and finally heated at low temperatures 120, 140, 160 and 180 ^oC for 6 h in autoclave. The effect of heating temperature on crystallite size and magnetic properties of ferrite was studied. The analysis of XRD, EDS and TEM data of samples confirmed that all of samples heated at these temperatures are crystalline with particle size of 6, 6.5, 7 and 8 nm, respectively. With the particles size below 10 nm, the nanoparticles of ferrite demonstrated the superparamagnetic properties, and could be applied effectively in various fields: medicine, treatment, military etc. The magnetic properties of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ ferrite measured by vibrating sample magnetometer (VSM) showed that the coercive force H_c and the remanence M_r of samples are about zero while the saturation magnetization M_s has values of 14.2, 25.4, 26.8 and 27.1 emu/g, consequently.

Keywords: crystalline nanoparticles**,** $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite, magnetic properties, superparamagnetism (SPM).

Classification number: 2.2.1; 2.10.2.

1. INTRODUCTION

The superparamagnetic nanoparticles of Zn-Ni-Fe ferrite system are used currently for special applications such as target-directed medicine, cancer treatment, contrast enhancer of magnetic resonance imaging, enhancement of radar wave absorption, ferro-fluid, etc. [1, 2]. Superparamagnetism (SPM) is a type of magnetism that occurs in small ferromagnetic or ferrimagnetic nanoparticles. Crystallite size of SPM is of around a few to 10 nanometers, depending on the material. In the superparamagnetic nature, ferromagnetic or ferrimagnetic nanoparticles have coercive force H_c = 0 and remanence M_r = 0, similar to paramagnetic materials, but their saturation magnetization M_s is many times higher than that of paramagnetic materials [3, 4].

There are several methods used for the synthesis of ferrite nanoparticles such as co-precipitation, sol-gel technique and hydrothermal method, etc. [5-7]. The Zn-Ni ferrites have been synthesized by chemical co-precipitation method with high annealing temperature [8-10] and by hydrothermal method [11-13]. A synthesis of cobalt ferrite assisted with the oleic acid is to avoid the agglomeration studied by Sonja Jovanović [7]. This research had synthesized the cobalt ferrite using hydrothermal method heating only at 180 ^{o}C for 16 h. The study indicated that, for the oleic acid concentration up to 0.25 M the average crystallite size decreased with the oleic acid concentration, while further addition of oleic acid had only a small influence on the average crystallite size. At the oleic acid concentration of 0.25 M, obtained particles were spherical, of about 6 nm in diameter and they were well-dispersed and non-agglomerated [7].

In the present paper, nanoparticles of $Zn_{0,8}Ni_{0,2}Fe_2O_4$ ferrite were first synthesized by chemical co-precipitation, then modified by 0.25 M oleic acid [7] and finally heated at different temperatures of 120, 140, 160 and 180^{o}C in 6 h (autoclave heating). This study aims to understand how the heating temperature influences on the crystallite size and magnetic properties of the ferrite.

2. EXPERIMENTAL

2.1. Chemicals

The chemicals such as $FeCl_3.6H_2O$ - Merck (Germany), $ZnCl_2$ - Merck (Germany), $NiCl_2.6H_2O$ - Merck (Germany), 1-Pentanol ($C_5H_{12}O$) - Merck (Germany), n-Hexane (C_6H_{14}) - (China), Oleic acid ($C_{18}H_{34}O_2$) - Sigma Aldrich (US) and Ethanol - (China) were used for the synthesis.

2.2. Synthesis of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite

Each salt type was dissolved in double distilled water to the concentration of 0.1 M. Solution of each salt was mixed and heated at 60 ^{o}C with a stirring speed of 500 rev/min. A 25 % ammonia solution was then added to the above mixture drop by drop while stirring kept constant. The addition of ammonia was stop when pH maintained at 8.5. To avoid agglomeration of particles, 0.25 M solution of oleic acid in pentanol dropped into the mixture at 60 ^{o}C with stirring. The mixture was then heated to 80 ^{o}C and stirring stopped when the smell of ammonia disappeared (about 1 h). Finally, to study the effect of heating temperature on crystallite size and magnetic properties of ferrite, the mixture was heated at temperatures of 180, 160, 140 and 120 ^{o}C for 6 h in autoclave. Products were obtained in the form of precipitates and then, separated from water by the magnet and washed several times by re-dispersing in n-hexane and precipitating with ethanol to remove salt residues and other impurities.

