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Analysis of the Electromagnetic Properties of 2000NN/2000NM Composites with Ferroelectric and Polymer Matrices

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Abstract—The results of studying the electrical properties of ferrite-dielectric composites containing inclusions of Mn-Zn and Ni-Zn spinel ferrites with the same initial magnetic permeability (grades 2000NM and 2000NN, respectively) and different electrical resistance are presented. Polymer and ceramic dielectrics with different values of dielectric permeability were used as matrices of composites: polystyrene (PS525), polyvinylidene fluoride (grade F2MB), lead zirconate titanate (PZT-21), and barium titanate (TBK-3). Experimental samples of composites were obtained by hot pressing (for a polymer matrix) or cold pressing with a binder (for a ferroelectric ceramic matrix). It has been shown that the radio-absorbing properties of the obtained composites strongly depend on the electrical properties of a dielectric matrix and on the electrical resistivity of a filler. The highest attenuation of electromagnetic waves of 25–27 dB in the frequency range of 4–5 GHz is observed for ferrite-polymer composites with a 2000NM semiconductor filler with a 6-mm-thick radio-absorbing material. For composites filled with a Mn-Zn ferrite, a pronounced shift in the dispersion region of magnetic permeability is also observed, which in turn changes the frequency position of peak radio absorption. For the composites with a ferroelectric matrix, the operating frequency range for both fillers was shifted toward the low-frequency region of 1–4 GHz with maximum attenuation of up to 22 dB at the same thickness of the material. It was experimentally confirmed that, at a weight content C_m of ferrite of 40 wt %, an increase in the dielectric permeability of the matrix results in a decrease in frequency f_c of the center of minimum absorption and in a decrease in minimum reflection coefficient $K_{\text{refl}}^{\min}$ at a metallic plate for a 2000NN filler with a high electrical resistance. For the composites with a 2000NM filler, the dependence of $K_{\text{refl}}^{\min}$ (ε' of the matrix) passes through a minimum. The obtained composites can be considered as effective radio-absorbing materials for the frequency range of 1–6 GHz with peak attenuation of an electromagnetic wave in the range of 14–27 dB and with the operating frequency band of 1.1–2.5 GHz (at a level less than 10 dB).

Keywords: ferrite-dielectric composites, Ni-Zn spinel ferrite 2000NN, Mn-Zn spinel ferrite 2000NM, radio-absorbing materials, matrix, filler, magnetic permeability, dielectric permeability, electrical resistivity

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INTRODUCTION

The problem of obtaining composite materials is relevant because of the need to develop new materials with unique functional and structural properties [1, 2]. The composite materials predominant in production and study are polymer composite materials (PCMs), in which polymers act as matrices that bind various reinforcing or functional fillers in the form of spheres, ellipsoids, threads, plates, fibers, etc. [1–3]. The resulting characteristics of PCMs depend on a large number of technological parameters of manufacturing and particular properties of components, but in the first approximation, one can emphasize the following properties: the distribution of inclusions over the matrix volume and the content of inclusions.

The need for obtaining PCMs that can absorb or shield electromagnetic radiation (EMR) is evident owing to the problems with electromagnetic compatibility of components in electronic equipment, electromagnetic contamination of the environment, etc. [3, 4]. The functional characteristics of radio-absorbing PCMs in the microwave range (attenuation, attenuation bandwidth, peak value of attenuation) depend on the physical parameters such as composite dielectric permeability ε^* and magnetic permeability μ^* and electrical conductivity σ. The study of the frequency spectra of these parameters can be used to predict the radio-absorbing characteristics of the material with reasonable accuracy. Note that the high values of ε^* and μ^* may indicate the intense processes of polarization and magnetization, in which some of the electromagnetic energy is consumed for the reorientation of dipoles. A high value of σ can cause eddy currents to occur in a material, which can also enhance its radio-absorbing characteristics.

The radio-absorbing characteristics of PCMs change in the presence of inclusions. Thus, the introduction in the PCM composition of magnetic oxides—ferrites [4, 5]—significantly increases magnetic losses, especially at the frequency of the natural ferromagnetic resonance (NFMR). Ferritic ceramic technology makes it possible to obtain a large assortment of different compositions with a wide range of magnetic properties [6], which makes it possible to produce a large number of radio-absorbing composite materials (RACMs) filled with ferrites. The ceramic technology can be used to produce both powders and bulk items that can be crushed (e.g., defective items). In addition, nanoparticles or ultrafine particles of ferrites [7, 8] can also be used as fillers of polymer-based RACMs. Note that the synthesis of nanomaterials is in most cases rather complicated, and their practical application is limited owing to a high cost and difficulty of the processes of obtaining fillers.

