Electromagnetic characteristics of composite materials based on hexaferrite powders and a silicone binder

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Abstract. This article studies the electromagnetic properties of composite materials based on hexaferrite powders and a silicone binder. The results of this study are presented. Samples of radiomaterials based on hexaferrite powders Z-, W-, M-type and silicone binder were made. The measurements were carried out in a frequency range from 100 MHz to 18 GHz. The frequency dependencies of complex permittivity and permeability are shown. Based on the data obtained, the electromagnetic response for composites of various thicknesses located in free space and on the metal was calculated. The composite located on the metal, which contains 80 wt.% BaCo$_{0.6}$Zn$_{1.4}$Fe$_{16}$O$_{27}$ and has a thickness of 2 mm, can reduce the level of reflected radiation by more than 100 times in the frequency range from 12.5 to 18 GHz. A composite material containing 80 wt.% BaCo$_{2.4}$Ti$_{0.4}$Fe$_{23.2}$O$_{41}$ is effective narrowband absorber (reduces reflection by more than 100,000 times) at a frequency of 11.6 GHz, at a thickness of 2.6 mm.

1. Introduction
In recent years, there has been growing interest in new radiomaterials that have prospects of application in microwave devices [1, 2] and ultra-high frequency devices [3, 4]. The transition to this area of operating frequencies leads to a decrease in the size of the equipment, but there are several problems. In particular, there is the problem of ensuring electromagnetic compatibility (EMC) of individual components of electronic equipment and all receiving-transmitting tract [5, 6]. The problem is much more complicated if it is necessary to solve the problem of constructing a multicomponent electromagnetic device with certain dimensions, weight, electromagnetic characteristics in the operating frequency band, etc. To solve this problem, the materials used as structural or functional in the development of electronic devices must have the necessary complex of physical and electromagnetic properties: low weight, hardness, elasticity, hydrophobicity, high reflection or absorption coefficient, large values of magnetic and dielectric constant etc. When solving specific EMC problems, these parameters can vary.

Continuous materials have large values of electromagnetic parameters, but, as a rule, a large weight. Therefore, when developing materials for high-frequency electronics, the use of composites is more acceptable. When creating them one can get a completely new material with a special set of properties. The values of complex permittivity and magnetic permeabilities of the composite depend on electromagnetic properties of raw materials, from degree of grinding, shape of particles and volumetric content of powder in matrix of binder [7].

The following materials are actively used as fillers for modern composite mixtures: powders of various metals [8], nanostructured magnetic materials [9], carbon nanoscale structures [10, 11], magnetic microwires [12] and others. Among the magnetic materials, hexagonal ferrites are especially...
distinguished. Their natural ferromagnetic resonance region characterized by significant changes in the values of the complex magnetic permeability is in the microwave range [13].

Therefore, the study of the electromagnetic characteristics of composite materials based on various types of hexaferrites is a current interest.

2. Materials and Methods

2.1. Materials

As a binder in the composites one can use epoxy resin, paint, varnishes, compounds, rubbers, silicones and other polymers. Each of these materials has different field of application, adhesion to the filler, and mechanical characteristics. As the binder, a silicone polymer matrix was used.

Hexagonal ferrimagnets with particle sizes less than 100 μm of three different types obtained by standard ceramic technology were used as an active phase of the composites. They have the following compositions:

- M-type: BaFe$_{12}$O$_{19}$;
- W-type: BaCo$_{0.6}$Zn$_{1.4}$Fe$_{16}$O$_{27}$;
- Z-type: BaCo$_{2.4}$Ti$_{0.4}$Fe$_{23.2}$O$_{41}$.

Composition and structure of materials were investigated by Shimadzu XRD 6000 X-ray diffractometer and XRF-1800 wavelength dispersion X-ray fluorescence spectrometer. All studied hexaferrites contain more than 92% of the main phase.

2.2. Obtaining experimental samples

For the manufacture of samples, the following scheme was used. The active phase and the binder were selected. The filler and binder were carefully weighed on a Shimadzu AUX - 320 balance (accuracy ~ 0.5 mg). After that, the components of the composite were combined in appropriate proportions (by weight) and thoroughly mixed until homogeneous. The resulting mixture was introduced with a specially made fluoroplastic form. The polymerization of the finished product was carried out at a room temperature for several hours. As a result, experimental samples were obtained in the form of toroidal washers with inner diameter $d_{in} = 3$ mm, external diameter $d_{ext} = 7$ mm and thickness $h = 3.5$–$4.5$ mm.

