A novel method for synthesis and characterization of Ni–Zn ferrite nanoparticles

Plutenko M.O.[1], Plutenko T.O.[2], Fedorchuk O.P.[2], V'yunov O.I.[2]

[1] Taras Shevchenko National University of Kyiv

[2] V.I. Vernadsky Institute of General and Inorganic Chemistry of the NAS of Ukraine

E-mail: taplutenko@gmail.com, Plutenko Tetiana Oleksandrivna

INTRODUCTION

Ferrites remain one of the most useful classes of microwave materials. Their relevance rises with the introduction of new generations' communications standards. Among them, the zinc-nickel (Zn-Ni) spinels are widely used in industry and have applications in catalysis, electrical and electronic devices, electrometallurgy, biotechnology [1]. Requirements for characteristics of materials rise and most of them can be solved by the development of new synthesis methods. The solid-state synthesis can't provide the chemical purity of products, low agglomeration, and small sizes. Another method, that can replace the solid-state route, is the co-precipitation from aqueous solutions. In this work, we synthesized Zn-Ni ferrites using microwave-assisted urea hydrolysis in DMFA. Compared with the co-precipitation from aqueous solutions this method has several advantages: microwave heating provides a faster reaction in a mixture while the use of DMFA as a solvent can provide lower boiling temperatures and effective filtration of a precipitate.

OBJECTIVES of this work are:

-to synthesize the $Ni_{1-x}Zn_xFe_2O_4$ (where $0 \le x \le 1$) system nanoparticles with the spinel structure using microwave-assisted urea hydrolysis (MWU);

-to synthesize $Ni_{1-x}Zn_xFe_2O_4$ particles by the co-precipitation from the aqueous solution;

-to investigate the properties of particles obtained by the MWU method and compare them with particles of ferrite synthesized by co-precipitation.

✓The aim of this work was the synthesis of Zn-Ni ferrite particles by a fast and simple method using microwave heating, urea, and DMF as a solvent, which shortens the synthesis time and allows obtaining small weak agglomerated particles that lower the ferrite synthesis temperature.

METHODOLOGY

MWU synthesis. A mixture of $FeCl_3 \cdot 6H2O$ (1.081 g, 4 mmol), $Me(NO_3)_2 \cdot 6H_2O$, Me = Zn, Ni (2 mmol), and urea (0.961 g, 16 mmol) was dissolved in 20 mL of dimethylformamide (DMF). The resulting solution was stirred on a magnetic stirrer for 10 minutes, and then treated with microwave irradiation (800 W, 4 times for 20 s), as a result the color of the mixture changed from light yellow to brown. The resulting suspension was cooled in air and filtered on a Schott fine-pore filter (class No. 4, pore diameter: 10-16 µm). The brown precipitate was washed on the filter with ethanol (2 times) and dried in an oven at a temperature of 90 °C for 2 hours.

Under the influence of microwave radiation, urea was hydrolyzed and turned into ammonia at the beginning of the MWU synthesis:

$$CO(NH_2)_2 + H_2O \rightarrow CO_2\uparrow + 2NH_3$$

The formed ammonia interacts with metal salts, forming metal hydroxides in several stages [2, 3]. First, iron(III) hydroxide is formed in the form of nanoparticles according to the equation:

$$FeCl_3 + 3NH_3 + 3H_2O \rightarrow 3NH_4Cl + Fe(OH)_3\downarrow$$

Such particles have a large surface area and can adsorb ions of other metals $Me^{2+} = Zn^{2+}, Ni^{2+}$. Subsequently, the adsorbed ions react with ammonia, forming zinc and nickel hydroxides:

$$Me^{2+}_{(adsorbed)} + 2NH_3 + 2H_2O \rightarrow 2NH_4^+ + Me(OH)_{2(adsorbed)}$$

The formed two-layer $Fe(OH)_3/Me(OH)_2$-nanoparticles have high surface energy, so they undergo aggregation in the future, forming larger agglomerates. Such agglomerates can be isolated from the reaction mixture by filtration. In general, the process of formation of such aggregates can be described by the equation:

$$Me(NO_3)_2 + 2FeCl_3 + 4CO(NH_2)_2 + 12H_2O \rightarrow 2NH_4NO_3 + 6NH_4Cl + 4CO_2\uparrow + \{Me(OH)_2 + 2Fe(OH)_3\}\downarrow$$