Ferrites are highly stable and resistant to atmospheric impacts and electromagnetic radiation. As polymer matrices, thermoplastic (polystyrene, polyethylene, polyvinyl chloride, polypropylene, polyvinyl alcohol) and thermosetting (epoxy resin) polymers are widely used, which exhibit low electrical conductivity and pronounced hydrophobicity and resistance to external impacts, respectively.

Oxide ferroelectrics, for example, barium titanate $BaTiO_3$ [9, 10], can serve as effective fillers for RACMs. In such materials, the presence of electrical dipoles causes polarization processes, which can considerably contribute to dielectric losses. Mixing magnetic or electrically conductive additives with ferroelectric inclusions may cause a synergistic effect of increased radio absorption.

The search for the optimum ratios of complex dielectric and magnetic permeabilities is mathematically implemented [11]. At the same time, the experimental data on the dependence of radio-absorbing characteristics on dielectric permeability are of interest, first of all, from a practical point of view.

The aim of this work is to study the influence of the weight content of a ferrite filler and its electrical properties on the electromagnetic and radio-absorbing properties of ferrite-dielectric composites.

EXPERIMENTAL

Industrial ferrites of grades 2000NN and 2000NM (chemical compositions $Ni_{0.32}Zn_{0.68}Fe_2O_4$ and $Mn_{0.58}Zn_{0.26}Fe_{0.16}Fe_2O_4$) were used as initial components, and polystyrene PS525, polyvinylidene fluoride (PVDF) F2MV, and ferroelectric ceramics TBK-3 (composition $Ba_{0.9}Ca_{0.1}TiO_3$ + 0.5CoO) and PZT-21 (composition $Pb(Zr_{0.4}Ti_{0.6})O_3$) were used as the matrices for composites. Note that the PVDF copolymer of grade F2MV (composition $–[CH_2—CF_2]_n–[CF_2—CF_2]_m–$, where $n = 71$ and $m = 29$) as a polymer material is widely used in the development of composites, since in addition to ferroelectric properties, it exhibits high structural characteristics [12–15].

The electromagnetic and radio-absorbing properties of the composites were studied on ring-shaped samples with outer and inner diameters of 16 and 7 mm and with the thickness of 6 mm. The rings with polymer matrices were manufactured as follows: polymer and ferrite powders were mechanically mixed until a homogeneous mixture was obtained; after loading into a stainless steel mold, the mixture was pressed to a pressure of 100 MPa and heated for 10 min at a temperature of 200°C (for polystyrene at 90°C). In the case of composites with the matrix of a ferroelectric powder, piezoceramic and ferrite powders were mixed with a binder of an aqueous solution of polyvinyl alcohol. The resulting mixture was also pressed without exposure to temperature, followed by drying at 60°C.

RESULTS AND DISCUSSION

The following dielectric materials were used as matrices: insulators (PS525, which is a nonpolar dielectric with a weak dipole moment) and ferroelectrics (F2MV, TBK, PZT). Oxides with a perovskite structure exhibit pronounced ferroelectric properties (after polarization of the ceramic), a high dielectric permeability, and a Curie point of ~120°C [16].

The frequency spectra of the dielectric permeability of the used dielectrics are shown in Fig. 1. It can be seen that the dielectric permeability of polymers is 10 times lower than that of ceramic oxide ferroelectrics owing to the presence of dipoles in the crystal lattice induced by its distortion. In the studied frequency range, no pronounced dispersion of dielectric permeability was observed. It is known that relaxation polarization (dipole, thermal) in ferroelectrics and polymers occurs in the range of $1–10^6$ Hz. For this reason, there are no noticeable frequency changes in the values of ε'. The change in the dielectric permeability in the range of 2–7 GHz for samples TBK-3 and PZT-21 is determined by the resonance processes in a measuring cell.

The study of the spectra of magnetic and dielectric permeability shows that the electrical properties of the ferrite filler and its content affect the pattern of the frequency spectra of composites and the values of ε^* and μ^*. These features, in turn, determine the radio-absorbing characteristics of composites.

The electrical properties of fillers are characterized by the fact that the used Mn-Zn ferrite can be considered as a semiconductor (electrical conductivity at direct current is 1 S/m), and Ni-Zn ferrite can be considered as a dielectric (electrical conductivity at direct current is 1.7×10^{-7} S/m). This is due to the presence of Fe^{2+} ions in Mn-Zn ferrite, which increase the conductivity (the Vervey hopping mechanism) [17].

