Preparation and Physical Properties of Opal Matrices with Nanoparticles of Titanium and Iron Oxides[*]

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The article considers specific features of the formation of nanocomposites based on the lattice packing of SiO_2 nanospheres (opal matrices) with clusters of titanium and iron compounds ($FeTiO_3$, $FeTi_2O_5$, TiO_2, Fe_2O_3) embedded into nanopores between spheres. For the formation of the nanocomposites samples of opal matrices with the sizes of single-domain regions > 0.1 mm3 were used. The diameter of the SiO_2 nanospheres was ~260 nm. Nanocomposites with the volume > 1 cm3 and 10–15% of interspherical nanospacing filled by crystallites of titanium and iron compounds were obtained. The composition and structure of the nanocomposites were studied by electron microscopy, X-ray diffraction and Raman spectroscopy. The dependence of the composition of the synthesized materials on the conditions of their preparation is shown. Results of measurements of the frequency dependences (within the range 1 MHz – 3 GHz) of the magnetic and dielectric characteristics of the obtained nanostructures are presented. Hysteresis loops were studied for the obtained samples.

Keywords: *nanocomposites, opal matrix, iron titanate, X-ray diffractometry, Raman spectroscopy, dielectric and magnetic properties.*

Introduction

Studies in the field of new materials with multiferroid properties are actively conducted in different countries. Multiferroics and multiferroid materials are being created now for the purpose of studying the possibility of their application in various multifrequency devices. It was found [1] that iron titanate ($FeTiO_3$) obtained at a high pressure shows ferromagnetic properties at temperatures below 120 K and spontaneous ferroelectric polarization, which is unusual for the known materials. Besides, iron titanate can show semiconductor and dielectric properties (its forbidden zone width is ~ 2.6–2.9 eV). The antiferromagnetic, magnetic and ferroelectric properties of multiferroic $FeTiO_3$ coexist at low temperatures. It can be used as a magnetic carrier and a magnetic sensor in memory devices, sensors, solenoids and other devices functioning as magnetic switches upon electric fields change [2]. It is assumed that creating a 3*D* lattice of clusters with sizes up to 50 nm from multiferroid materials will allow expanding the frequency range of their

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application, because frequency restrictions, as a rule, are caused by dispersion of dielectric and magnetic permeability typical of massive materials.

A perspective method for obtaining solid-state nanocomposites is introducing various compounds into porous matrixes with nanosized cavities. Nanocomposites based on filled porous matrixes have a number of considerable advantages related to the possibility of setting the size and relative positioning of nanoparticles by choosing matrixes with certain geometry of cavities. Besides, nanoparticles in cavities are protected against the environmental influence. Ordered *3D* nanolattices of multiferroic crystallites can be created with the use of opal matrixes (three-dimensional three-layered cubic structures based on latticed packing of X-ray amorphous SiO_2 nanospheres close in diameter) due to filling the interspherical cavities with multiferroics.

The composition, structure, optical, electric and magnetic properties of $FeTiO_3$ are markedly affected by the synthesis conditions [3]. In order to fill pores the method of synthesizing compounds directly in the porous matrix is widely used. Despite its complexity this method gives the amplest opportunities for obtaining nanocomposites with different characteristics. Synthesis in the nanodimensional space of interspherical cavities of opal matrixes helps stabilizing high-temperature phases at low temperatures and decreasing the temperature of the synthesized substance formation [4]. A disadvantage of the method of synthesis of cavities is the production of several phases of various structure, which requires careful development of the synthesis conditions and control of the properties of the obtained composites.

Previously, opal matrixes were obtained. In their interspherical cavities titanium oxide crystallites, as well as titanates of metals and rare earth elements were synthesized. The structure and physical properties of these matrixes were studied [5–7].

This work presents the results of studying the interrelation of conditions of formation and composition, structure, dielectric and magnetic properties of nanocomposites based on opal matrixes, in the interspherical cavities of which Fe and Ti oxide nanoparticles were synthesized.

