DOI 10.30898/1684-1719.2020.3.15
UDC 539.2

NANOSTRUCTURED MATERIALS BASED ON OPAL MATRIXES AND MAGNETIC OXIDES Ni(Co)-Zn-Fe

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The paper is received on March 18, 2020

Abstract. The conditions for the formation of opal matrixes representing the lattice packing of spheric particles SiO_2 with diameter ~260 nm ($\Delta d < 4\%$) and single-domain size (regions with proper packing of spheric particles) $\geq 0{,}1$ mm^3 are presented. The processes for obtaining of 3D magnetic nanocomposites by synthesis of NiXZn1-XFe2O4 and CoXZn1-XFe2O4 crystallites in communicating spatially ordered inter-spherical voids, occupying ~ 26% of the volume of the opal matrix, are shown. The composition and structure of nanocomposites were researched by electron microscopy and X-ray diffractometry. The results of using samples of magnetic nanocomposites containing Ni0.5Zn0.5Fe2O4 and Co0.5Zn0.5Fe2O4 crystallites of 15–50 nm in size as inserts in Y circulators are discussed.

Key words: Nanocomposites, opal matrix, spinel, 3D packaging of nanocrystallites, magnetic characteristics.

Introduction

At present the intensive research are making to find new materials with magnetic properties. Implementation of magnetic materials as 3D nano-lattice of crystallites with sizes of 10–50 nm will make it possible to expand the frequency range of their application, since the frequency limitations are usually connected with the dispersion of the dielectric and magnetic permeability typical for bulk materials. New direction in development of 3D nanocomposites is the introduction of different compounds into porous matrixes with the cavities of nanometer range. To fill the nanocavities of the porous matrix with different substances, the method for synthesis of compounds directly in the cavities is usually applied.

Opal matrixes are promising as a porous matrix with an ordered lattice of nanocavities [1, 2]. Opal matrix is the correct packaging of spheric particles of amorphous SiO_2 and spheric particle diameters depending on formation conditions can vary within specified limits from ~200 up to ~700 nm [2–5]. Under stable parameters for producing of opal matrixes, the scatter in diameters is < 4%. Opal matrixes are characterized by connected regular network of nanocavitiess between SiO_2 spheric particles. A system of connected and spatially ordered inter-sphere cavities takes ~26% opal matrix volume. Opal matrixes, the nanocavities of which are filled with nanoparticles of different substances, are metamaterials that have the new properties (that are difficult to achieve for monolithic substances) and are adaptable for development of phase velocity control devices in a wide frequency range [3, 6–8]. The periodic structure of the nanoparticle arrangement in the opal matrix significantly changes the microwave properties of the material. The developed metamaterials with spatial dispersion of properties allow us to apply new solutions in the development of electronics devices in the frequency range from tens of GHz to units of THz. Opal matrix-based nanocomposites are advanced in electronic engineering for solid-state microwave devices, as well as for directional X-ray and acoustic wave sources [6, 7, 9–11].

In present work Co(Ni)-Zn-Fe oxides with spinel structure were selected as a magnetic substance [12]. There are investigated the composition and magnetic properties of nanocomposites based on opal matrixes, in nanocavities of which $Ni_XZn_{1-X}Fe_2O_4$ and $Co_XZn_{1-X}Fe_2O_4$ crystallites synthesized. Previously, there have been investigated the structure and magnetic properties of opal matrixes in nanocavities of which the metals and magnetic oxides of complex composition were synthesized [2, 13–15]. The disadvantage of the synthesis method in the nanocavities of the porous matrix is the production of multiphase material that requires careful processing of the conditions for synthesis and control of the obtained nanocomposite properties. Understanding of the features of substance crystallization in the opal matrix nanocavities, promotes creation of metamaterials with controlled functional properties [2, 4, 5].

Our research goal is to obtain and study the relationship of structural features with the magnetic properties of nanocomposites based on opal matrixes, nanocavities of which filled with the $Ni_XZn_{1-X}Fe_2O_4$ and $Co_XZn_{1-X}Fe_2O_4$ crystallites.