At the last stage of synthesis, a mixture of hydroxides is sintered to form spinel:

$$Zn(OH)_2 + Ni(OH)_2 + 4Fe(OH)_3 \rightarrow 2Zn_{0.5}Ni_{0.5}Fe_2O_4 + 8H_2O$$

Co-precipitation synthesis. The Zn-Ni particles have been synthesized by the chemical co-precipitation method. The mix of $FeCl_3 \cdot 6H_2O$ (5.406 g, 20 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (1.454 g, 5 mmol), and $Zn(NO_3)_2 \cdot 6H_2O$ (1.487 g, 20 mmol) was dissolved in 50 ml of the distilled water. The resulting solution was stirring 30 min at 60 °C and then 50 ml of NaOH solution (3.200 g, 80 mmol) was added dropwise. After 60 min, the aging process was completed, and the resulting mixture was cooled down to room temperature under constant stirring. The mixture was filtered off on the glass filter and washed with distilled water and ethanol.

After precipitation, the suspension was heated to 80 °C for 1 hour. The precipitate was filtered off from the mother liquor and washed. The resulting product was dried at the temperature of 110–120 °C. The final product was obtained after heat treatment of the precipitate in an air atmosphere at different temperatures for two hours.

Investigation methods:

- X-ray diffraction (XRD);
- Fourier-transform infrared spectroscopy (FTIR);
- transmission electron microscopy – energy dispersive spectroscopy (TEM – EDS);
- Mössbauer spectroscopy;
- magnetic parameters measurement using a vibrating magnetometer.

RESULTS AND DISCUSSION

Fig 1. demonstrates the XRD patterns of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite, synthesized using MWU (Fig. 1a), calcined at different temperatures. The single-phase $Zn_{0.5}Ni_{0.5}Fe_2O_4$ product is formed during the MWU synthesis after 450 °C, in the case of co-precipitation synthesis the spinel structure forms after 650 °C.

FTIR spectra of Zn-Ni ferrites for all samples are given in figure 1b. It reveals the two absorption bands at around 600, 400 cm^{-1} corresponding to tetrahedral and octahedral vibrations, which provides information about the formation of cubic structure. The vibration *v*1 at the tetrahedral site is caused by the stretching of M-O and oxygen bond while that of *v*2 at the octahedral site is by the bending of M-O.

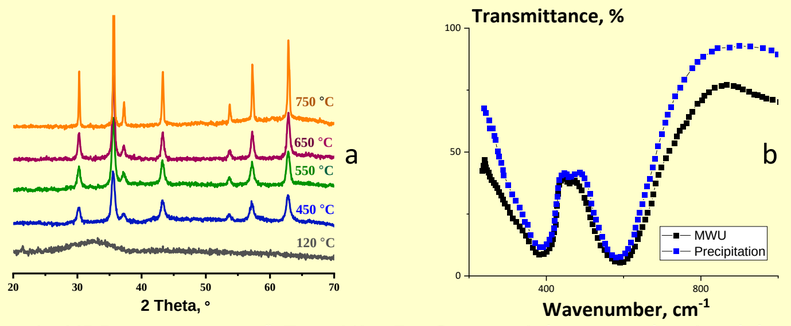

Fig. 1. XRD patterns of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ particles, synthesized by the MWU method, after the heat treatment at different temperatures (a) and FTIR spectra of nanoparticles synthesized by two methods (b).

Median size of synthesized ferrite particles is 26 and 47 nm for MWU and co-precipitation methods respectively (Fig. 2).

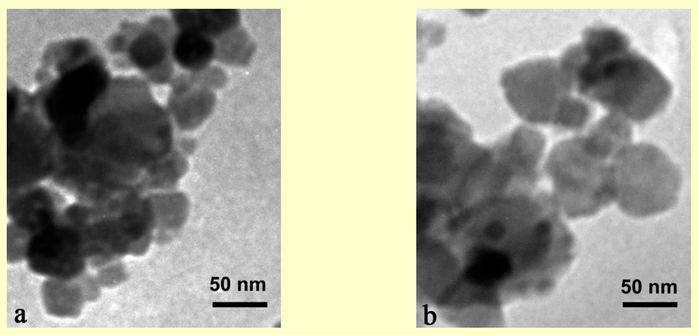

Fig. 2. TEM images of particles synthesized by the MWU (a) and co-precipitation (b) methods.

Le Bail method (Fig. 3) was used to determine lattice parameters of ferrite particles. Crystal lattice parameters increase with Zn content (Fig. 4a). This fact indicates, that Zn enters the crystal lattice.