Experimental

Nanocomposites preparation. We used opal matrixes as a porous matrix. They consisted of spheres of X-ray amorphous silicon dioxide 260–270 nm in diameter. The structure of opal matrixes is the closest packing with a factor of space filling with SiO_2 nanospheres ~ 74% (~ 26% of the volume of opal matrixes is the share of octahedral and tetrahedral interspherical cavities) [8]. The structure of consecutively close-packed layers of SiO_2 nanospheres and of the substance filling the interspherical cavities of opal matrixes is considered in [5]. According to calculations on the assumption of rigid spheres, octahedral and tetrahedral cavities have sizes (diameters of the spheres inscribed in them) of ~ 110 and ~ 60 nm (~ 0.41 *d* and ~ 0.22 *d*), respectively. If the shape of SiO_2

spheres is ideal, cavities in the opal matrix are connected with channels having the shape of a triangle with concave walls in section [5].

Opal matrixes were obtained by hydrolysis of tetraethyl orthosilicate $Si(OC_2H_5)_4$ with an ethanol solution in the presence of $NH_3 \cdot H_2O$ as a catalyst. In the course of the hydrolysis, fine branched polymeric particles of silicon dioxide are formed at first. Due to internal polycondensation they are transformed into amorphous spherical particles. The surface of contact of SiO_2 spherical particles in such a structure is close to a dot. Then a number of operations for hardening the samples were sequentially performed. In case of hydrothermal hardening of opal matrixes at high temperature and pressure silicon dioxide is transferred into the zone of contact of spherical SiO_2 particles resulting in the formation of stable −Si−O−Si− bonds. Note that in real opal matrixes that underwent hardening the sizes of cavities and channels are less than theoretical.

Samples of nanocomposites based on the opal matrixes containing Fe and Ti oxide nanoparticles were prepared in two stages. At the first stage, the opal matrixes were impregnated with a solution of iron nitrate in a 15% $TiCl_3$ solution in a 10% aqueous solution of hydrochloric acid (to fill the interspherical cavities) and subjected to low-temperature treatment at 400°C. The described procedure including impregnation and low-temperature treatment was repeated up to 9 times. At the second stage, the filled opal matrixes were subjected to high-temperature treatment in various modes: in H_2 atmosphere at 800–1000°C; in the air at 1200°C; sequentially in H_2 at 1000°C and in the air at 1200°C. Controlled heat treatment of the nanocomposites in H_2 was carried out with the use of an “Otzhig TM-6” installation developed in the Research Institute of Precision Machine Manufacturing, Zelenograd [7]. The installation provided automatic processing of samples in a heating chamber according to a preset program. Parameters of the samples heat treatment in H_2 were as follows: preliminary purge of the reaction chamber with nitrogen (20 min); heating at rate of 600 deg/h in hydrogen flow at a pressure of 5 atm; keeping for 1–2 h in hydrogen flow at 800–1000°C (hydrogen pressure: 3–5 atm); cooling in hydrogen to 250°C. High-temperature treatment of the samples in the air was carried out at 1200°C in a tube furnace.

Methods of studying the structure, and composition and measuring the dielectric and magnetic characteristics of the nanocomposites. The structure of the opal matrixes was studied with the use of a Carl Zeiss Supra 40-30-87 scanning electron microscope (SEM). The crystal phases of the Fe and Ti compounds synthesized in the interspherical cavities of the SiO_2 nanospheres were identified with the use of an *ARL X*'tra diffractometer (Thermo Fisher Scientific) [Cu *k*α radiation, energy-dispersive solid-state detector with a Peltier cooler, sample rotation, step size 0.02°, continuous mode (1 deg/min.)]. The synthesis process (the nanocomposites composition and structure) were monitored also by Raman scattering spectroscopy with the use of a LabRAM *HR* 800 (HORIBA Jobin-Yvon) laser spectrometer (632.8 nm line of a He-Ne laser; laser power

<300 mW; beam spot area ~ 4 μm; analyzed layer depth ~ 3 μm) equipped with a *THMS* 600/720 detachable device for samples heating (Linkam Scientific Instruments).