The formation of ferrite nanoparticles passed a two-step process. In the first step, hydroxide nanoparticles were co-precipitated from the metal salts and ammonia solution and then were capped from each other by oleic acid (*co-precipitation step*). The oleic acid initially reacted with the ammonia to form ammonium oleate. Additional heating could decompose ammonium oleate to ammonia gas and oleate ions, which can be attached to and surround the hydroxide nanoparticles. The mentions above can be expressed in the following chemical reactions:

$$0.2Ni^{2+} + 0.8Zn^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow 0.2Ni(OH)_2 0.8Zn(OH)_2 2Fe(OH)_3\downarrow \quad (1)$$

$$NH_4OH + C_{17}H_{33}COOH\ (heating) \rightarrow C_{17}H_{33}COONH_4 + H_2O \quad (2)$$

$$C_{17}H_{33}COONH_4\ (heating) \rightarrow C_{17}H_{33}COOH + NH_3 \quad (3)$$

$$C_{17}H_{33}COO + Ni^{2+}/Zn^{2+}/Fe^{3+}\ (heating) \rightarrow C_{17}H_{33}COO(Ni/Zn/Fe) \quad (4)$$

The second step consists of transformation of hydroxides into nanoferrites occurring when the samples were heated at appropriate temperatures in autoclave (*ferritization step*) as follows:

$$0.2Ni(OH)_2 0.8Zn(OH)_2 2Fe(OH)\ (heating) \rightarrow Ni_{0.2}Zn_{0.8}Fe_2O_4 + 4H_2O \quad (5)$$

At this step, the crystalline nanoparticles of ferrite are formed and grow up. The growth of ferrite nanoparticles is hindered by capped layer of metal oleate. As a result, crystalline nanoparticles of ferrite can be obtained at appropriate heating temperature.

2.3. Characterization

Structure of ferrite was studied by X-ray diffraction (XRD). Microstructure was observed by Transmission Electron Microscope (TEM). Chemical composition of ferrite was determined by Energy Dispersive X-rays Spectroscopy (EDS). Magnetic properties of ferrite were measured by Vibrating Sample Magnetometer (VSM).

3. RESULTS AND DISCUSSION

3.1. Chemical composition

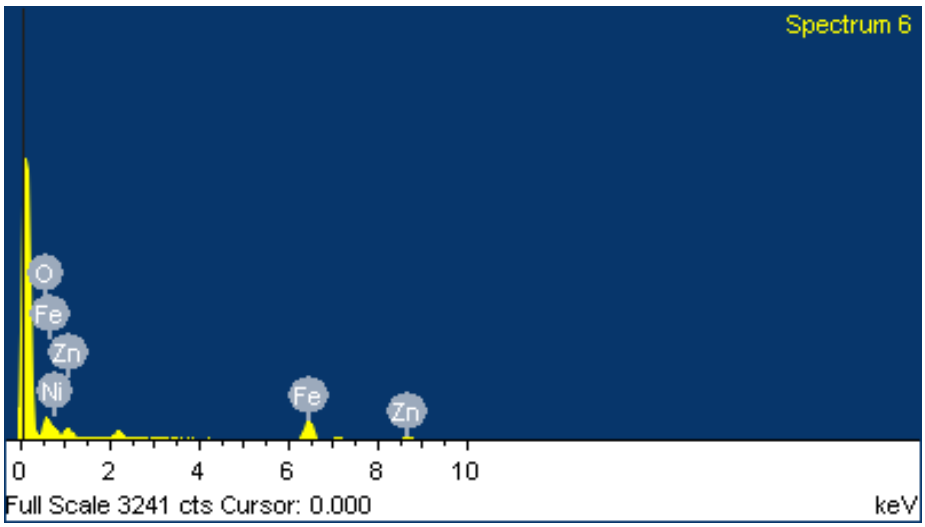

Figure 1. The EDS spectrum of $Zn_{0,8}Ni_{0,2}Fe_2O_4$ samples heated at 180 ^oC.