Experimental methods

Opal matrixes were manufactured under the temperature 310–350 K from the emulsion, prepared by mixing 1 part of 25% aqueous solution of ammonium hydroxide (NH_4OH), 50 parts of ethanol (C_2H_5OH) and 1,6 parts of orthosilicic acid tetraester ($Si(OC_2H_5)_4$). The chemical substances used in the manufacturing of the opal matrixes were removed from the samples by heat treatment in vacuum (770–970 K; ~ 1 Pa). After vacuum heat treatment, the opal matrixes were hardened at the temperatures up to 1400 K and pressures> 0.2 MPa, and the transfer of SiO_2 to the contact area of the spheric particles took place.

Opal matrix based nanocomposites were manufactured in two stages. At the first stage, nanocavities of opal matrixes were repeatedly filled with aqueous solutions of nitrates Fe, Zn, Ni or Co and the heat treatment were made under 570–770 K. At the second stage, opal matrixes with introduced substances had heat treatment with 970–1470 K for 4–24 hours in air. Low-temperature heat treatment led to the formation of X-ray amorphous and crystalline phases of the different modifications, and high-temperature heat treatment promoted the crystallization of phases of a given composition.

The structure of opal matrices and nanocomposites based on them were studied using raster and transmission electron microscopes (SEM and TEM) Carl Zeiss Supra 40-30-87 and JEM 200C. Substances synthesized in nanocavities of opal matrixes were identified using an X-ray diffractometer *XRD*-6000 (Cu *k*α-radiation).

Magnetic measurements performed with the installation MPMS-XL under the temperatures 2 K and 300 K [12]. Measurement of the losses, signal suppression between output ports of the circulator and reflection coefficient in the frequency range 28–37 GHz were made using Y-circulator (Type ФВЦН1-42, Russia) at Penza Artillery Engineering Institute named after N.N. Voronov. Disc-shaped nanocomposites were used [16, 17].

Results and discussion

Structure of opal matrixes and nanocomposites based on its. Samples of opal matrixes with a volume up to 3 cm^3 with spheric particle diameter of SiO_2 ~ 260 nm ($\Delta d \approx 4\%$) and single domain size (region of the correct packing of spheric particles) $\geq$ 0.1 mm^3 were manufactured (Fig 1*a*). The fragmentation of the opal matrix sample demonstrated the accuracy of the spherical shape of SiO_2 particles and the absence of deformation at the places of their point contact (Fig. 1*b*). Spheric particles of SiO_2 form a lattice having inter-sphere tetrahedral (*T1*, *T2*) and octahedral (*Oc*) nanocavities (Fig. 2*a*). At Fig. 2*b* (left), on the polyhedral faces, concaves of inter-sphere cavity sections are presented, and on the right the synthesized material completely filled the nanocavities is demonstrated. The synthesized substances of the considered nanocomposites filled <20% of inter-sphere cavities (Fig. 3).

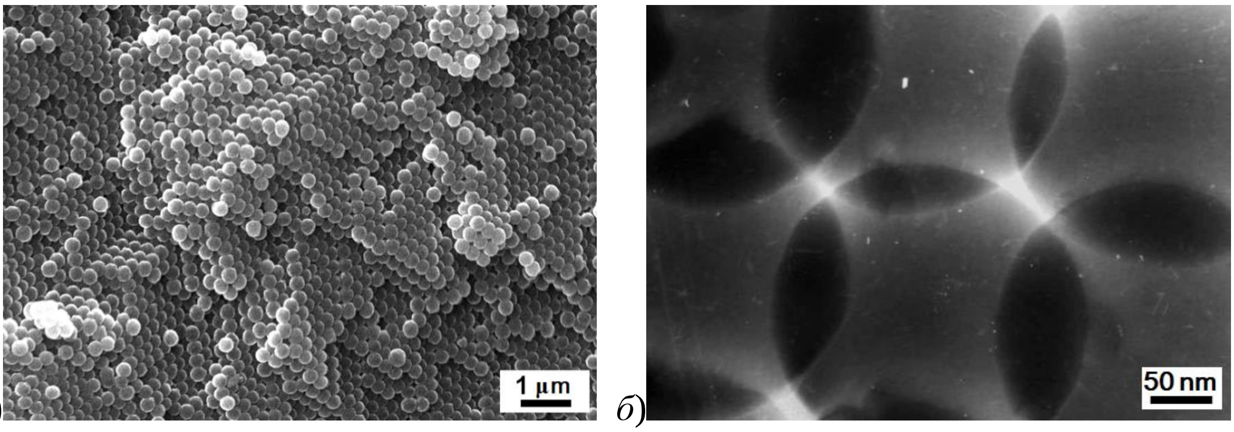
a)


Fig. 1. *a*) SEM image of the opal matrix sample surface. *b*) TEM image of a single layer of SiO_2 spheric particles (the spheric particle layer is angled to the figure surface).

