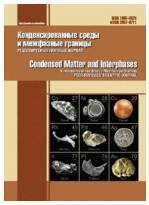

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Structural and magnetic properties of Ho-doped $CuFe_2O_4$ nanoparticles prepared by a simple co-precipitation method

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Abstract

Nanocrystalline copper (II) ferrite with a spinel structure doped with holmium was synthesized by co-precipitation using an aqueous solution of NaOH as a precipitant and subsequent annealing at 800°C for 60 min. The doping limit was determined by X-ray phase analysis. The similarity of the real and nominal compositions of the doped samples was established by energy-dispersive X-ray spectroscopy using a scanning electron microscope. The obtained particles had an approximately spherical shape, and their size was 40–70 nm (X-ray phase analysis, transmission electron microscopy). The introduction of Ho^{3+} cations to x = 0.15 into a $CuFe_2O_4$ spinel lattice led to a decrease in the average size of crystallites, an increase in the coercive force of nanopowders, and a decrease in excess magnetization and saturation magnetization. Synthesized $CuFe_{2-x}Ho_xO_4$ (x = 0, 0.1 and 0.15) nanopowders were magnetically hard materials with high coercive force.

Keywords: $CuFe_2O_4$, Ho-doping, Co-precipitation method, Magnetic properties

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1. Introduction

The synthesis and study of the characteristics of nanomaterials now attracts a lot of attention, since nanoparticles possess a set of properties different from those of macrosized analogues [1–5]. Among the magnetic materials, nanocrystalline ferrites with an MFe_2O_4 type spinel structure (M = Co, Ni, Zn, Cu) are distinguished by high values of magnetic permeability, saturation magnetization, and are used to create new multifunctional materials, such as high-frequency devices, due to a decrease in the energy of Foucault's currents and, accordingly, an increase in the duration of their operation [4, 6–9]. In addition, ferrites with a spinel structure are cheaper and more stable (in time and temperature) compared to metals and alloys.

Ferrites with an MFe_2O_4 spinel structure doped with various metal cations are usually synthesized by methods such as sol–gel technology [6–9], hydrothermal synthesis [10], solid phase reaction [11], or coprecipitation with the addition of organic compounds [12]. The studies [4, 13] describe the features of the formation of nanopowders of ferrites – spinels MFe_2O_4 (M = Zn, Co, Ni) by a simple co-precipitation method via the hydrolysis of cations in boiling water followed by the addition of appropriate precipitants in the absence of surface active substances (SAS). According to literature, $CuFe_2O_4$ in the form of nanocrystals doped with holmium ($CuFe_{2-x}Ho_xO_4$), were not synthesized in a similar way.

Thus, the purpose of this study was the synthesis and investigation of the magnetic properties of nanocrystalline ferrite – copper (II) spinel, doped with holmium, formed by a simple chemical coprecipitation method.

2. Experimental

The starting materials were aqueous solutions of copper (II), iron (III), and holmium (III) nitrates (analytical grade reagents) with molar ratio Cu^{2+} : Fe^{3+} : Ho^{3+} = 1 : (2-x) : x (x = 0, 0.1, 0.15, and 0.2). An aqueous solution of NaOH was used as a precipitant. An aqueous solution of a mixture of $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Ho(NO_3)_3 \cdot 5H_2O$ (50 mL) was added dropwise to 450 mL of boiling water with stirring using a magnetic stirrer. After the introduction of salts, boiling was continued for another 10 min, while the solution acquired a brown-red colour, then the system was cooled to room temperature, and the 5% NaOH solution was added dropwise until the complete precipitation of Cu^{2+}, Fe^{3+} and Ho^{3+} cations similarly to [13–14]. The resulting precipitate was stirred for 60 min and then precipitated within 15 min. After separation on a vacuum filter, the precipitate was washed with distilled water until pH ~ 7.0 was reached and dried at room temperature. Annealing was carried out in a muffle furnace at 800°C for 60 min. Such an annealing regime was chosen based on the results of [13, 15].

The phase compositions of the samples were determined using X-ray phase analysis (XRD, D8-ADVANCE diffractometer, CuK_α-radiation, λ = 1.5406 Å, 2θ = 10–80°). The average crystal size (D_{av}, nm) of $CuFe_{2-x}Ho_xO_4$ samples was calculated using the Scherrer formula.