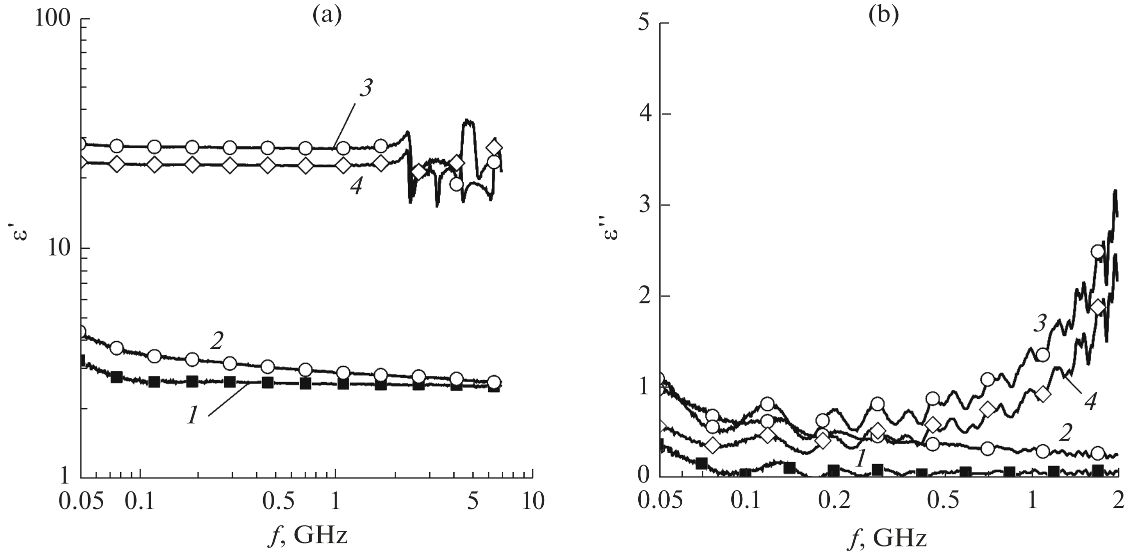

Fig. 1. High-frequency spectra of the (a) real ε' and (b) imaginary ε'' parts of the dielectric permeability of (*1*) PS525, (*2*) F2MV, (*3*) PZT, and (*4*) TBK-3 dielectrics.

Figure 2 shows the spectra of the dielectric and magnetic permeability of the ferrite rings 2000NM and 2000NN. Despite the same values of the initial permeability, the high-frequency magnetic permeabilities are very different. A decrease in magnetic permeability with an increase in the EMR frequency is associated with a lag in the following of magnetic moments to the alternating field. The decrease is especially pronounced upon the resonance process (NFMR and the domain-wall resonance).

The measured initial magnetic permeability of ceramic rings 2000NM and 2000NN was 1755 and 2041 (induction coercive force was ~15 A/m; saturation magnetic induction was 0.24 and 0.16 T). A sharp decrease in dielectric permeability ε' for ferrite 2000NM can be due to the influence of eddy currents or an excess of the frequency of hoppings between Fe^{2+} and Fe^{3+} ions [18]. Since the ferrite ceramic is characterized by such parameters as initial magnetic permeability, saturation induction, and coercive force, it can be confirmed that the used ferrite materials exhibited almost the same magnetic characteristics.

Note that, in comparison with the magnetic permeability spectra of the ferrite ceramic, a frequency shift in the dispersion region of μ*(*f*) for composites is observed. In composites with a high content of Mn-Zn ferrite inclusions ($C_m > 60\%$), a weak dispersion of ε*(*f*) is also observed [19–22].

The spectra of the magnetic permeability for the composites F2MV/2000NM and F2MV/2000NN are shown in Fig. 3. It can be seen that, for a composite with magnetic inclusions of 2000NM (Fig. 3b), the dispersion frequency estimated from the maximum value of μ'' noticeably shifts toward the low-frequency region. Note that, for composites with PS525, the features of the frequency spectra are similar, but there is a difference in the value of magnetic permeability.

The electrical properties of ferrite inclusions can affect the pattern of the spectra of dielectric permeability. Figure 4 shows that the frequency dependences for F2MV/2000NM exhibit a weak dependence on frequency in the range of 1–7 GHz. This is especially pronounced for high contents.

