Synthesis, Structure and Properties of Zn$_{0.3}$Ni$_{0.7-x}$Co$_x$Fe$_2$O$_4$ Ferrite

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Abstract. The article presents the results of a study of ferrite Zn$_{0.3}$Ni$_{0.7-x}$Co$_x$Fe$_2$O$_4$, where $x = 0–0.6$ in increments of 0.2. The samples were obtained by solid-phase synthesis in a tube furnace with silicon carbide heaters at a temperature of 1150 °C for 5 hours. X-ray phase analysis showed that all the samples obtained are monophasic and have a spinel structure. X-ray structural analysis revealed that the substitution of cobalt atoms for nickel atoms leads to a monotonic increase in the parameters (a and V) of the unit crystal lattice. The elemental composition of the synthesized samples was monitored using an energy dispersive analyzer installed on a Jeol JSM 7001F scanning electron microscope. The aim of this work was to obtain new monophasic samples using previously developed technology.

1. Introduction

Since 1950, ferrites based on solid solutions of NiFe$_2$O$_4$ and ZnFe$_2$O$_4$ found its application in industry [1]. Nowadays with the development of technology, the ferrites under investigation are used everywhere. For example, to suppress electromagnetic interference and incoming noise, to prevent external vibrations using cores made of Ni-Zn ferrite. Particular attention was given to ferrite tubes, which are a core with a hole through which passes current-carrying wire. Ferrites are one of the most important magnetic materials since they have a wide possibility of their technological application. Such materials are used in magnetic cores for high frequency transformers in many microwave components. They are also magnetically resistant materials that are difficult to demagnetize and relatively inexpensive.

Nickel-zinc-cobalt (Ni-Zn-Co) ferrites are affordable materials having the necessary magnetic and electrical properties for high frequency applications in the radio frequency domain. The studied ferrites have high electrical resistivity, low eddy current losses, high magnetic permeability, relatively high Curie temperature and high saturation magnetization. Also, cores of this type are used in visualization devices, audio equipment, telecommunications devices, automotive electronics and various cable systems. Parts in the form of rods are used for radio antennas, chokes, inductors, transformers, as well as power filters and DC signal filters. Flat core can suppress microprocessor radiation noise, prevent resonance and suppress communication when connecting two microprocessors, suppress electromagnetic interference through a cable from electrical equipment when connecting to a flat cable [2, 3].

Depending on the scope and achievement of certain properties, nickel-zinc ferrites get certain method, and if necessary, are doped with ions of other elements that change properties. Currently,
several methods for obtaining Ni-Zn ferrites, the most famous of them are methods: solid-phase synthesis, co-precipitation, sol-gel, spontaneous combustion, etc. [4–8].

By analyzing modern scientific literature, you can find many publications in which, in addition to research on Ni-Zn ferrite, they explore ferrite with the addition of alloying elements. The result is substitution of a part of the ions of the starting components by doping ions elements. The most widely studied properties of nickel-zinc ferrites with alloying with Al [9, 10], Cu [11–13], Cr [14–16], Co [4, 17], Nd [18, 19], etc. Also, in addition to one alloying element, the possibility of creating a material in which ions of the initial matrix of 2 or more elements are replaced is actively introduced in research papers [20–22]. After a review of the literature data, a solid-phase synthesis method was chosen to obtain samples, as well as an alloying element for the initial composition of Zn$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$ ferrite. Such synthesis conditions make it possible to obtain samples of new compositions and properties.

2. Experimental part

The first stage of the study is the synthesis of a series of samples with the general formula Zn$_{0.3}$Ni$_{0.7-x}$Co$_x$Fe$_2$O$_4$, where $x$ – takes values from 0 to 0.6 in increments of 0.2. Solid-phase synthesis was chosen as a method of obtaining the material. The components of the original mixture - iron oxide Fe$_2$O$_3$, nickel oxide NiO, zinc oxide ZnO, cobalt oxide CoO were mixed in the mass ratio shown in table 1. After mixing the components in a ball mill to a homogeneous powder, the samples were compacted on a hydraulic press. The final stage of the synthesis is the ferritization of pressed samples in a tube furnace with silicon carbide heaters. The sintering process was carried out at a temperature of 1150 °C for 5 hours of isothermal exposure. Sintering temperature is selected based on the analysis of literature data. The basic composition of Zn$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$ has a relatively high temperature of the second-order phase transition [1].

| №  | Formula               | wt. %     |
|----|----------------------|-----------|
|    | NiO                  | ZnO       | CoO   | Fe$_2$O$_3$ |
| 1  | Zn$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$ | 22,1183 | 10,3279 | –          | 67,5538 |
| 2  | Zn$_{0.3}$Ni$_{0.5}$Co$_{0.2}$Fe$_2$O$_4$ | 18,9566 | 10,3269 | 3,1696    | 67,5469 |
| 3  | Zn$_{0.3}$Ni$_{0.3}$Co$_{0.4}$Fe$_2$O$_4$ | 15,7956 | 10,3258 | 6,3385    | 67,5400 |
| 4  | Zn$_{0.3}$Ni$_{0.1}$Co$_{0.6}$Fe$_2$O$_4$ | 12,6352 | 10,3248 | 9,5068    | 67,5332 |

The chemical composition and surface morphology of the samples were investigated on a scanning electron microscope Jeol JSM 7001F equipped with an Oxford INCA X-max 80 X-ray spectrometer for elemental analysis.