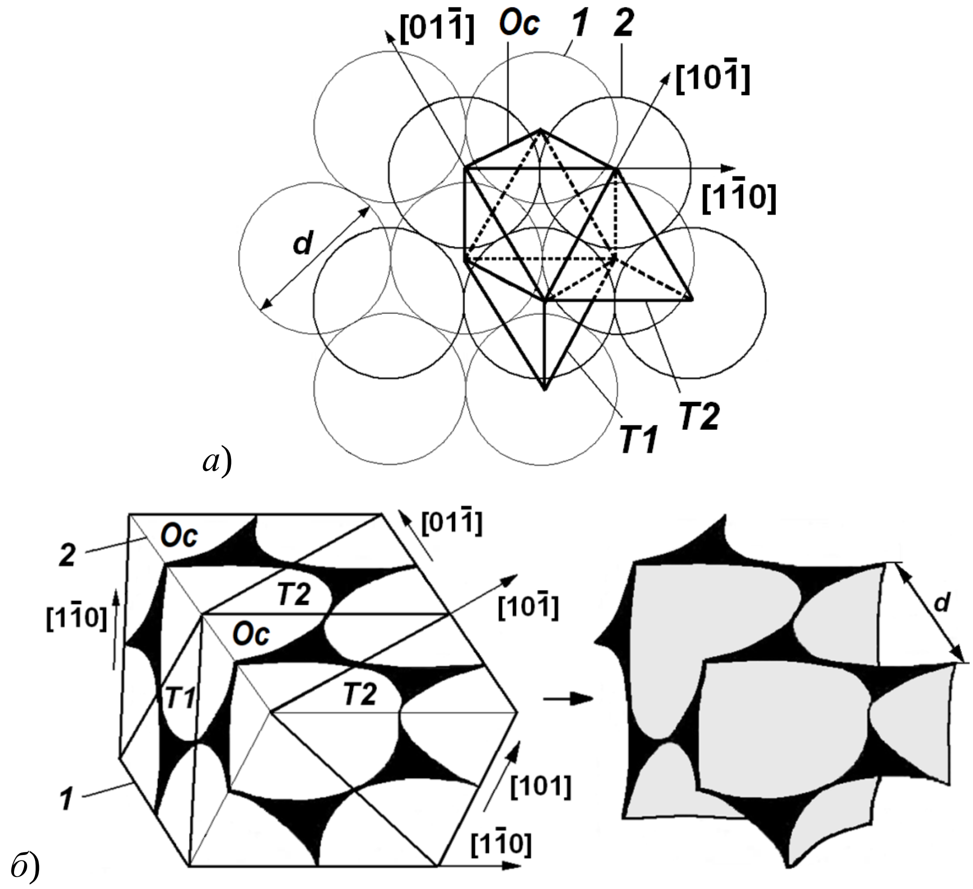


Fig. 2. *a*) Two (*1*, *2*) levels of SiO_2 spheric particles, forming inter-sphere nanocavities.

b) Volume fragment of nanocomposite (left) and the substance filled nanocavities (right).