The dependences of magnetic and dielectric permeabilities on the content at a frequency of 100 MHz are shown in Fig. 5. For the complex magnetic permeability of composites, it can be noted that the values of μ' were different at fixed contents because of different filling of the volume with inclusions and because of the features of the distribution of components. The selected mixing method makes it not possible to completely avoid contact of ferrite inclusions with each other, which results in electrical and magnetic percolation. As a result, the number of open channels through the composite thickness can be different, which affects the permeability values in the microwave region. Owing to the higher ε' values of Mn-Zn ferrite, the composites with its addition exhibit a more pronounced increase in this parameter with increasing content.

Figure 6 shows the spectra of the reflection coefficient on a metal plate of the obtained composites (the thickness is 6 mm). For the PS525/2000NN composite, the attenuation does not exceed 5 dB for all contents; therefore, the spectra $K_{refl}(f)$ are not presented.

We found that the most pronounced radio-absorbing characteristics are exhibited by the following composites: F2MV/2000NM, $C_m = 40\%$ ($K_{refl}^{min} = -26$ dB, f_c = 4.1 GHz, $\Delta f(-10$ dB$)$ = 2.5 GHz);

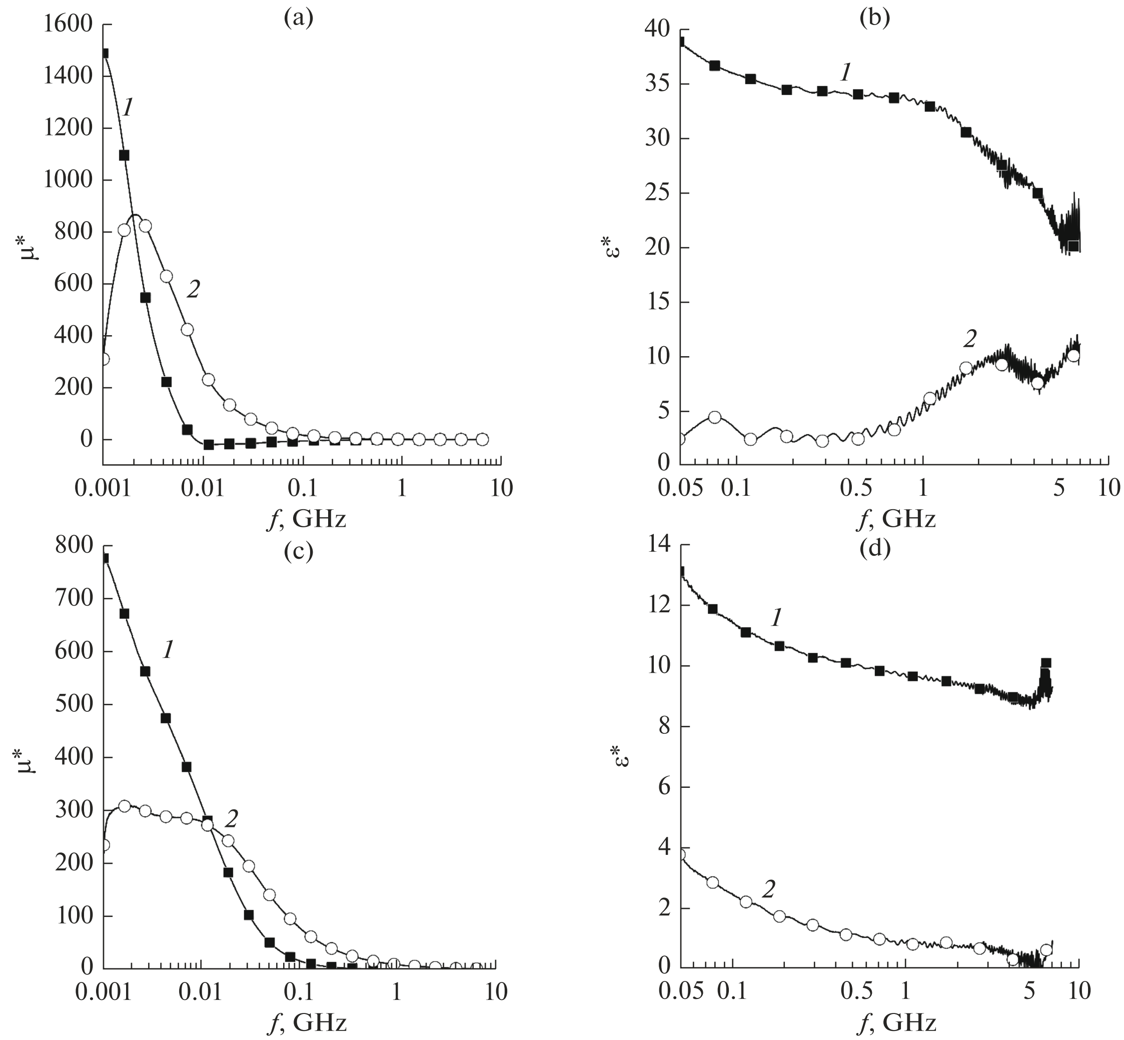

Fig. 2. High-frequency spectra of complex magnetic μ* and dielectric ε* permittivity ((*1*) real and (*2*) imaginary parts) of (a, b) 2000NM and (c, d) 2000NN ferrimagnetics, respectively.