The frequency profiles (in the range from 1 MHz to 3 GHz) of the real and imaginary components of dielectric permittivity (ε', ε'') and of magnetic susceptibility (μ', μ''), as well as the loss-angle tangent ($tg\delta_\varepsilon$, $tg\delta_\mu$) of the nanocomposites were measured with the use of an Agilent N5260A controller and a E4991A Agilent analyzer. Magnetization was measured with the use of a Quantum Design SQUID magnetometer.

Results and Discussion

Structure of nanocomposites based on opal matrixes. In order to form nanocomposites we used samples of opal matrixes with a volume of > 1 cm^3 and a diameter of SiO_2 nanospheres of $d \approx$ 260 nm (Δd <5%, the size of monodomain areas > 0.1 mm^3) (Figure 1). The various phase composition and structure of the phases of the materials synthesized at high-temperature treatment depended on the composition of the impregnating solutions, the number of impregnations and the conditions of the nanocomposites heat treatment. The substances obtained in the interspherical cavities by low heat treatment are X-ray amorphous metal oxides that partially crystallize upon high-temperature treatment. The synthesized oxides based on Fe and Ti filled up to 15% of the volume of the opal matrixes interspherical cavities.

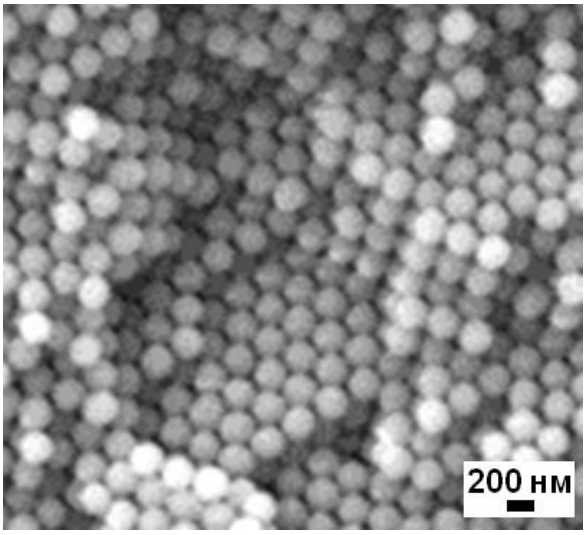


Figure 1. SEM-image of the surface of the formation of a bulk sample of an opal matrix – ordered packing of SiO_2 nanospheres.
[нм means nm]

The X-ray diffractograms of the nanocomposites having a degree of the interspherical cavities filling ~ 10% and ~ 15% (6 and 9 impregnations) and subjected to high-temperature treatment in H_2 at 800–1000°C, and also consecutively in H_2 at 1000°C and in the air at 1200°C show the existence of the following crystal phases: $FeTi_2O_5$ (spatial group *Bbmm*); TiO_2-rutile *($P4_2/mnm$)* and TiO_2-

anatase *(I4₁/amd)* (Figures 2 and 3, where TiO_2-r and TiO_2-a are TiO_2-rutile and TiO_2-anatase, respectively). The size of areas of $FeTi_2O_5$ crystallites coherent dispersion was 24–38 nm, and that of titanium oxides, 15–60 nm, which is less than the diameters of the spheres inscribed in the tetrahedral and octahedral cavities of the opal matrixes. In some cases depending on the impregnating solutions concentration, when annealing in H_2 at temperatures $\leq$ 800°C, Fe_2O_3-hematite *(R-3c)* forms (Figure 3, curve *1*). High-temperature annealing in the air at 1200°C is followed by the formation of SiO_2 crystal phases in small concentrations (recrystallization of X-ray amorphous silicon dioxide): SiO_2-christobalite ($P4_12_12$); SiO_2 (*I2/a*) etc. [4].