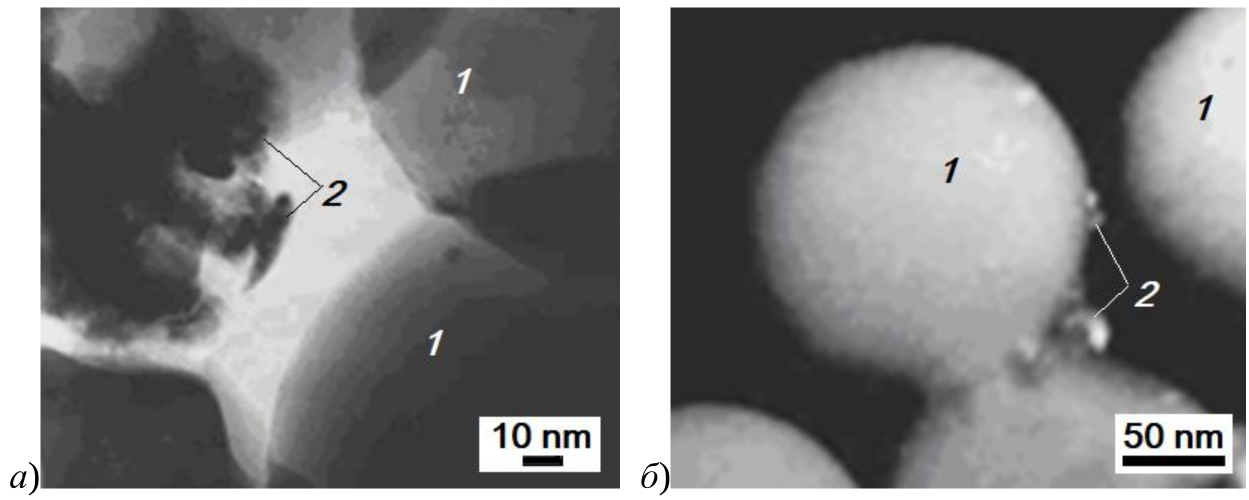


Fig. 3. TEM images of nanocomposites based on opal matrixes containing crystallites in nanocavities: *a*) $Co_XZn_{1-X}Fe_2O_4$; *b*) $Ni_XZn_{1-X}Fe_2O_4$ (*1* – spheric particles SiO_2; *2* – synthesized crystallites).

Phase composition of nanocomposites. Phase transformations, including crystallization of different type compounds, depended on the heat treatment conditions (temperature and duration), as well as on the chemical properties of the intermediate compounds, their thermal stability, and their ability to interact with SiO_2. Analysis of X-ray diffraction patterns demonstrated the presence of crystalline phases $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Co_{0,5}Zn_{0,5}Fe_2O_4$ in the nanocavities of the opal matrixes. Crystallite size (X-ray coherent scattering regions) of the substances synthesized in nanocavities was 15–50 nm. The crystallite size was determined by diffraction peak broadening in X-ray diffraction patterns according to the Selyakov-Scherrer formula. Along with the presented crystalline phases with spinel structure, several crystalline iron-containing phases were obtained: Fe_3O_4 (magnetite, space group $Fd3m$) and Fe_2O_3 ($R\bar{3}c$). During the interaction of compounds based on Co and Fe, X-ray amorphous substances were formed with small inclusions of crystalline phases Fe_3O_4 (magnetite) and $CoFe_2O_4$ (spinel structure). Recrystallization of X-ray amorphous silica with the formation of crystalline phases SiO_2 and the interaction of the synthesized substances with SiO_2 were not detected. In addition to crystalline phases, the studied samples contained X-ray amorphous phases. Similar results of crystallization in nanocavities were observed during the synthesis of the other compounds, for example, $Ni_{0,35}Zn_{0,65}Fe_2O_4$ and $Co_{0,35}Zn_{0,65}Fe_2O_4$. The crystallinity degree (concentration of the crystalline phase in the mixture of amorphous and crystalline components) of the synthesized substances with the composition $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Co_{0,5}Zn_{0,5}Fe_2O_4$ depended on the heat treatment conditions and in some cases reached 60% (by volume). The crystallite size did not depend on the degree of crystallinity of the synthesized substances. Crystallites of substances with spinel structure according to X-ray phase analysis had an equiaxial shape. The uncontrolled crystallization of iron oxides (Fe_2O_3 and Fe_3O_4) and the presence of X-ray amorphous phases compound the selection of the concentrations of the nitrate salt solutions used for the synthesis of substances of given compositions.

Magnetic characteristics. The moment of different $Ni_XZn_{1-X}Fe_2O_4$ and $Co_XZn_{1-X}Fe_2O_4$ nanocomposite samples was measured. At Fig. 4 there are demonstrated the hysteresis loops obtained from nanocomposites containing $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Co_{0,5}Zn_{0,5}Fe_2O_4$ crystallites are presented. The hysteresis loops of these nanocomposites in magnetic field region ~ 300 Oe are presented at the inset to Fig. 4.