F2MV/2000NN, C_m = 80% ($K_{\text{refl}}^{\text{min}}$ = −14 dB, f_{c} = 5.8 GHz, Δ*f*(−5 dB) = 5.5 GHz); PS525/2000NM, C_m = 60% ($K_{\text{refl}}^{\text{min}}$ = −27.5 dB, f_{c} = 4.3 GHz, Δ*f* (−10 dB) = 2.5 GHz); TBK-3/2000NN ($K_{\text{refl}}^{\text{min}}$ = −23 dB, f_{c} = 3.5 GHz, Δ*f* (−10 dB) = 1.1 GHz). The PS525/2000NM and F2MB/2000NM composites exhibit similar spectra of the reflection coefficient at C_m = 40 and 60%, respectively. However, the determination of the apparent density of the rings showed that the density of the F2MB/2000NM composite is 3.08 g/cm^3, while that of PS525/2000NM is 3.4 g/cm^3. Taking this into account, it can be confirmed that, as a radio-absorbing material (RAM), it is more preferable to use a composite with a F2MV matrix, since it is preferable for the RAM to be as lightweight as possible. We also note a shift in the center of the peak f_{c} for composites with conducting Mn-Zn ferrite with an increase in its content. For Ni-Zn ferrite, no shift of the peak was observed.

The spectra of the reflection coefficient on a metal plate for composite rings were used to obtain the dependences of some parameters of these spectra on the dielectric permeability of the matrix. The dependences of $K_{\text{refl}}^{\text{min}}$ and K_{refl} at a given frequency of 0.1 GHz and the position of the center of the absorption minimum f_{c} on dielectric permeability ε' of the matrix are shown in Fig. 7 (C_m = 40%). Clearly, the peak value of $K_{\text{refl}}^{\text{min}}$ passes through the minimum, but the position of the minimum is different for composites with Mn-Zn- and Ni-Zn-ferrite. For the dependence of f_{c} for composites with 2000NM inclusions, the drop of the curve is more pronounced. Note also that, for composites with Ni-Zn ferrite, K_{refl} at frequencies >3 GHz weakly depends on ε' of the matrix,

