Hydrothermal Synthesis of Cobalt Ferrite Nanosized Powders

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Abstract. Cobalt ferrite powders are synthesized by the co-precipitation technology, combined with the hydrothermal synthesis method and crystallite size, specific surface area (SSA), magnetic properties of synthesized products are obtained. All the synthesized ferrites are nanocrystalline single phase materials with crystallite size of 10-16 nm the SSA of 60±5 m\textsuperscript{2}/g and the calculated particle size of 20±2 nm. Synthesized Co ferrites are characterized by the saturation magnetization $M_S$ of 59-60 emu/g, remanent magnetization $M_r$ of 23 emu/g and coercivity $H_c$ of 570-650 Oe.

1. Introduction

Recently ferrites have received an increased scientific and commercial interest. The most significant and popular usage of ferrites are in optics, electronics, mechanics and other technical fields \cite{1}. Ferrites are also of great importance in medicine, for biomedical purposes and in chemical catalysis. More information appears about hyperthermia in scientific articles. With this method, ferrite nanoparticles are introduced in living organism and in controlled conditions nanoparticles are transported to the cancer zones in organism, and in magnetic field with thermal treatment, cancer cells are eliminated \cite{2}.

The properties of nanomaterials vary from it morphology, particle size and microstructure and it is important to analyze methods of synthesis of nanoparticles, as well as obtain new metal oxides with new properties. Materials in the form of nanowires, nanosheets, etc., are especially important, because of their improved optical, electronic and magnetic properties allowing to extend application limits.

Ferrites with spinel structure are significant materials in development of several technological applications, where materials with high density and low porosity are necessary \cite{3}. Ferrites, as most of ceramic materials, are obtained in solid phase reactions from different oxides. By improving nanotechnology, several liquid phase and gas phase synthesis methods have been developed – hydrolysis, hydrothermal synthesis \cite{4}, pyrolysis, microwave synthesis \cite{1}, co-precipitation method \cite{5}, sol-gel method \cite{6}, combustion \cite{7} and plasma synthesis \cite{8}.

In this research the cobalt ferrite nanopowders synthesis have been prepared by hydrothermal method and their mechanical and magnetic properties have been studied.
2. Experimental

Synthesis of cobalt ferrite nanoparticles was performed by the co-precipitation technology, combined with the hydrothermal synthesis method. By the hydrothermal method cobalt ferrites were synthesized using reagent grade chemicals: FeCl₃·6H₂O, urea, Co(NO₃)₂·6H₂O, NaOH. Urea was hydrolyzed for 3 hours in the solution of FeCl₃ (molar ratio 3:1) at 70-75 °C. Cobalt nitrate was added to the cooled reaction mixture. The molar ratio FeCl₃·6H₂O : Co(NO₃)₂·6H₂O was corresponding to the stoichiometry of the metal ions in ferrite. Stirring the suspension continuously with the 40% solution of NaOH, cobalt hydroxide is slowly precipitated until pH of the suspension is of 9-10, then inserted in the ultrasound bath for 20 min and after it treated for 24 h at 40 °C. The precipitate is washed by decanting with distilled water until the presence of Cl⁻ ion can not been registered. The volume of hydroxides mixture is reduced by decanting until 250 ml which are poured into the reaction vessel inserted in the autoclave. Then the obtained mixture of hydroxides was treated hydrothermally at different regimes (T = 200-250 °C, t = 1-3 h, p = 17-17,5 MPa). After hydrothermal treatment the formed precipitate is filtered by the water jet pump using the membrane filter, precipitate is washed by distilled water and dried at 40 °C.

Ferrite nanopowders were prepared for sintering as follows: 3 wt. % stearic acid is mixed mechanically with ferrite nanopowder sample for 1 h in planetary mills (400 rpm, vessel material ZrO₂, milling ball material ZrO₂) by using isopropanol as dispersing environment. After mixing samples were dried in an oven at 80 °C and sieved. For pressure-less sintering samples were pressed (200 MPa) in pellets with diameter of 12 mm and height of 4 – 6 mm. Stearic acid was burned out at 600 °C. Samples were sintered for 2 h at isothermal conditions in air atmosphere at the temperature range from (1000 – 1200) °C (10 °C/min).

All samples were analyzed by the X-ray diffractometer Advance 8 (Bruker AXS). Measuring parameters: CuKα radiation (1.5418 Å), range (10 – 70) 2Θ°, increment 0.02 2Θ°, time per step 1 s, to reduce background effects the SolX detector was used. Crystallite size was determined by the Scherrer’s equation. Magnetic properties of the synthesized ferrites were analyzed by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM). SSA was measured with the BET single point method. Measurements were made at the boiling point of liquid nitrogen (−196 °C), the adsorbing gas was Ar (~7 % Ar gas mixture in He gas).

3. Results and discussion

The characteristics of synthesized ferrite products are given in Table 1 and in Figures 2 – 3. It is found that all by hydrothermal synthesis obtained ferrites, except sample No 1 (synthesized 1 h at 200 °C - this sample shows also FeOOH phase), are nanocrystalline stoichiometric single phase materials (Fig. 2) with specific surface area of (55 – 63) m²/g and calculated particle size of 20±2 nm (Fig. 3). The crystallite size in ferrite is of 10-16 nm. None of the obtained samples No 2-6 show other additional phases (commonly magnetite, maghemite, hematite or other metal oxides), which proves that obtained samples are of high purity.

With the increase of the temperature and the time of the hydrothermal treatment, the magnetic properties (saturation magnetization Ms, remanent magnetization Mr, emu/g and coercivity Hc, Oe) are also increasing (Table 1).