The shape and size of the particles were determined using transmission electron microscopy (TEM, electron microscope JEM-1400).

The actual qualitative and quantitative elemental composition of the samples was studied by energy dispersive X-ray spectroscopy (EDX) using an FE-SEM S-4800 scanning electron microscope. The quantitative elemental composition was determined as the average of the values obtained at five different points of each sample.

The hysteresis loop and magnetic characteristics of $CuFe_{2-x}Ho_xO_4$ (x = x = 0, 0.1, 0.15 and 0.2) nanopowders at room temperature, including saturation magnetization (M_s,), coercive force (H_c, Oe) and residual magnetization (M_r) were recorded using a Microsene EV11 magnetometer with a vibrating sample under the action of a magnetic field in the range from –16,000 to +16,000 Oe.

3. Results and discussion

X-ray diffraction patterns of powders of a nominal composition of $CuFe_{2-x}Ho_xO_4$ (x = 0, 0.1, 0.15, and 0.2), obtained by co-deposition after annealing at 800°C for 60 min are shown in Fig. 1. For samples with values x = 0, 0.1 and 0.15, peaks corresponding to the standard peaks of $CuFe_2O_4$ spinel phase (JCPDS: 04-001-9258; Copper Iron Oxide) were obtained. On the diffraction pattern of a sample with a nominal degree of doping

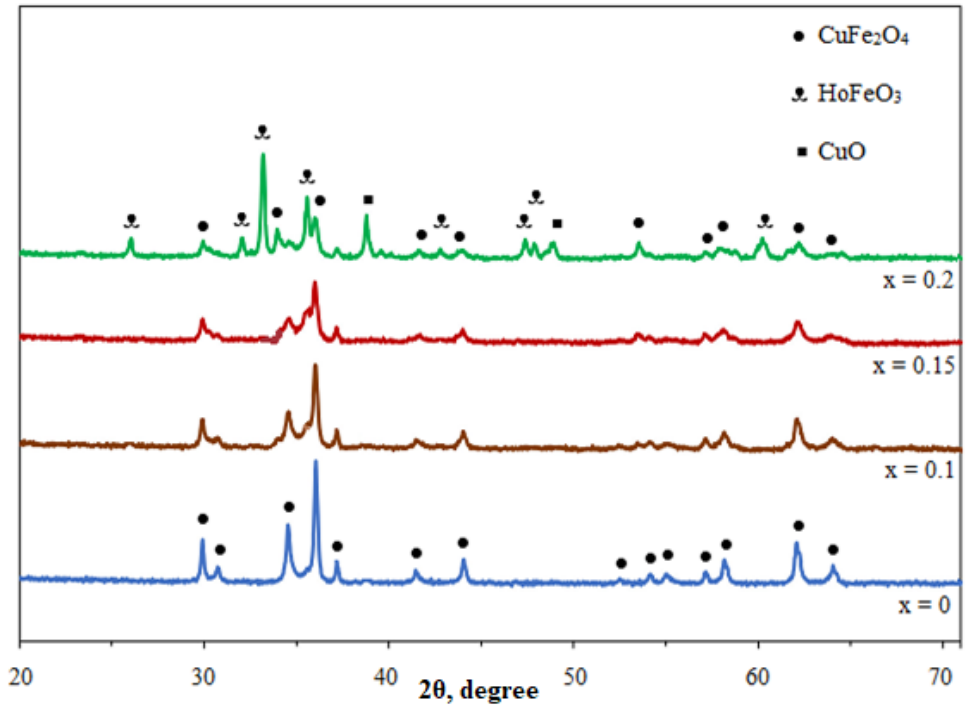

Fig. 1. X-ray diffraction patterns of samples of nominal composition $CuFe_{2-x}Ho_xO_4$ synthesized by co-precipitation after annealing at 800°C for 60 min

x = 0.2 in addition to the peaks of the phase with the copper(II) spinel structure $CuFe_2O_4$, peaks corresponding to the following phases: CuO (JCPDS: 04-004-5685; Copper Oxide) and $HoFeO_3$ (JCPDS: 01-084-8725; Holmium Iron Oxide) were revealed.