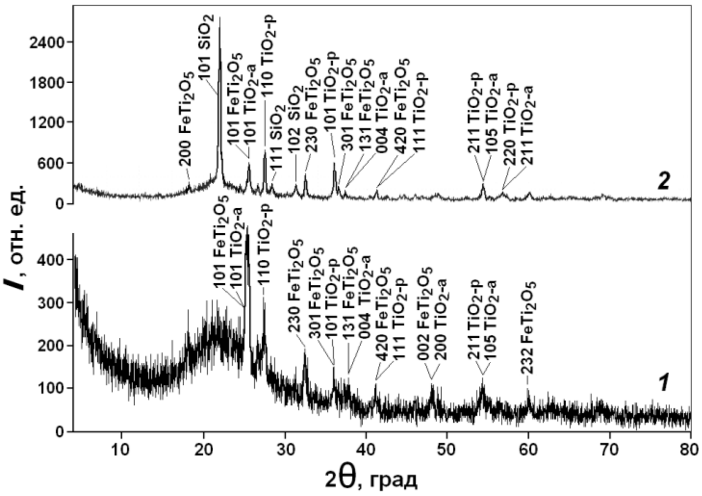


Figure 2. X-ray diffractograms of opal matrixes with crystallites synthesized in the interspherical cavities based on Fe and Ti oxides (the cavities were filled by ~ 10%) obtained upon heat treatment: *1* – in H_2 at 1000°C; *2* – in the air at 1200°C

[отн. ед. means Rel. units; град means deg; TiO_2-р means TiO_2-r]

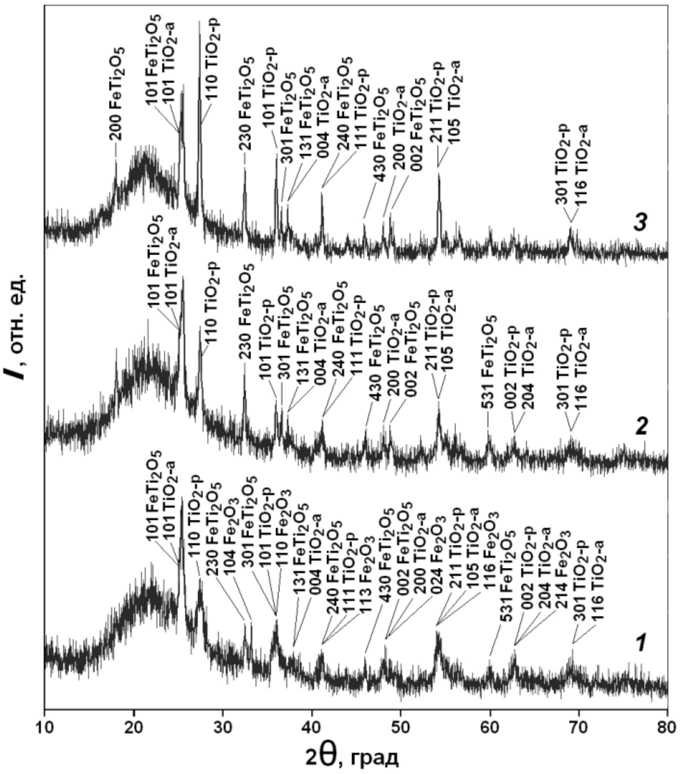


Figure 3. X-ray diffractograms of opal matrixes with crystallites synthesized in the interspherical cavities based on Fe and Ti oxides (the cavities were filled by ~ 15%) obtained upon heat treatment in H_2 at temperatures: *1* – 800°C; *2* – 900° C; *3* – 1000°C.
[отн. ед. means Rel. units; град means deg; TiO_2-р means TiO_2-r]

Changes in the phase relationships in the conditions of limited geometry of interspherical cavities are illustrated by changes in the Raman spectra. The Raman spectra of the nanocomposites containing crystallites of Fe and Ti oxides are presented in Figure 4. The width and position of the bands in the Raman spectra of the obtained substances change depending on the synthesis conditions determining the crystallites structure and size. The Raman spectra show bands of the phases $FeTiO_3$, $FeTi_2O_5$, TiO_2-rutile and TiO_2-anatase. The changes in the position of the bands in the Raman spectrum of TiO_2-anatase and TiO_2-rutile nanostructured phases are caused by the composition deviation from stoichiometry [9].