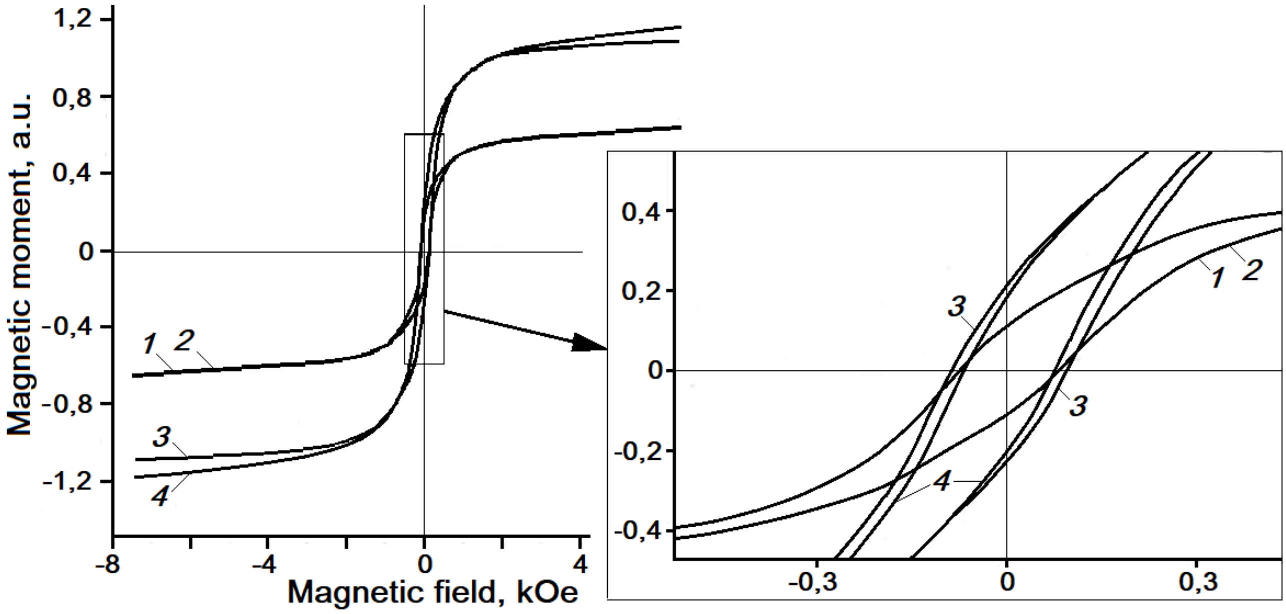


Fig. 4. Hysteresis loops for nanocomposites based on opal matrixes, nanocavities of which filled with $Ni_{0,5}Zn_{0,5}Fe_2O_4$ (*1*, *3*) and $Co_{0,5}Zn_{0,5}Fe_2O_4$ crystallites (*2*, *4*). Measurement temperature 300 K (*1*, *2*) and 2 K (*3*, *4*).

A hysteresis loop typical for ferromagnets is observed, while the value of the coercive force indicates the nanostructured magnetic phase. The result interpretation complexity is due to the multiphase nature and differences in the crystallite sizes of the substances synthesized in the nanocavities. The values of coercive forces in the case of nanocomposites, containing $Ni_XZn_{1-X}Fe_2O_4$ and $Co_XZn_{1-X}Fe_2O_4$ crystallites, indicate on special ferromagnetic ordering. Measurements of samples obtained under different conditions of high-temperature heat treatment demonstrated that there is an impact on the measured parameters by the crystalline phase concentration in the composition of the synthesized substances.

The characteristics of Y-circulator with a cylindrical insert made of magnetic nanocomposites based on opal matrixes, the nanocavities of which contain $Ni_XZn_{1-X}Fe_2O_4$ or $Co_XZn_{1-X}Fe_2O_4$ crystallites, have been investigated. The measurement results for nanocomposite samples containing crystallites with the composition $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Co_{0,5}Zn_{0,5}Fe_2O_4$, as well as X-ray amorphous metal oxide phases, are presented at Fig. 5 **[16, 17]**. The Y-circulator, modified by the authors, with samples of nanocomposites based on opal matrixes, the nanocavities of which are filled with crystallites $Ni_XZn_{1-X}Fe_2O_4$ and $Co_XZn_{1-X}Fe_2O_4$, has demonstrated better signal suppression between circulator output ports, lower values of straightforward losses, a wider passband in comparison with industrial Y-circulator with ferrite (grade 1СЧ4 (Russia), Ni-Zn-spinel), having signal suppression equal to 20-23 dB, with straightforward losses ~ 0.3 dB. Application of nanocomposites based on opal matrixes, the nanocavities of which are filled with $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Co_{0,5}Zn_{0,5}Fe_2O_4$ crystallites provides the improvement of the pointed Y-circulator characteristics in comparison with application of ferrite on $\geq 20\%$.