Thus, experimental samples were prepared, which contained 80 wt.%. ferrite powders: BaFe$_{12}$O$_{19}$, BaCo$_{0.6}$Zn$_{1.4}$Fe$_{16}$O$_{27}$ and BaCo$_{2.4}$Ti$_{0.4}$Fe$_{23.2}$O$_{41}$.

We used the silicone that combines high adhesive properties with flexibility and ductility, and hexaferrite powders of various structural types possible to create a number of magnetic elastomers.

2.3. Measuring equipment

The electromagnetic properties of the obtained composites were measured by the waveguide method with the inclusion of a coaxial cell with an inner diameter $d_{in} = 3$ mm and external diameter $d_{ext} = 7$ mm. The vector network analyzer P4M-18 produced by the company “Micran” acted as a measuring installation. The measurements were carried out according to the “transmission” scheme (Figure 1).

The “transmission” (Figure 1a) measurement scheme allows one to measure the values of the coefficients of the scattering matrix. In other words, to determine the value of parameters $S11$, $S12$, $S21$, $S22$ and their phase. These $S$-parameters determine the coefficients of reflection and transmission of an electromagnetic wave through a sample placed in the measuring cell (Figure 1c) having forward direction and reverse passage. Based on the measured $S$-parameters with phase, the spectra of complex permeability and permittivity can be calculated. For this, a modified Becker-Jarvis technique is used [14].
3. Results and discussion

As a result of the measurements, the complex permeability and permittivity of composite samples based on 80 wt.% hexaferrite and silicone binder were obtained. The frequency dependences of the real and imaginary parts of the complex permeability and permittivity composites are shown in Figure 2.

The constructed comparative dependence shows that in the frequency band from 0.1 to 6 GHz, Z-type hexaferrite has a larger value of the real part of magnetic permeability than W and M-types. In the frequency range from 6 GHz, W-type hexaferrite has a greater value of the real part of the magnetic permeability. M-type hexaferrite has the lowest complex permeability values. On the frequency dependences of complex magnetic permeability there are several areas where real part decreases and there are maxima on the imaginary part. In the case of W-type hexaferrites (BaCo0.6Zn0.4Fe16O27) and Z-type (Ba2Co4Ti0.4Fe23.2O41), two dispersion regions are observed. This is due to the manifestation of domain wall resonance at a frequency of the order of 1.3 GHz and natural ferromagnetic resonance (NFMR) at frequencies of 4 GHz and 11.5 GHz for W- and Z-type hexaferrites, respectively. This is consistent with the literature on this class of materials. The NFMR region for BaFe12O19 hexaferrite is found at frequencies of the order of 50 GHz [13].
The real parts of permittivity are ε'≈5.5–6.0 rel. units in the entire investigated frequency range. The values of the imaginary parts of permittivity have no singularities. Their values are ε''≈0.1–0.5 rel. units. The absence of permittivity dispersion regions indicates that in the studied frequency range only electronic polarization is present in composite materials.

Based on the obtained data on the values of the complex magnetic and dielectric permittivity, the electromagnetic response from the sample layer can be calculated. The electromagnetic response was simulated from a layer of material located in the free space and on the metal (R). Distribution plots were obtained for the corresponding coefficients depending on the thickness and frequency of the layer.

For modeling, the materials with the highest values of the complex magnetic and dielectric constant were selected. These are magnetic elastomers with a content of 80 wt.% of type W and Z hexaferrites. Figure 3 shows the simulation results of the electromagnetic response from a layer of materials in free space. These materials are able to effectively shield electromagnetic radiation. Composite material based on hexaferrite W-type shielding more than 80% of radiation at frequency range from 7 to 13 GHz with a thickness more than 4 mm. Composite material based on hexaferrite Z-type shielding more than 80% of radiation at frequencies above 13 GHz with a thickness of more than 3 mm. Maximum reflection (more than 60%) is observed for a composite with ferrite Z-type with thickness of 1-2 mm at frequencies from 16 to 18 GHz and with thickness of more than 3 mm at frequencies from 5 to 8 GHz. More than 50% of the radiation is absorbed at frequency range from 5 to 17 GHz at a thickness more than 4 mm for W-type hexaferrite and at frequencies more than 11 GHz at a material thickness more than 2 mm for Z-type hexaferrite.