Heat treatment in the air at 1200°C leads to an increase in the concentration of the $FeTiO_3$ phase. In this case, the opal matrix can be described as a continuous material containing a *3D*-sublattice of $FeTiO_3$ crystallites with a size of coherent X-ray scattering areas of < 1 nm. This does not allow to identify them by X-ray diffractometry. Figure 4 (a curve *4*) shows the Raman spectrum of the nanocomposite. The spectrum contains bands, the position of which is close to the position of the bands in the spectrum range of nanocrystalline $FeTiO_3$ [10] (see the table).

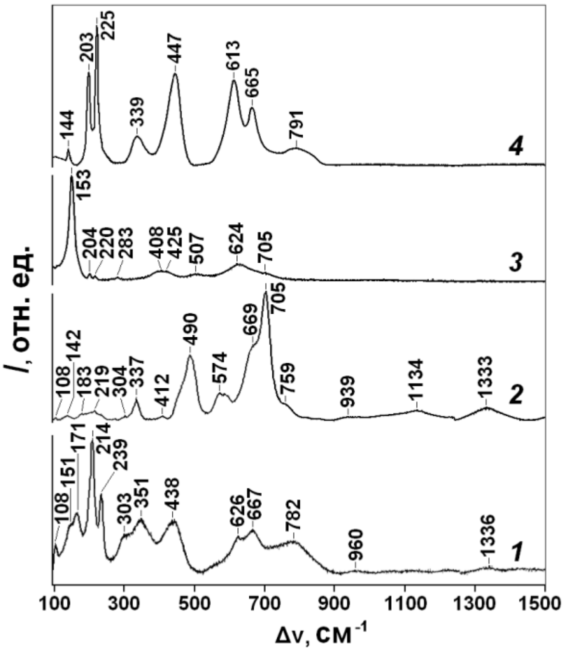


Figure 4. Raman spectra of nanocomposites obtained by heat treatment:
1 – in H_2 at 1000°C; *2, 3* – in the air at 1200°C;
4 – sequentially in H_2 at 1000°C and in the air at 1200°C.
[отн. ед. means Rel. units; см means cm]

Raman spectra of nanocrystalline $FeTiO_3$

Vibrational mode $FeTiO_3$	Shift of Raman bands, $\Delta\nu$, cm^{-1}	
	Exp. data	Lit. data [10]
A_{1g}	144	144
E_{1g}	203	200
E_{2g} or E_{3g}	225	224
A_{2g} or A_{3g}	339	336
A_{4g}	447	443
E_{4g}	615	612
E_{5g}	665	662

The Raman spectra of $FeTiO_3$ contain bands associated with the oscillatory modes of the bonds in iron oxides characterized by $\Delta\nu$ equal to 225, 339, 447, 613 (Fe_2O_3-hematite) and 665 cm^{-1} (Fe_2O_3-maghemite). An indistinct band at $\Delta\nu$ 791 cm^{-1} relates to X-ray amorphous silicon dioxide and SiO_2-christobalite phase.

The common bands at $\Delta\nu$ 138–146, 220–235, 246–258, 286–298, 425–439 and 633–647 of cm^{-1} typical of titanium dioxide can be found in the Raman spectra of the nanocomposites based on the opal matrixes, the interspherical cavities of which are filled with titanium oxides (TiO_2 and TiO), as well as with such multiferroics as rare earth element (RZE) titanates: oxotitanates of general formula R_2TiO_5 and dititanates $R_2Ti_2O_7$, where R is an RZE (Er_2TiO_5, La_2TiO_5, $Dy_2Ti_2O_7$, $Gd_2Ti_2O_7$, $Pr_2Ti_2O_7$, $Tb_2Ti_2O_7$, $Yb_2Ti_2O_7$); lithium-zinc and bismuth dititanates ($Li_2ZnTi_3O_8$ and $Bi_2Ti_2O_7$); lead titanates ($PbTiO_3$ and $PbTi_3O_7$) [5–7].