Figure 1 shows EDS spectra of $Ni_{0,2}Zn_{0,8}Fe_2O_4$ sample heated at 180 ^oC which confirm appearing of Fe, Zn, Ni and O.

Table 1 shows chemical composition of $Ni_{0,2}Zn_{0,8}Fe_2O_4$ samples heated at 180^oC compared with theoretical composition. There is also a little difference of compositions found which can be negligible.

Table 1. Chemical composition of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ sample heated at 180 ^oC.

Element	Weight by EDS (%)	Theoretical weight (%)
O K	25.20	26.71
Fe K	45.99	46.74
Ni K	5.01	4.84
Zn K	23.81	21.70

3.2. Microstructure

Crystal structure of samples was studied by XRD. Figure 2 shows diffraction patterns for as-synthesized samples heated at different temperatures: 120, 140, 160 and 180 ^oC for 6 h in autoclave. Observed diffraction peaks of the heated samples are corresponding to the (220), (311), (400), (422), (511) and (440) standard powder diffraction lines of Fe-Zn-Ni ferrite [14]. The sample heated at 120 ^oC is not completely crystallized because only three diffraction peaks with low intensity are observed. Thus, it is believed that the ferritization occurs completely at temperatures from 140 to 180 ^oC, i.e. at lower temperature than that reported in other works using the same method [11, 13, 15].

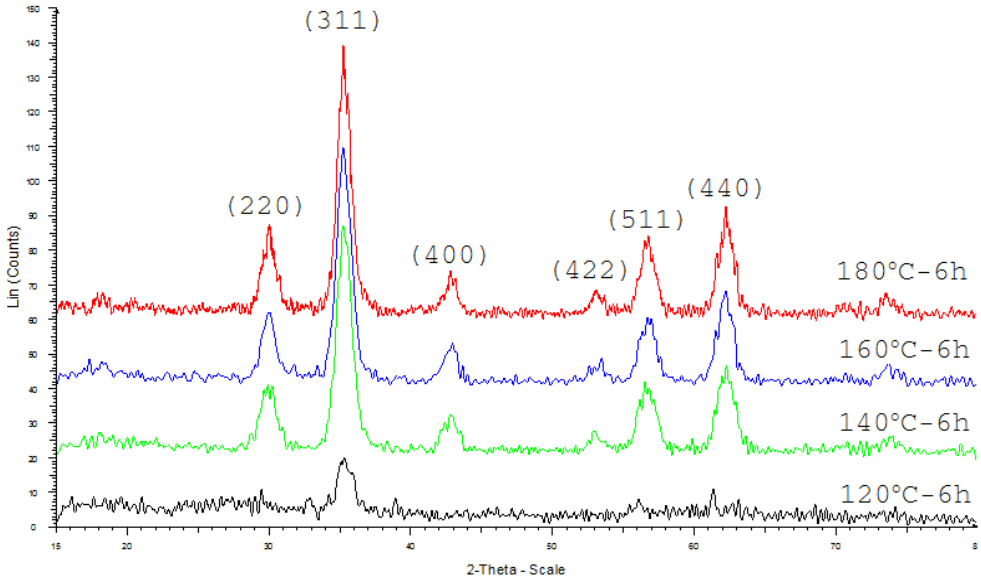

Figure 2. XRD pattern of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ samples heated at different temperatures.

The crystallite size of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite was determined by Scherrer formula [16]:

$$d = \frac{K\lambda}{\beta.\cos\theta}\ ; \qquad (6)$$

where d is average crystallite size; K = 0.9; $\lambda_{Cu\text{-}K\alpha}$ = 1.54056 Å; β - FWHM in radians; θ - Wulf-Bragg angle ($2\theta = 35.23^o$).

Values of average crystallite size and corresponding β of heated samples are shown in Table 2.