The calculation of the reflection coefficient from a composite material located on a metal surface is of the greatest interest. For this, the plane-wave approximation and formula (1) were used. We considered a thin, infinite flat layer of material on an ideally reflecting surface, onto which an electromagnetic wave is incident perpendicularly from free space.

\[
R = \frac{Z_{\text{in}} - 1}{Z_{\text{in}} + 1},
\]

where \(Z_{\text{in}} = i \cdot Z_{\text{tg}}(kd)\) - input impedance at the free space – absorber interface, \(k = \frac{2\pi f \sqrt{\varepsilon'' \mu''}}{c}\) - wave number, \(Z = \frac{\mu' + \mu''}{\sqrt{\varepsilon' + \varepsilon''}}\) - wave resistance of a flat layer, provided that it is on the metal; \(\varepsilon\) is the dielectric constant, \(\mu\) is the magnetic constant, \(c\) is the speed of light in vacuum, \(f\) is the frequency.

Plots of the surface with level lines for reflection coefficient from a composite material located on metal were obtained. The distribution of the reflection coefficient from the frequency and layer thickness for composite materials containing 80 wt.% hexaferrites W- and Z-type in silicone binder are shown (Figure 4).

The graph shows that a coating based on a composite with 80 wt.% hexaferrite W-type located on metal surface and has a thickness of 2 mm, can reduce the level of reflected radiation by more than 100 times in the frequency range from 12.5 to 18 GHz. A composite material containing 80 wt.% BaCo\(_{2.4}\)Ti\(_{0.4}\)Fe\(_{23.5}\)O\(_{41}\) is effective narrowband absorber (reduces reflection by more than 10,000 times) at a frequency of 11.6 GHz, at a thickness of 2.6 mm. Also, this material can be used as an extremely efficient narrow-band absorber at frequencies of 10.3 GHz with a thickness of 6.7 mm, while the maximum attenuation of radiation can reach -43.7 dB (more than 10,000 times). Composite with 80 wt.% hexaferrite Z-type located on metal surface and has a thickness of 2 mm, can reduce the level of reflected radiation by more than 10 times in the frequency range from 6 to 14 GHz. Also, this material can be used as an extremely efficient narrow-band absorber at frequencies of 10.3 GHz with a thickness of 2.6 mm, while the maximum attenuation of radiation can reach -52.3 dB (more than 100,000 times).

For a composite based on the M-type hexaferrite, the maximum decreases the level of reflected radiation reaches only -3 dB (50%) with a large thickness (8-9 mm) and frequency (15-16 GHz).
Figure 3. Electromagnetic response in free space from composite material containing 80 wt.% $\text{BaCo}_{0.6}\text{Zn}_{1.4}\text{Fe}_{16}\text{O}_{27}$ (a, c, e), $\text{BaCo}_{2.4}\text{Ti}_{0.4}\text{Fe}_{23.2}\text{O}_{41}$ (b, d, f)
Figure 4. Dependence of reflection coefficient from a composite material located on a metal surface on frequency and thickness for composites containing 80 wt.% BaCo$_{0.6}$Zn$_{1.4}$Fe$_{16}$O$_{27}$ (a), BaCo$_{2.4}$Ti$_{0.4}$Fe$_{23.2}$O$_{41}$ (b) in silicone binder

4. Conclusions
The obtained dependences make it possible to characterize a composite material based on silicone with the addition barium ferrites W- and Z- type as effective broadband and narrowband absorbers of electromagnetic radiation in various frequency ranges. The composite located on the metal, which contains 80 wt.% BaCo$_{0.6}$Zn$_{1.4}$Fe$_{16}$O$_{27}$ and has a thickness of 2 mm, can reduce the level of reflected radiation by more than 100 times in the frequency range from 12.5 to 18 GHz. A composite material containing 80 wt.% BaCo$_{2.4}$Ti$_{0.4}$Fe$_{23.2}$O$_{41}$ is effective narrowband absorber (reduces reflection by more than 100,000 times) at a frequency of 11.6 GHz, at a thickness of 2.6 mm.

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