Heating the obtained samples in the air to 550°C (with the use of the Raman spectrometer detachable device for samples heating) shows intensity redistribution and strips broadening, the sample containing $FeTiO_3$ nanocrystallites not showing bands attributed to $FeTi_2O_5$ and to other phases (Figure 5). Note that X-ray diffractometry revealed only the maxima corresponding to titanium oxides and $FeTi_2O_5$. It is possible to assume that the synthesis of Ti and Fe compounds in the interspherical cavities of the opal matrix produces $FeTiO_3$ particles with a size of coherent dispersion areas about 1 nm, which does not allow seeing them in the X-ray diffractograms because of dimensional broadening of the diffraction maxima.

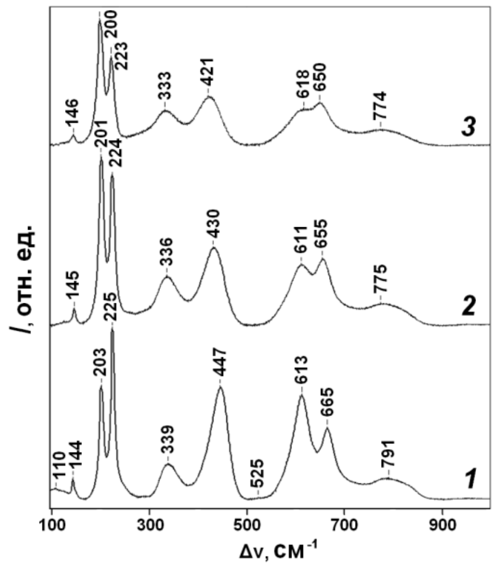


Figure 5. Raman spectra of the opal matrix, the interspherical cavities of which are filled with $FeTiO_3$ nanocrystallites. (The sample was obtained by thermal treatment sequentially in H_2 at 1000°C and in the air at 1200°C). The Raman spectra were recorded at the following temperatures: 20°C (*1*); 300°C (*2*); 550°C (*3*).
[отн. ед. means Rel. units; см means cm]

Dielectric and magnetic properties of studied materials. The results of the studies on the frequency dependencies of the real and imaginary components of dielectric permeability, of magnetic susceptibility and the loss-angle tangent of the opal matrixes with the crystallites of Fe and Ti compounds synthesized in the interspherical cavities are presented in Figures 6–8.

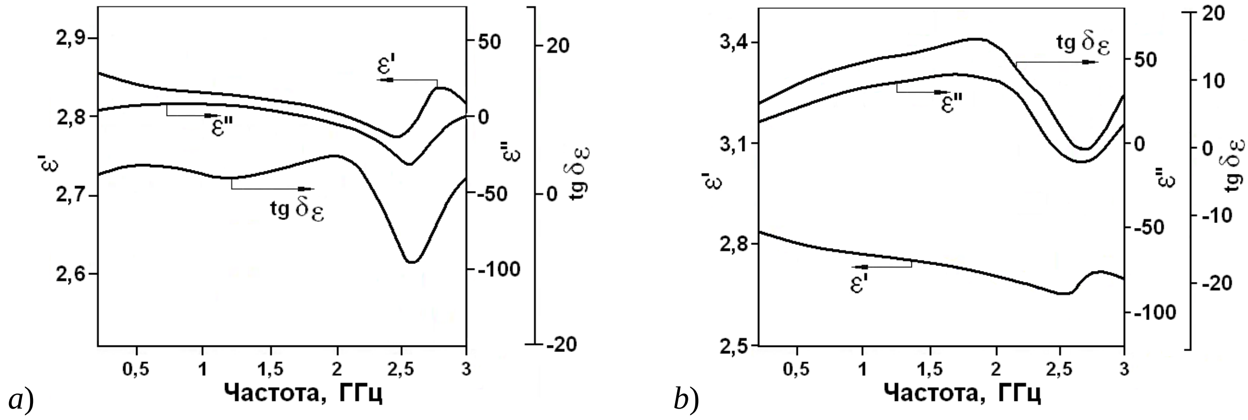


Figure 6. Frequency dependencies of the real (ε ′) and imaginary (ε ″) components of dielectric permeability and the loss-angle tangent of the opal matrixes with a degree of filling of interspherical cavities: *a)* ~ 10%; *b)* ~ 15%.
[Частота, ГГц means Frequency, GHz]