Slight weight changes (~ 1,5 mass %) and minor exo-effect in the temperature range of 250-350 °C has been found by the thermal analysis. The total change of the weight after treatment to the constant weight was ~ 7 mass %, therefore it is recomendated to calcinate the sample for 1 h at 400 °C. The crystallite size and SSA after calcinating change insignificantly (Table 2). After thermal treatment at higher temperatures the SSA of the ferrites has a tendency to decrease, while the crystallite size increases. This could be explained that particles are re-crystallizing and growing at higher temperatures, so the SSA is decreasing (Figure 4). With increase of temperature of thermal treatment, saturation magnetization of the ferrites increases (Figure 5).
Table 1. Characteristics of CoFe$_2$O$_4$ nanopowders prepared at different regimes.

| No | MODE, °C/h | SSA, m$^2$/g | $d_{50}$, nm* | Crystallite size, nm | XRD phases       | Magnetic properties |
|----|------------|--------------|---------------|---------------------|------------------|---------------------|
|    |            |              |               |                     |                  | $M_s$, emu/g | $M_r$, emu/g | $H_c$, Oe |
| 1  | 200/1      | 58           | 20            | 10                  | CoFe$_2$O$_4$, FeOOH | 13,2       | 2,6        | 105,1     |
| 2  | 200/3      | 59           | 19            | 13-14               | CoFe$_2$O$_4$     | -          | -          | -         |
| 3  | 230/1      | 63           | 18            | 10-13               | CoFe$_2$O$_4$     | 50,0       | 10,2       | 494,0     |
| 4  | 230/3      | 55           | 21            | 15-16               | CoFe$_2$O$_4$     | 58,9       | 17,8       | 643,4     |
| 5  | 250/1      | 61           | 19            | 12-13               | CoFe$_2$O$_4$     | 57,3       | 17,3       | 565,5     |
| 6  | 250/3      | 62           | 18            | 10-12               | CoFe$_2$O$_4$     | 59,8       | 16,8       | 574,2     |

*calculated from SSA

Figure 2. XRD patterns of the CoFe$_2$O$_4$ nanopowder prepared at:
1 – 200 °C, 1h; 2 – 230 °C, 1h; 3 – 250 °C, 1h.

Figure 3. Electron microscopy images of CoFe$_2$O$_4$ obtained by the hydrothermal method.
Figure 4. Specific surface area (SSA) and crystallite size of CoFe$_2$O$_4$ as functions of hydrothermal treatment temperature.

Table 2. Properties of synthesized CoFe$_2$O$_4$ nanopowders (sample No 3) after thermal treatment (2 h at different temperatures).

| Heating temperature, °C | SSA, m$^2$/g | d$_{50}$, nm* | Crystallite size, nm | XRD phases | Magnetic properties |
|-------------------------|--------------|--------------|---------------------|------------|--------------------|
| Raw powder              | 63           | 18           | 10-13               | CoFe$_2$O$_4$ | M$_s$, emu/g       |
|                         |              |              |                     |            | M$_r$, emu/g       |
|                         |              |              |                     |            | H$_c$, Oe          |
| 400                     | 54           | 21           | 10-11               | CoFe$_2$O$_4$ | 50,0               |
|                         |              |              |                     |            | 10,2               |
|                         |              |              |                     |            | 494,0              |
| 600                     | 40           | 29           | 19-20               | CoFe$_2$O$_4$ | 50,1               |
|                         |              |              |                     |            | 12,6               |
|                         |              |              |                     |            | 390,1              |
| 800                     | 26           | 44           | 43-45               | CoFe$_2$O$_4$ | 62,8               |
|                         |              |              |                     |            | 22,4               |
|                         |              |              |                     |            | 757,0              |

*calculated from SSA

Figure 5. The magnetic properties of the sample No. 3 after thermal treatment at 400 (1), 600 (2) and 800 (3) °C.
After thermal treatment at 800 ºC the magnetic saturation increased to 72 emu/g, which is close to the values of the standard bulk material (80 emu/g for \(\text{CoFe}_2\text{O}_4\)) [10].

Sintering of nanosized \(\text{CoFe}_2\text{O}_4\) powder was made at 1000, 1100 and 1200 ºC. Some properties of the sintered ferrites are shown in Table 3. By increasing the sintering temperature, the size of nanograins and magnetization increases while coercivity decreases. In comparison to the ferrite nanopowders, obtained by hydrothermal method, the sintered materials have higher magnetization and lower coercivity, which could be explained with particle size and also crystallite size increase.

**Table 3.** Properties of \(\text{CoFe}_2\text{O}_4\) (sample No 3) after 2h sintering.

| Heating temperature, ºC | Density, % | Open porosity, % | Crystallite size, nm | Magnetic properties |
|-------------------------|------------|------------------|---------------------|-------------------|
| Raw powder              | -          | -                | 10-13               | 50,0, 10,2, 494,0 |
| 1000                    | 81,3       | 14,2             | 75                  | -                 |
| 1100                    | 94,3       | 0,8              | 90-95               | 77,0, 20,7, 492,8 |
| 1200                    | 95,0       | 0,1              | 150                 | 81,3, 14,1, 168,6 |

4. Conclusions

Single phase cobalt ferrite nanopowders can be successfully synthesized by the hydrothermal synthesis method. The average particle size of the nanopowders obtained by this method is in the range of 20 ± 2 nm (SSA of 60 ± 5 m²/g). The magnetic saturation values of these samples depend on hydrothermal synthesis temperature and time and reach up to 59-60 emu/g. After thermal treatment at 800 ºC the magnetic saturation increased to 72 emu/g, which is close to the values of the standard bulk material (80 emu/g for \(\text{CoFe}_2\text{O}_4\)).

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