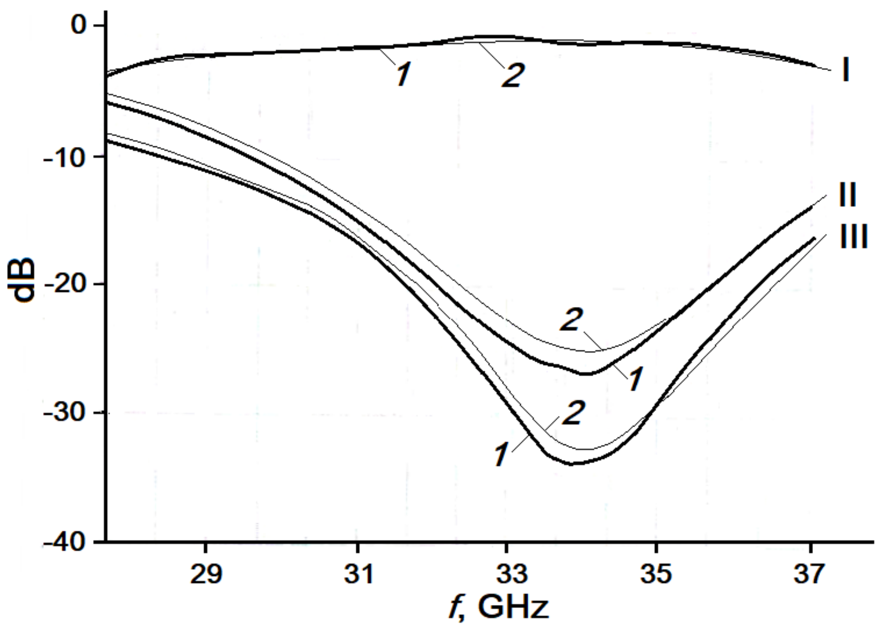


Fig. 5. Measurement of the losses (I), reflection coefficient (II) and signal suppression between output ports (III) in frequency range 28–37 GHz for Y-circulator with nanocomposites samples based on opal matrixes, the nanocavities of which filled with crystallites $Ni_{0,5}Zn_{0,5}Fe_2O_4$ (*1*) and $Co_{0,5}Zn_{0,5}Fe_2O_4$ (*2*).

CONCLUSION

The conditions are demonstrated for the opal matrix formation (3D packages of amorphous SiO_2 spheric particles with a diameter of ~ 260 nm), which form an ordered system of intersphere nanocavities, as well as nanocomposites based on opal matrixes containing 3D lattice of magnetic substance crystallites with compositions: $Ni_XZn_{1-X}Fe_2O_4$ and $Co_XZn_{1-X}Fe_2O_4$, filled the nanocavities.

Magnetic substances synthesized in opal matrix nanocavities had crystallite sizes (X-ray radiation coherent scattering regions) 15–50 nm. The crystallinity degree for a number of samples exceeded tens of volume percent. The crystallites of most of the synthesized substances had a shape close to equiaxial, while the crystallite size did not depend on the synthesized substance crystallinity degree. Understanding of the crystallization features in the nanocavities of opal matrixes, during manufacturing of given compositions of the synthesized substances provides the development of metamaterials with controlled functional property values, which are promising for future device applications.

We investigated the characteristics of the Y-circulator with nanocomposite samples based on opal matrixes, the nanocavities of which are filled with crystallites of composition $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Co_{0,5}Zn_{0,5}Fe_2O_4$. The improvement of ≥ 20% in the characteristics of the Y-circulator in comparison with the use of ferrite (Ni-Zn spinel) is demonstrated.

Present research is supported by RFBR (grants 18-07-00282 A and 18-29-02076 mk).

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For citation:
Belyanin A.F., Bagdasaryan A.S., Bagdasaryan S.A., Pavlyukova E.R.. Nanostructured materials based on opal matrixes and magnetic oxides Ni(Co)-Zn-Fe. *Zhurnal Radioelektroniki - Journal of Radio Electronics*. 2020. No. 3. Available at http://jre.cplire.ru/jre/mar20/15/text.pdf. DOI 10.30898/1684-1719.2020.3.15