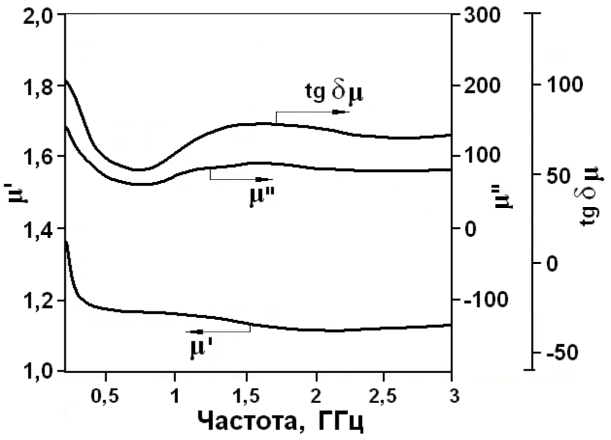
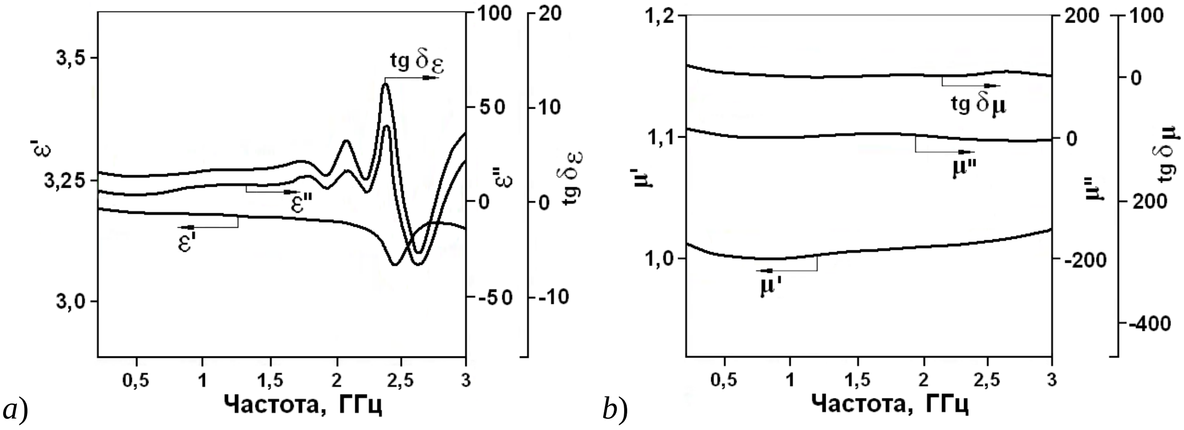


Figure 7. Frequency dependencies of the real (μ′) and imaginary (μ″) components of magnetic susceptibility and the loss-angle tangent of the opal matrix, the interspherical cavities of which are filled by ~ 15%
[Частота, ГГц means Frequency, GHz]



a)

b)

Figure 8. Frequency dependencies of the real and imaginary (ε ′ and ε ″) components of dielectric permeability (a) and magnetic susceptibility (μ′ and μ″) (b) and the loss-angle tangent of the opal matrix, the interspherical cavities of which are partially filled with crystallites of Fe and Ti oxides. (According to Raman spectroscopy the sample does not contain a $FeTiO_3$ phase.)
[Частота, ГГц means Frequency, GHz]

In can be seen from Figures 6–8 that dielectric losses are low in all the range and just slightly depend on frequency. The dielectric dispersion of frequencies in the microwave range is poorly resolved. Perhaps all the main changes occur at low frequencies. The studied materials are so-called "bad" dielectrics with high losses and pronounced relaxational polarization. The dielectric losses and conductivity at high frequencies just slightly differ from the parameters of the opal matrix with unfilled interspherical cavities. Measurements of the samples obtained at various synthesis temperatures showed that the concentration of crystal phases in the synthesized substances affects the measured parameters.