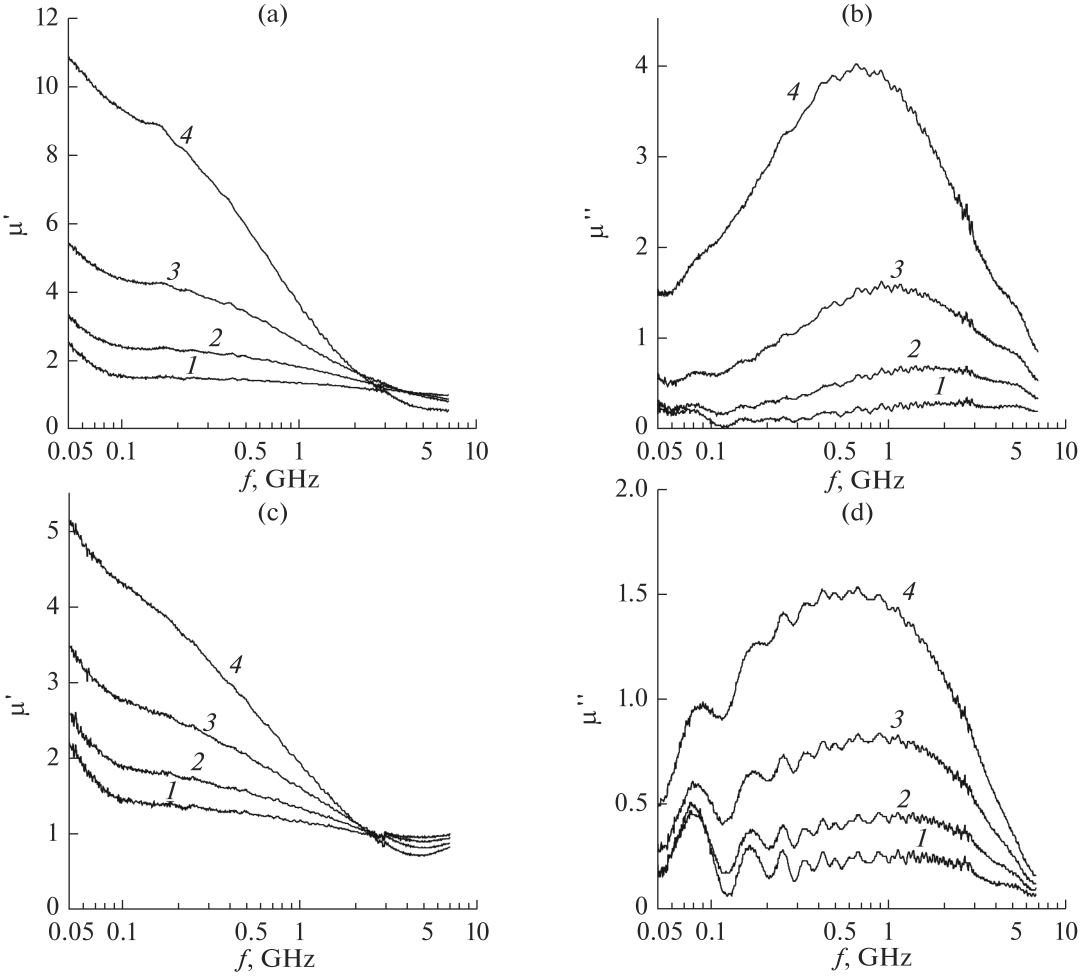

Fig. 3. Frequency dependences of the real μ' and imaginary μ'' parts of the magnetic permeability of (a, b) F2MV/2000NM and (c, d) F2MV/2000NN composites with the content of (*1*) 20, (*2*) 40, (*3*) 60, and (*4*) 80%.

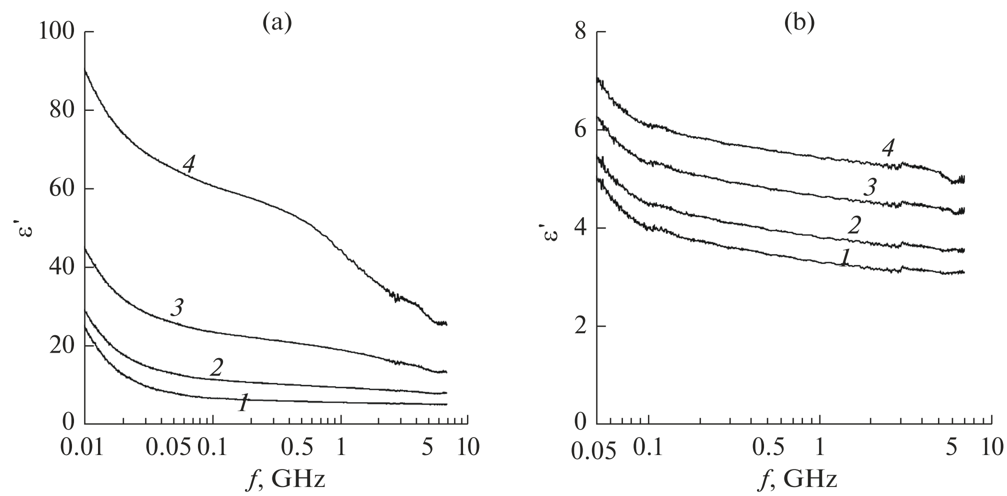

Fig. 4. Frequency spectra of dielectric permeability ε' of (a) F2MB/2000NM and (b) F2MB/2000NN composites with the content of (*1*) 20, (*2*) 40, (*3*) 60, and (*4*) 80%.