Table 2. Average crystallite sizes of heated samples determined by Scherrer formula.

Samples	2θ (degree)	β (FWHM) (radian)	Crystallite size (nm)	Average crystallite size (nm)
Heated at 180 ^{o}C / 6 h	35.23	1.042	7.9	8 ± 1
Heated at 160 ^{o}C / 6 h	35.23	1.176	7.1	7 ± 1
Heated at 140 ^{o}C / 6 h	35.23	1.213	6.8	6.5 ± 1
Heated at 120 ^{o}C / 6 h	35.23	1.299	6.4	6 ± 2

For TEM analysis of heated ferrites, the powder specimens were dispersed in n-hexane and then, treated by ultrasonication for about 30 min. A few drops of the suspension were made on a carbon-coated copper grid and left to dry in the air. Figure 3 shows the TEM images of samples heated at different temperatures for 6 h in autoclave. All of samples had the particles size arranged from 6 – 8 nm, this is the same size as reported in other works [7,13].

The average crystallite size of heated $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite nanoparticles were also analyzed by software TEM image J and were shown in Table 2.

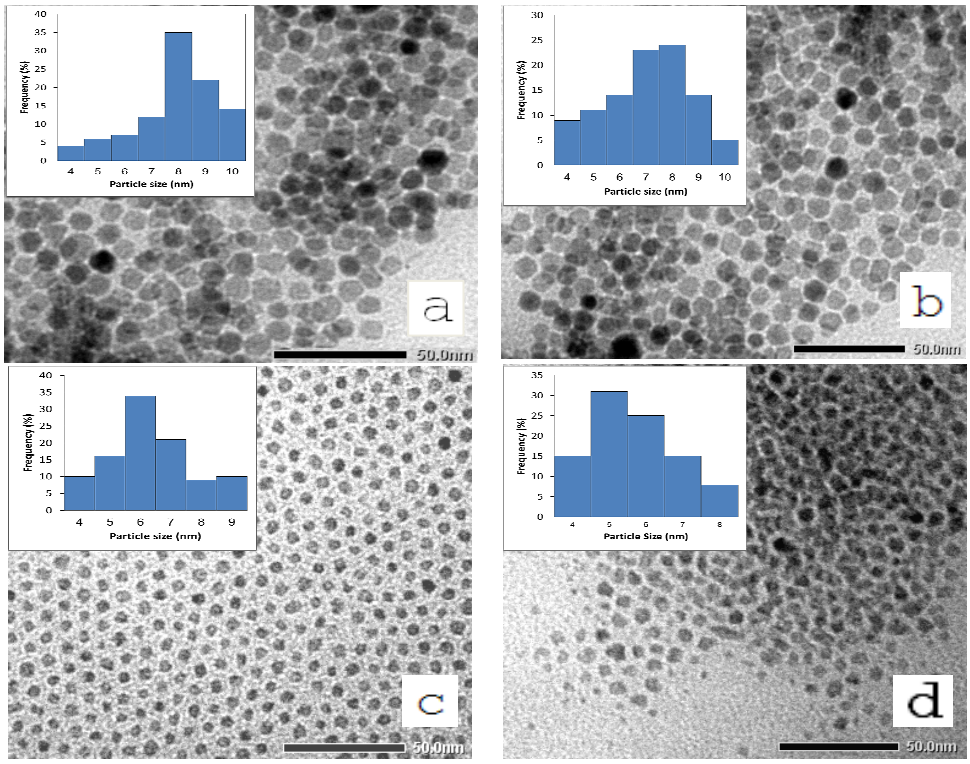

Figure 3. TEM images of samples heated at: (a) 180, (b) 160, (c) 140 and (d) 120 ^{o}C.

Comparing the average crystallite size of heated samples determined by Scherrer formula and analyzed by software TEM image J (Tables 2) shows very good agreement.

It has also demonstrated that increase of heating temperature from 120 up to 180^{o}C leads to increasing the average crystallite size of ferrite from 6 to 8 nm. This may be explained by the growth of crystallite nanoparticles of ferrites with temperature.