At low temperature, the samples containing $FeTiO_3$ clusters show hysteresis loops caused by ferromagnetism. The studied nanocomposites showed two magnetic phase transitions [11]: one at ~

345 K, and the second, near ~ 50 K. According to [9] the magnetization of the $FeTiO_3$ nanoparticle system in a field of 1 kOe at temperatures ~ 30 K was about 0.1 $A \cdot m^2/kg$. The magnetization of the studied sample in this temperature range in the field of 1 kOe depended on the quantity of the $FeTiO_3$ clusters, and when the cavities were filled by ~ 15% of the volume, magnetization was equal to ~ 0.01 $A \cdot m^2/kg$. This property indicates that the quantity of the $FeTiO_3$ phase in the studied sample is much less than the full volume of the substance filling the interspherical cavities.

The change in the temperature dependence of sample susceptibility at ~ 50 K can be interpreted as the transition to the anti-ferromagnetic state in $FeTiO_3$ nanoparticles that are present in the interspherical cavities of the opal matrix. However, bulk $FeTiO_3$ does not show ferromagnetic properties. The crystalline phases found by X-ray diffraction do not show noticeable magnetic properties in the temperature ranges where magnetic phase transitions can be seen.

Conclusion

Specific features of the formation of nanocomposites based on lattice packings of SiO_2 nanospheres (opal matrixes) containing clusters of Fe and Ti oxides in the interspherical cavities were considered. Samples of nanocomposites based on the opal matrixes containing nanoparticles of Fe and Ti oxides were prepared in two stages including low-temperature heat treatment (at 400°C) and high-temperature heat treatment (in H_2 at 800–1000°C and/or in the air at 1200°C). High-temperature heat treatment (in the air and in hydrogen) of the nanocomposite samples obtained under various conditions of impregnation and low-temperature treatment can lead to the formation of various concentrations of crystalline phases of Fe and Ti oxides. Changes in the phase ratios under the conditions of limited geometry of the interspherical cavities are illustrated by changes in X-ray diffractograms and Raman spectra. The X-ray diffractograms indicate the formation of iron dititanate $FeTi_2O_5$ and titanium oxides TiO_2 with the structure of rutile and anatase in the cavities. The bands of $FeTiO_3$ phase appear in the Raman spectra. Its concentration increases upon heat treatment in the air at 1200°C, and the opal matrix can be described as a continuous material containing a *3D* sublattice of $FeTiO_3$ crystallites with a size of coherent X-ray scattering regions < 1 nm. The synthesized oxides based on Fe and Ti filled up to 15% of the volume of the interspherical cavities of the opal matrixes.

The results of the studies on the frequency dependencies (in the range from 1 MHz to 3 GHz) of the real and imaginary components of dielectric permeability, magnetic susceptibility and loss-angle tangent of the opal matrixes with the crystallites of Fe and Ti oxides synthesized in the interspherical cavities show that dielectric losses are low in all the range and hardly depend on frequency. The studies allowed to determine the interrelation between the microwave characteristics and the phase structure of the nanocomposites containing the crystalline phases of $FeTiO_3$, $FeTi_2O_5$

and titanium dioxides, as well as to obtain data necessary for using such non-crystalline non-uniform materials with spatial modulation (dispersion) of dielectric parameters in the nanometer range.

The nanoparticles synthesized in the cavities showed weak ferromagnetic properties below 345 K. At a low temperature the samples containing $FeTiO_3$ clusters show hysteresis loops caused by ferromagnetism. The magnetization of the studied samples in the specified temperature range in a field of 1 kOe depended on the quantity of $FeTiO_3$ clusters. When ~ 15% of the cavities volume was filled, magnetization was equal to ~ 0.01 $A{\cdot}m^2/kg$.

Understanding the specific features of phase transformations and crystallization in the cavities of the opal matrixes upon the synthesis of materials with preset composition and structure allows creating metamaterials with controlled values of functional properties and operating characteristics.

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