Thus, according to XRD data, the limit for the doping of ferrite – copper spinel with holmium from x = 0.15 to x = 0.2 after annealing at 800 °C for 60 min was established. The limiting level of doping was due to the difference in the ionic radii of the substituted element and the dopant, the ionic radius Ho^{3+} (r = 1.04 Å) was much larger than the ionic radius of Fe^{3+} (r = 0.65 Å) [16–17]. An increase in the degree of doping in the $CuFe_2O_4$ lattice led to a decrease in the value of the angle 2θ for the peak with the highest intensity (Table 1). This once again indicates the successful doping of copper spinel ferrite with holmium and incorporation of the latter into the $CuFe_2O_4$ lattice. The analysis of the crystal sizes determined using the Scherrer formula [18] based on X-ray diffractometry data showed a decrease in D_{av} with an increase in the degree of doping of copper ferrite with Ho^{3+} ions from x = 0 to x = 0.15, followed by an increase at x = 0.2 (Table 1). Such an anomaly at x = 0.2 could be related to the phase inhomogeneity of the samples when two impurity phases appear (CuO and $HoFeO_3$) (Fig. 1), which causes an error in the calculation using the Scherrer formula. The reduction of the average crystal size of $CuFe_{2-x}Ho_xO_4$ (D_{av}) with an increase in the content of Ho^{3+} cations from x = 0.0 to x = 0.15 is explained by the fact that the substitution of Fe^{3+} cations (r = 0.65 Å) by Ho^{3+} cations with a large ionic radius (r = 1.04 Å) causes

Table 1. Characteristics of $CuFe_{2-x}Ho_xFeO_4$ samples synthesized by co-precipitation after annealing at 800 °C for 60 min

Samples, nominal composition	2θ, °	D_{av}, nm	H_c, Oe	M_r, emu/g	M_s, emu/g
$CuFe_2O_4$	36.0510	54.6	940.72	13.03	23.64
$CuFe_{1.9}Ho_{0.1}O_4$	36.0301	46.2	1320.11	10.81	21.32
$CuFe_{1.85}Ho_{0.15}O_4$	36.0119	37.8	1501.12	9.15	18.29
$CuFe_{1.8}Ho_{0.2}O_4$	35.5868	42.9	1317.82	6.40	13.14

an increase in the defectiveness of the lattice and, accordingly, increased internal stresses, as a result of which the growth of crystals is inhibited. Similar results were observed in the study [19], in which the substitution of Fe^{3+} in the $CuFe_2O_4$ lattice by doping with Ce^{3+} cations (r = 1.14 Å) led to a decrease in the average crystal size from 25.36 to 18.53 nm with a change in x from 0.0 to 0.5.

Determination of the real elemental composition of $CuFe_2O_4$ and $CuFe_{1.85}Ho_{0.15}FeO_3$ samples showed that peaks were observed only for the elements Cu, Fe, O, and Ho, and their content was very close to the nominal composition. Impurities of other elements were not revealed (Fig. 2).

TEM images of $CuFe_2O_4$ (A) and $CuFe_{1.85}Ho_{0.15}O_4$ (B), nanopowders annealed at 800°C for 60 min are