3.3. Magnetic properties

Figures 4 shows magnetization curves of nanoferrite samples crystallized at 120, 140, 160 and 180 ^{o}C.

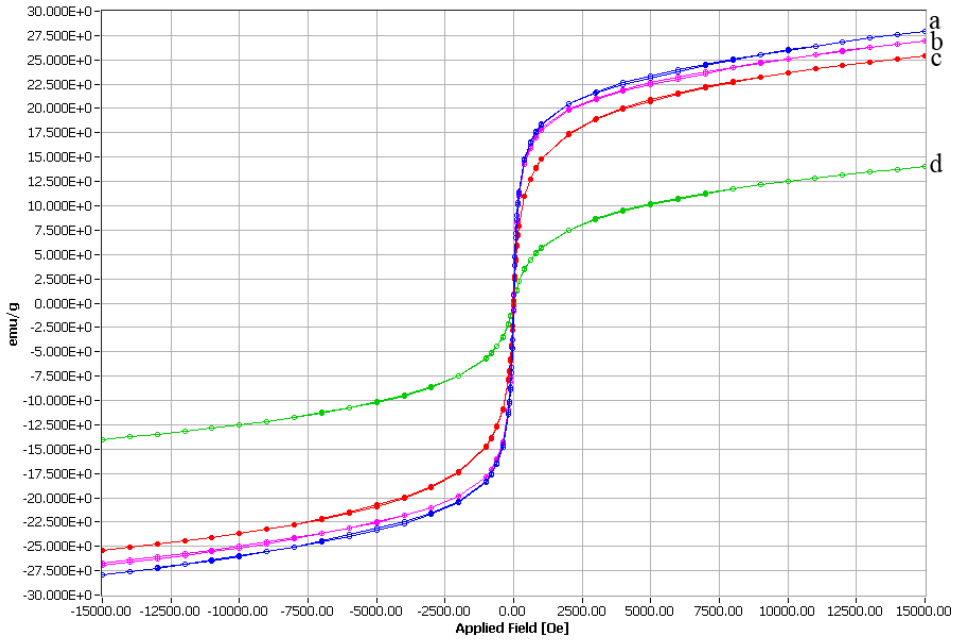

Figure 4. Magnetization curves of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ ferrite crystallized at:
(a) 180; (b) 160, (c) 140 and (d) 120 ^{o}C.

The measured magnetic properties of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite nanoparticles such as coercive force (H_c), remanence (M_r) and saturation magnetization (M_s) are given in Table 3. It has shown that all heated samples having zero coercive force H_c and remanence M_r are of superparamagnetic nature. These values showed the superparamagnetism of the nanoferrite [3, 12].

Superparamagnetic nature of the ferrite may be attributed by their small crystalline size [3, 4]. As mentioned above, crystallite size of SPM is around a few to 10 nanometers. With such a small crystallite size, the crystalline nanoparticles have greater thermal energy than magnetic anisotropic energy and the magnetic moment of nanoparticles fluctuates like in paramagnetic materials [3, 4].

Table 3. Magnetic properties of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ samples crystallized at 120, 140, 160 and 180 ^oC.

Samples	M_r (emu/g)	M_s (emu/g)	H_c (Oe)
Crystallized at 180 ^oC	≈ 0	27.12	≈ 0
Crystallized at 160 ^oC	≈ 0	26.81	≈ 0
Crystallized at 140 ^oC	≈ 0	25.39	≈ 0
Crystallized at 120 ^oC	≈ 0	14.20	≈ 0

In addition, Tables 2, 3 also show that when the crystallization temperature dropped from 180 down to 120 ^oC, the crystallite size decreased from 8 to 6 nm and corresponding saturation magnetization decreased from 27.12 down to 14.20 emu/g. The more heating temperature reduced, the smaller is crystallite size of ferrite and the lower saturation magnetization observed. This is explained by the growth of crystalline nanoparticles of ferrite as temperature increased and the proportionality of magnetic energy to crystal volume.