The data about phase composition and lattice parameters were investigate on powder X-ray diffractometer Rigaku Ultima IV in the angular range 2θ from 15° to 90° with the scanning speed 2 °/min.

The Curie temperature was determined on a Netzsch STA 449 F1 Jupiter differential scanning calorimeter (DSC) in platinum crucibles in an argon atmosphere. The Curie temperature is the temperature corresponding to the temperature of a phase transition of the second kind. Ferromagnetic and paramagnetic modifications have different heat capacities. The peak of the DSC curve corresponds to this transition. Therefore, DSC measurements are sufficient for determination of the Curie temperature [23].

3. Results and discussion

Table 2 shows the elemental composition of the synthesized samples, as well as the gross formulas calculated from it. From table 2 it is seen that the elemental composition of the synthesized samples is in good agreement with the initial charge of the samples. An insignificant mismatch of the given
composition with the obtained data is due to the fact that when zinc is heated to the sintering temperature, intense volatilization of zinc and oxygen loss occur [1].

Table 2. The elemental composition recorded in three spectra.

| №  | Chemical composition, atom, % | Calculated formula         |
|----|------------------------------|----------------------------|
|    | O   | Fe   | Co | Ni | Zn |          |
| 1  | 47,66 | 37,13 | -  | 11,10 | 4,11 | Zn_{0,27}Ni_{0,73}Fe_2O_4 |
| 2  | 47,91 | 36,47 | 3,75 | 7,58 | 4,29 | Zn_{0,27}Ni_{0,49}Co_{0,24}Fe_2O_4 |
| 3  | 48,40 | 35,62 | 7,01 | 4,68 | 4,29 | Zn_{0,27}Ni_{0,29}Co_{0,44}Fe_2O_4 |
| 4  | 48,21 | 34,82 | 10,72 | 1,94 | 4,31 | Zn_{0,28}Ni_{0,11}Co_{0,63}Fe_2O_4 |

The microstructure of the surface of the samples consists of many crystallites of various sizes, sintered together. Crystallites have a characteristic inherent of cubic syngony.

X-ray phase analysis showed that all prepared samples are monophasic and have a spinel structure. In fig. 1 presents x-rays of the studied samples.

Due to the fact that Zn and Co atoms have different ionic radii, when Zn atoms (r (Ni^{2+}) = 0.49 Å [24]) are replaced by Co atoms (r (Co^{2+}) = 0.58 Å [24]), the crystal lattices - the growth of unit cell parameters.

![Figure 1. X-ray diffraction patterns of the Ni_{0,3}Zn_{0,7-x}Co_{x}Fe_2O_4 system.](image)

Figure 2 shows the dependence of the change in the parameter $a$ and the volume $V$ of the unit cell on the degree of cobalt substitution. The graph shows that the values monotonically increase with increasing concentration of the substitute element. This is due to the difference in the ionic radii of cobalt and zinc.
Figure 2. The dependence of the crystal lattice parameters $a$, $V$ on the degree of substitution with cobalt.

DSC curves were obtained at a heating rate of 20 °/min to a temperature of 800 °C. The sample weighed was 150 mg. Figure 3 shows DSC curves of samples. Figure 3 shows that in the temperature range 200–600 °C, all samples have an endothermic process.

The inflection point of the DSC curve corresponds to the temperature of the ferromagnet – paramagnet phase transition (Curie temperature).

Figure 3. DSC curves of Ni-Zn-Co ferrite.

4. Conclusions
A set of physicochemical parameters has been worked out to ensure the production of nickel-zinc-cobalt ferrite $\text{Zn}_{0.25}\text{Ni}_{0.75}\text{Fe}_2\text{O}_4$ with a spinel structure. The optimal temperature regime of the solid-phase reaction was determined: temperature $T = 1150$ °C, duration 5 h.
A technology has been developed for producing ferrites of a new chemical composition with spinel structure. Thermal analysis was carried out; samples were studied on a differential scanning calorimeter. The analysis determined the Curie temperature of the samples. Controlling the Curie temperature of the material will allow the use of these ferrites in various temperature conditions.

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Acknowledgments
The reported study was funded by RFBR, project number 20-38-70057.