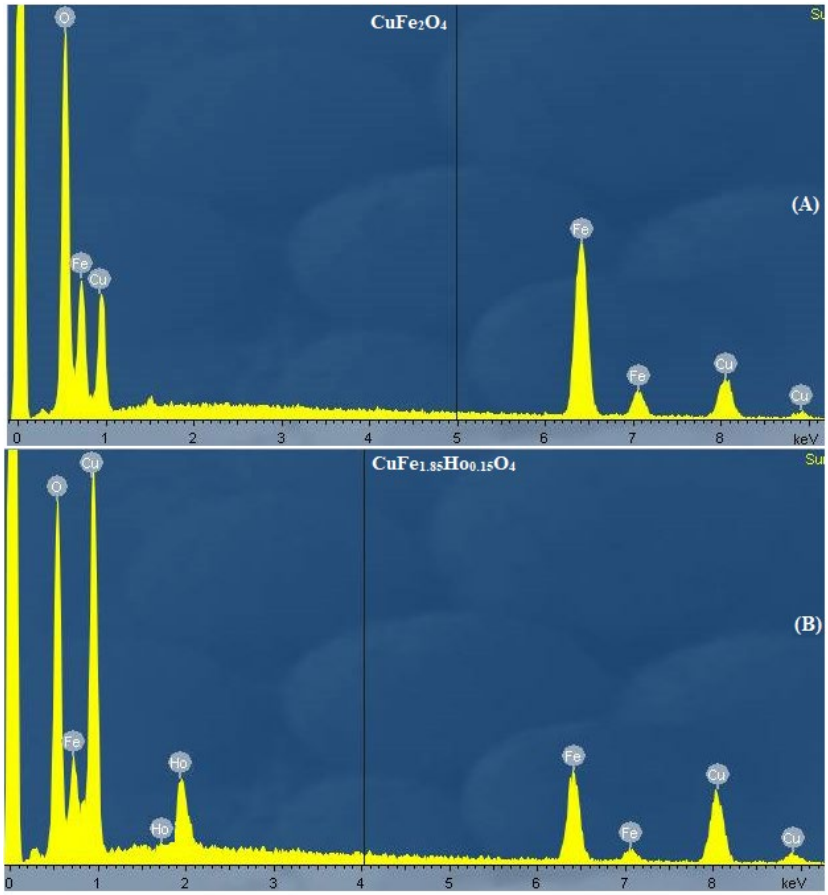

Fig. 2. EDX - X-ray diffraction patterns of $CuFe_2O_4$ (A) and $CuFe_{1.85}Ho_{0.15}O_4$ (B), samples synthesized by co-precipitation after annealing at 800 °C for 60 min

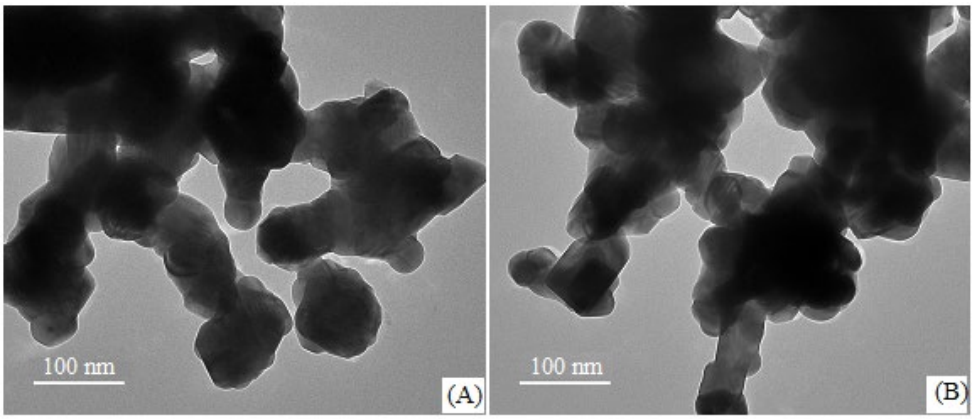

Fig. 3. TEM images of $CuFe_2O_4$ (A) and $CuFe_{1.85}Ho_{0.15}O_4$ (B), nanoparticles synthesized by co-precipitation after annealing at 800 °C for 60 min

shown in Fig. 3. It can be seen that the obtained particles have an approximately spherical shape, and their size was 40–70 nm. The particles were mainly aggregated.

A study of the magnetic characteristics at room temperature showed that the doping of crystal lattice of spinel $CuFe_2O_4$ with Ho^{3+} affected not only the structural characteristics of crystals, but also the magnetic properties of $CuFe_{2-x}Ho_xO_4$ nanopowders (Fig. 4 and Table 1).

Magnetic parameters such as excess magnetization (M_r, emu/g) and saturation magnetization (M_s, emu/g) of $CuFe_{2-x}Ho_xO_4$ samples (nominal composition x = 0, 0.1, 0.15, and 0.2) after annealing at 800 °C for 60 min decreased with increase in Ho^{3+} content, but the coercive force (H_c, Oe) increased with increase in dopant content. An increase in the coercive force is explained by the fact that an increase in the dopant content in $CuFe_2O_4$ crystals led to an increase in their magnetic anisotropy [20–21]. Regardless of the dopant content, the synthesized $CuFe_{2-x}Ho_xO_4$ nanopowders had high values of magnetic characteristics: H_c = 940.72÷1501.12 Oe, M_r = 13.03÷6.40 emu/g, M_s = 23.64÷13.14 emu/g, which opens up prospects for their application as magnetically hard materials for the manufacture of permanent magnets or magnetic recording on hard disks and tapes [20].