4. CONCLUSIONS

Superparamagnetic nanoparticles of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite have successfully been synthesized by chemical co-precipitation, modifying with oleic acid 0.25 M to avoid the agglomeration and hydrothermal heating at low temperatures 120 – 180 ^oC for 6 h in autoclave. The lowest temperature determined for completing the ferritization is 140 °C. The presence of the oleic acid enables control the size of particles and keeps the particle to be separated. The superparamagnetic nanoparticles of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite have crystallite size of nearly (6÷8) nm, zero coercive force H_c and remanence M_r and saturation magnetization M_s of about (14÷27) emu/g.

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REFERENCES

1. Alex Goldman - Modern ferrite technology, Springer Science, Business Media Inc., 2006, p. 438.
2. Lu A. H., Salabas E. L. and Schuth F. - Magnetic nanoparticles: synthesis, protection, functionalization and application, Angewandte Chemie-Internl. Ed. **46** (8) (2007) pp. 1222-1244.
3. Manuel Benz - Superparamagnetism: Theory and Applications, Research gate, December 14, 2012.
4. Meizhen Gao, Wen Li, Jingwei Dong, Zhirong Zhang and Bingjun Yang - Synthesis and characterization of superparamagnetic Fe_3O_4@SiO_2 core-shell composite nanoparticles, World Journal of Condensed Matter Physics **1** (2011) 49-54.
5. Kumar S., Sharma A., Singh M., and Sharma S. P. - Simple synthesis and magnetic properties of nickel-zinc ferrite nanoparticles by using Aloe vera extract solution, Applied Science Research **5** (6) (2013) 145-151.

6. Bhattacharjee K., and Ghosh C. K. - Novel synthesis of $Ni_xZn_{1-x}Fe_2O_4$ ($0 < x < 1$) nanoparticles and their dielectric properties, J. Nanopart. Res. **13** (2011) 739-750.
7. Jovanovich S., Spreitzer M., Tramsek M., Trontelj Z. and Suvorov D. - The effect of Oleic acid concentration on the physicochemical properties of cobalt ferrite nanoparticles, J. Phys. Chem. C **118** (25) (2014) 13844-13856.
8. Din Israf Ud, Tasleem, S., Naeem, A., Al Kaisy, Ghassan M. J., Al Kaisy, M. J. - Zinc Ferrite Nanoparticle Synthesis and Characterization, Effects of Annealing Temperature on the Size of nanoparticles; Australian Journal of Basic and Applied Sciences **7** (4) (2013) 154-162.
9. Rao P. B. C., Setty S. P. - Electrical properties of Ni-Zn nano ferrite particles, International Journal of Engineering Science and Technology **2** (8) (2010) 3351-3354.
10. Date S. K., Joy P.A, Anil Kumar P. S., Sahoo B., and Keune W. - Structural, magnetic and Mössbauer studies on nickel-zinc ferrites synthesized via a precipitation route, Phys. stat. sol. (C) **1** (12) (2004) 3495–3498.
11. Makovec D. and Drofenik M. - Hydrothermal Synthesis of Manganese Zinc Ferrite Powders from Oxides, J. Am. Ceram. Soc., **82** (5) (1999) 1113–1120.
12. Zahraei Maryam, Monshi A., Maria del Puerto Morales, Shahbazi-Gahrouei D., Amirnasr M., Behdadfar B. - Hydrothermal synthesis of fine stabilized superparamagnetic nanoparticles of Zn^{2+} substituted manganese ferrite, Journal of Magnetism and Magnetic Materials **393** (2015) 429–436.
13. Sridhar Komarneni - Microwave-Hydrothermal Synthesis of Nanophase Ferrites, J. Am. Ceram. Soc. **81** (11) (1998) 3041–43.
14. Jiles D. - Introduction to magnetism and magnetic materials, Publ. by Chap.-Hall, 1994, p. 430.
15. Repko A., Nizˇnˇansky D., Poltierova´-Vejpravov J.- A study of oleic acid-based hydrothermal preparation of $CoFe_2O_4$ nanoparticles, J. Nanopart Res. **13** (2011) 5021–5031.
16. Cullity B. D. - Element of X-ray diffraction, Adison - Wesley, 1956, p. 531.