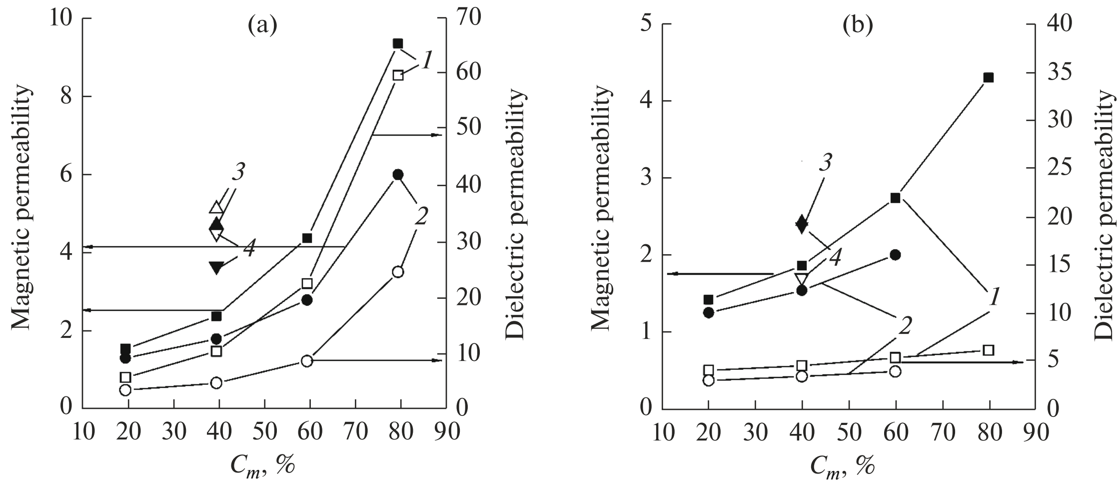

Fig. 5. Dependences of the magnetic and dielectric permeability on content C_m in (*1*) F2MV, (*2*) PS525, (*3*) PZT-21, and (*4*) TBK-3 composites at the frequency f = 100 MHz for (a) 2000NM and (b) 2000NN ferrite filler.

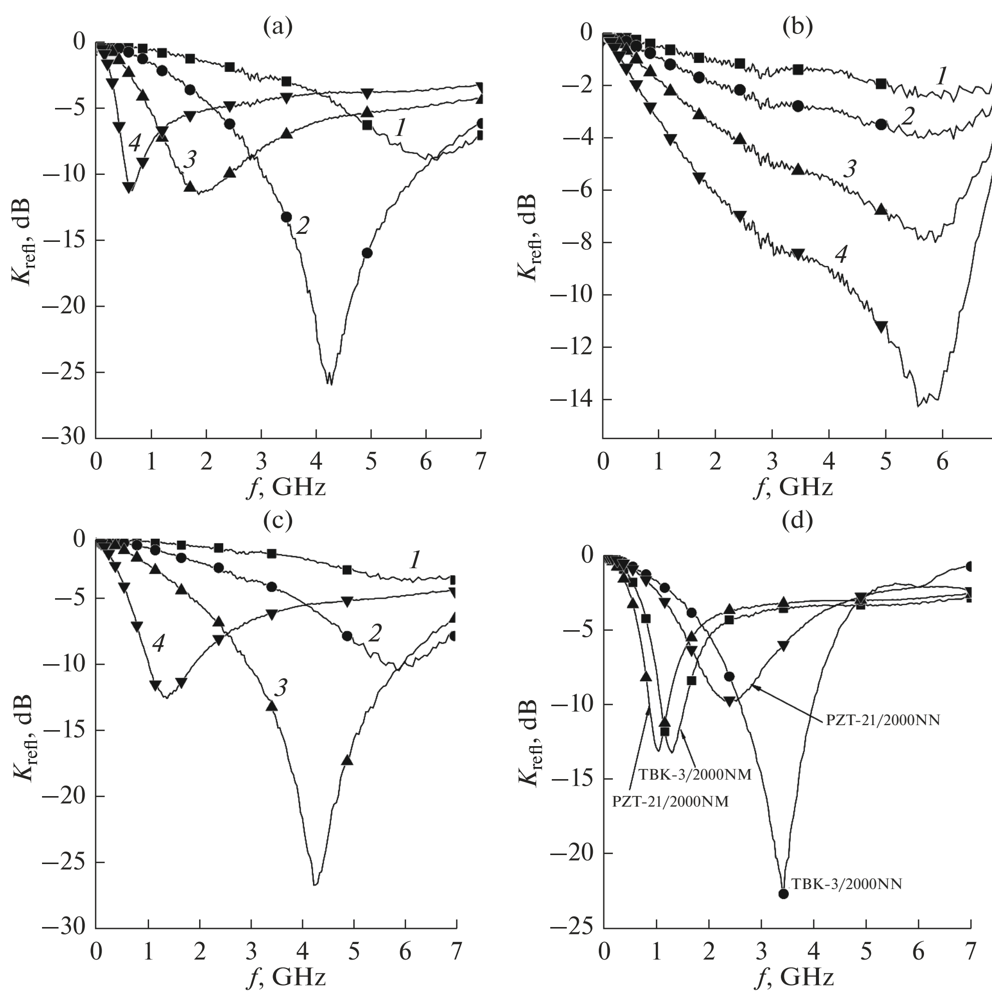

Fig. 6. Frequency spectra of reflection coefficient K_{refl} of (a) F2MV/2000NM, (b) F2MV/2000NN, and (c) PS525/2000NM composites (with the content of (*1*) 20, (*2*) 40, (*3*) 60, and (*4*) 80%), and (d) TBK-3 and CTS-21 composites with C_m = 40%.