4. Conclusions

Ferrite nanopowders $CuFe_{2-x}Ho_xO_4$ (x = 0, 0.1 and 0.15) were synthesized by a simple co-precipitation method, using a 5% NaOH aqueous solution as the precipitant. The obtained $CuFe_{2-x}Ho_xO_4$ samples after annealing of the precipitates at 800°C for 60 min had an average particle size of 40–70 nm. Doping limit of spinel ferrite $CuFe_2O_4$ with Ho^{3+} was detected at a nominal value of x = 0.15. The reduction of the average size (D_{av}) of $CuFe_{2-x}Ho_xO_4$ crystals with an increase in the content of Ho^{3+} cations from x = 0.0 to x = 0.15 is explained by the fact that the substitution of Fe^{3+} cations (r = 0.65 Å) by Ho^{3+} cations with a large ionic radius (r = 1.04 Å) causes an increase in the defectiveness of the lattice and, accordingly, increased internal stresses, as a result of which the growth of crystals is inhibited. Synthesized $CuFe_{2-x}Ho_xO_4$ nanoparticles are characterized by higher values of the coercive force and excess magnetization and, accordingly, are magnetically hard materials.

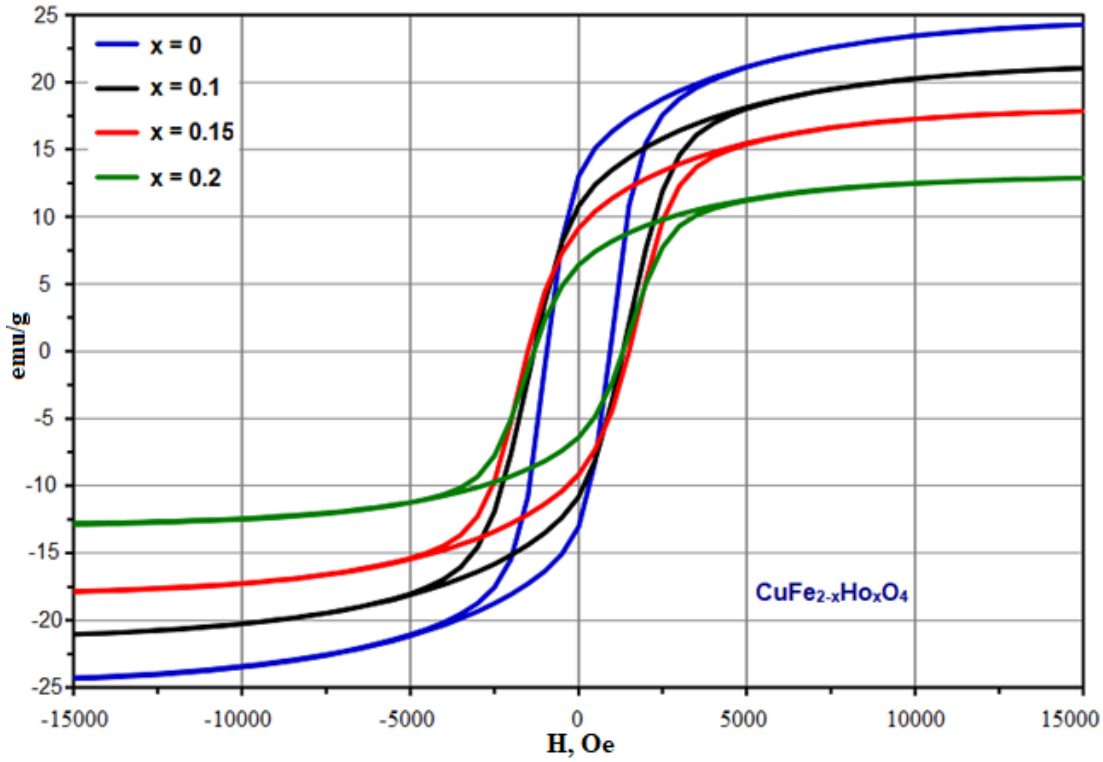

Fig. 4. Field dependences of the magnetization of $CuFe_{2-x}Ho_xO_4$ nanopowders synthesized by co-precipitation after annealing at 800 °C for 60 min

Author contributions

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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