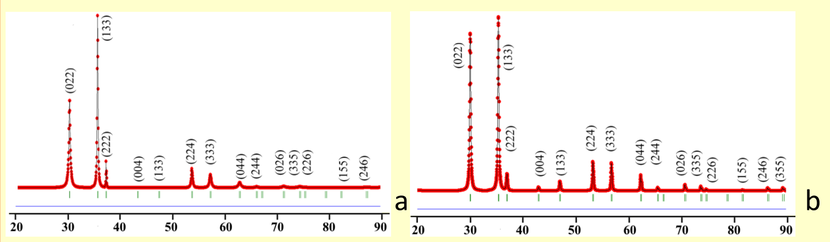

Fig. 3. Le Bail refinement of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite powders, synthesized using MWU (a) and by co-precipitation (b) methods.

Also, the Mössbauer spectrum of ferrimagnetic particles demonstrates two sextets (4b). It indicates, that Fe ions are introduced in two positions (tetrahedral and octahedral sublattices) of spinel. Thus, a solid solution of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ with the spinel structure was formed.

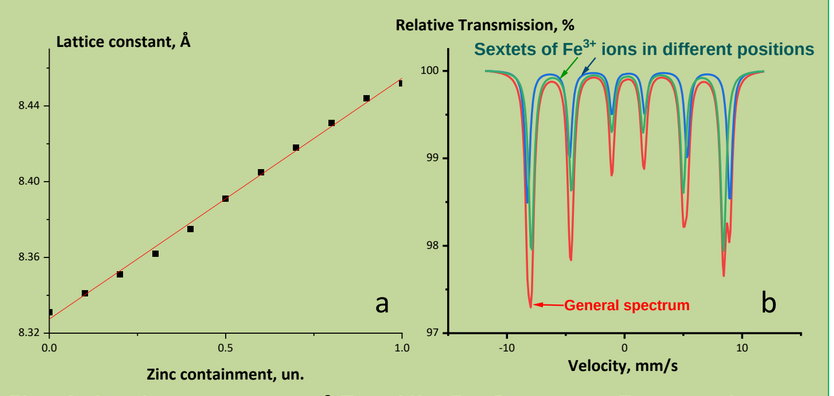

Fig. 4. Lattice constant of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ versus Zn containment (a) and Mössbauer spectrum (b) of particles, synthesized using MWU.

While synthesis conditions changed significantly, the magnetic properties changed slightly (Fig. 5). Saturation magnetization is 45.6, 44.8 Am^2/kg and coercive force is 1.3 and 3 kA/m (MWU and co-precipitation methods respectively). Magnetically softer particles are preferred for high-Q materials.

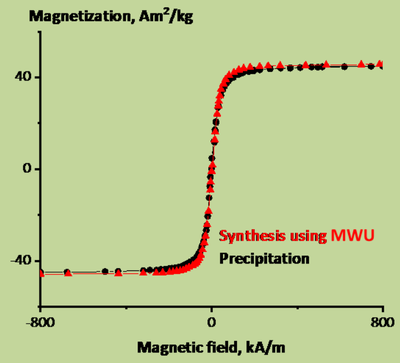

Fig. 5. Hysteresis loop of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ particles synthesized using MWU.

CONCLUSIONS

The formation temperatures of single-phase spinels synthesized using microwave-assisted urea (MWU) hydrolysis and co-precipitation from aqueous solutions were determined by X-ray analysis. Materials synthesized using MWU have lower particle formation temperatures (a difference of 200 °C). Such a difference is the result of rapid heating of reagents to high temperatures under the influence of microwave radiation. This factor promotes a fast nucleation rate, reduces reaction time. Microwave treatment reduces the time required for synthesis. As a result, the ferrite particles have a smaller size (26 vs. 47 nm) and a higher uniformity. With an increase in zinc content, the parameter of the unit cell increases uniformly by Vegard's law. Mössbauer spectroscopy showed that the cations in the sub-lattice are distributed randomly. Obtained materials are magnetically soft, and have a high saturation magnetization: the magnetization differs little while coercive force differs by about 3 times (1.3 and 3 kA/m) and is lower for the particles synthesized by MWU methods.

Reached changes make Zn-Ni particles more applicable in films and high-quality coatings deposition.

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References:

[1] S. Bindra Narang, K. Pubby, Nickel Spinel Ferrites: A Review, Journal of Magnetism and Magnetic Materials (2020), doi: https://doi.org/10.1016/j.jmmm.2020.167163

[2] X. Li, G. Wang, Journal of Magnetism and Magnetic Materials 321 (2009) 1276–1279. doi: https://doi.org/10.1016/j.jmmm.2008.11.006

[3] X. Li, Q. Li, Z. Xia, W.X. Yan, Journal of Alloys and Compounds 458 (2008) 558–563. doi: https://doi.org/10.1016/j.jallcom.2007.04.214