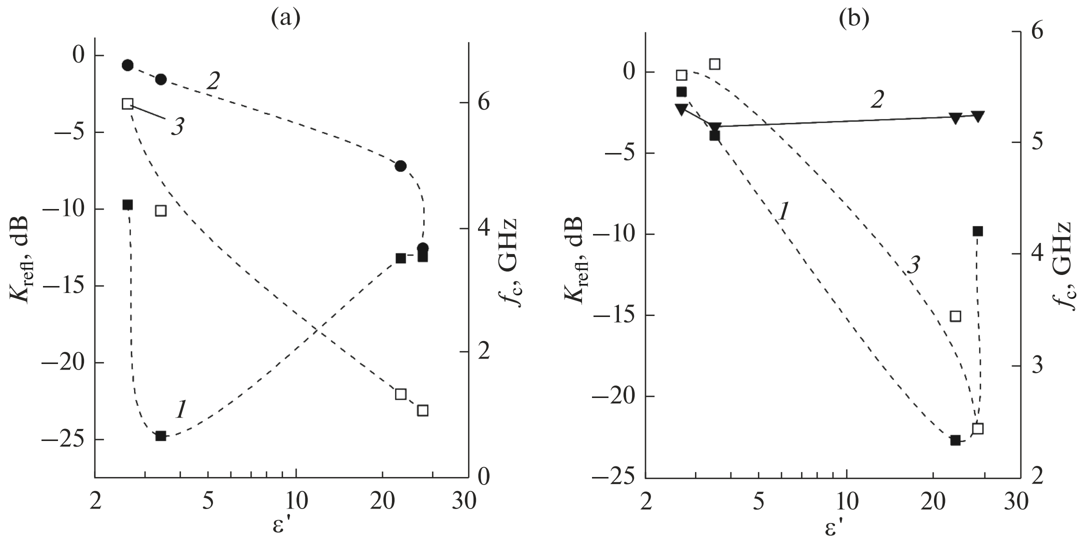

Fig. 7. Dependences of the parameters of spectra $K_{\text{refl}}(f)$ on dielectric permeability ε' of the matrix with the filler (a) 2000NM and (b) 2000NN: (*1*) $K_{\text{refl}}^{\text{min}}$, (*2*) K_{ref} at a given frequency of 0.1 GHz, and (*3*) position f_c of minimum absorption.

and for composites with Mn-Zn ferrite, a decay of the curve K_{refl}(ε') is observed at frequencies up to 1 GHz.

CONCLUSIONS

Analysis of the electrophysical and radio-absorbing properties of ferrite-dielectric composites shows that the electromagnetic properties of such composites are considerably determined by the electrophysical properties of ferrite inclusions. The high electrical conductivity of Mn-Zn ferrite causes a pronounced dependence of ε' on the content of inclusions and a frequency shift in the dispersion region of magnetic permeability. These features of electromagnetic characteristics, in turn, affect radio absorption in the obtained samples. At the same time, the radio-absorbing properties of composites also depend on the dielectric properties of the matrix. It can be confirmed that, for composites with 2000NN and 2000NM, there is a certain value of the dielectric permeability of the matrix making it possible to maximize the radio-absorbing characteristics. For composites filled with Mn-Zn ferrite with a matrix dielectric permeability of 2.5–3 and a weight content C_m = 40–60%, the peak attenuation can reach 25 dB at a frequency of 4.2 GHz. An increase in the content of ferrite 2000NM and an increase in the dielectric permeability of the matrix result in the deterioration of the radio-absorbing properties of composites. For the 2000NN-based composites with ε' of the matrix of 2.5–3, only the composites with C_m = 80% exhibit pronounced radio-absorbing characteristics. The TBK-3/2000NN composite exhibits excellent characteristics, with a minimum reflection coefficient reaching –22 dB at a frequency of 3.5 GHz. Thus, a series of the obtained composites can be considered as radio-absorbing materials for the frequency range of 1–6 GHz with maximum attenuation of electromagnetic radiation in the range of 14–27 dB and an operating frequency band (less than 10 dB) in the range of 1.1–2.5 GHz.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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