Interaction of microwave radiation with composites containing nanosized hexaferrite, multiferroics, carbon nanostructures and silicon binder

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Abstract: A new composite consisting of nanosized powders of hexaferrites $BaFe_{12}O_{19}$ (BaM), multiferroics $Co_{1.6}Zn_{1.4}W+CaTiO_3$ (30%), carbon nanostructures (powder mixture of carbon nanotubes, fullerenes, squamous structures and amorphous carbon) and silicone binder absorbs microwaves. Varying the concentration of each component in the composite materials changes the characteristics of a coating from reflective to absorbing electromagnetic radiation. Adding a layer with multiferroics to a composite material significantly improves the coatings as protective layer from microwaves.

Keywords: nanotechnology; composites; carbon nanostructures; multiferroics; hexaferrites; absorption properties; microwave measurements.

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1 Introduction

In recent years, interest in new radio materials is growing. They are used extensively in microwave technology devices. Using higher frequencies can significantly reduce the geometrical dimensions and weight of radio elements, help to achieve compaction of their location, reduce power consumption and extend the functionality of the equipment. However, there are problems with electromagnetic compatibility of electronic equipment [1] and with protection of biological objects from the action of microwave radiation [2]. The latter problem is especially relevant.

Experimental researches on the biological effects of prolonged exposure to high-frequency fields were conducted by WHO and many independent researchers. There identified several specific diseases associated with microwave radiation. They are functional changes in: the brain, reproductive organs, cardio vascular system, endocrine and immune systems [3–5]. Commission of the International Agency for Research on Cancer (IARC, 2002) published the conclusion that the influence of the electromagnetic field is associated with the possible carcinogenicity [5]. There are many cases of correlation between exposure to electromagnetic fields and the occurrence of leukaemia [6]. The mechanism of radiation influence on the human body has not been defined yet, but doctors recommend limiting the use of mobile phones, especially by children [6]. But people cannot refuse using electronic devices. Therefore, actual current task is development of means of protection from exposure to high-frequency electromagnetic radiation. All these reasons led to the search for new materials with the necessary properties for the modern electronics.

These materials must be lightweight, hard, flexible and waterproof. Also, they have to possess high reflectance/absorption and great values of permittivity or permeability. For specific problem of electromagnetic compatibility solution, these properties can vary.

Solid materials have great values of the electromagnetic parameters but they are heavy. Composite materials have the required set of properties. Therefore, the composites are used for design of materials for high-frequency electronics. The composites are materials with a particular set of properties. It is known that ferromagnetic oxide, soot, iron carbonyl, dielectrics, etc., are suitable fillers for new composite mixtures. Ferroelectrics and multiferroics are used for new radio absorbers. Carbon nanostructures (nanotubes, fullerenes, nanofibres, nanowires and carbon onion structures) and ferrite nanopowders are also used for this purpose.

A new promising material for application in electronic devices is carbon nanostructures (CNS) [7]. CNSs have special characteristics, namely high conductivity, low bulk density, mechanical strength, ductility and low thermal conductivity. CNSs are used for developing of high-strength and lightweight coverage. Moreover, we can get reflective and absorptive coating by changing the concentration of the CNS [8,9].

Ferrites with hexagonal crystal structure (hexaferrite) have a natural ferromagnetic resonance in the microwave region. Hexaferrites have great changes of the complex permeability in the microwave region. The properties of hexaferrites depend on the method of composition production [10], shape and size of the particles [11,12] and the mixture structure [13]. It is possible to obtain new lightweight materials based on hexaferrites.

Multiferroics are materials that combine ferromagnetic and ferroelectric structure. They are being actively investigated [14].

Therefore, this paper focuses on composite materials based on nanosized powders of hexaferrite, carbon nanostructures and multiferroics.

2 Experimental section

2.1 Means of measurement

The structure of the materials was determined by X-ray analysis. Images were obtained on X-ray Diffractometer Shimadzu XRD 6000 with copper radiation (CuKα) and Wavelength Dispersive X-Ray Fluorescence Spectrometer XRF-1800. Powder samples and composites samples were studied. Shooting modes are tube voltage of 40 kV, anode current of 30 mA, goniometer speed when shooting is 2 deg/min and X-ray diffraction is $2\theta = (20 \div 60)^{\circ}$.

The structure of material was studied by optical microscope and by scanning electron microscopy. Electron-microscopic measurements were carried out with a scanning electron microscope with a focused ion beam QUANTA 3D.

Electromagnetic characteristics of materials were measured by a cavity resonator method. Agilent's E8363B vector network analyser was used to measure electromagnetic response of the rectangular cavity. The sample for measuring was a long and thin rod $2 \times 2 \times 70\ \text{mm}^3$. Complex permeability and permittivity were calculated using the approximation of the perturbation method. Frequency dependence of reflection coefficients was calculated.

2.2 Experimental samples

To select a binder, it is necessary to know the required properties of the composite, such as hardness, flexibility and elasticity. As the binder we used silicone polymer matrix, which integrates high adhesive properties with flexibility and lightness.

To create samples, we used the following scheme. There were a filler and a binder. The filler and the binder were weighed on Shimadzu AUX-320 Analytical Balance (error ~ 0.5 mg). Thereafter, the composite components were mixed in the appropriate parts (by weight). Then, the mixture was blended until homogeneous state (using an ultrasonic disperser and a magnetic stirrer). Manufactured mixture was placed in a special mould. Finished composite sample is a thin rod. Polymerisation of the finished product was carried out for several hours at room temperature.

The samples of composites based on polymer matrix were studied in this paper. They contain:

- Hexaferrite powders $BaFe_{12}O_{19}$ (BaM) with the sizes of the particles of 100–1000 nm.
- Carbon nanostructure (powder mixture of carbon nanotubes, fullerenes, squamous structures and amorphous carbon). They are made from a hydrocarbon gas using microwave energy [15]. For the measurements, we selected three types of nanopowder containing carbon nanostructures:
  - the original, obtained directly at the output of the device
  - annealed at T = 800ºC for 2 hours
  - the milled solid remainder.
- Multiferroic ultrafine powder with a grain size of about 100 nm and a particle size not more than 4 µm. For this research, we took the sample of thecomposition $BaCo_{0.6}Zn_{1.4}Fe_{16}O_{27}+CaTiO_3$ (30%), where the first component is hexaferrite W-type and the second is ferroelectric.

Figure 1 shows the microstructure of hexaferrite, multiferroics (a, b) and composite materials based on hexaferrite and multiferroics (c, d). Analysis of the morphological features of the sample shows that along with the particles in the form of hexagonal plates there are quasispherical grain form or octahedral particles, which are characteristics of cubic ferroshpineles.

Samples of powders of the hexagonal ferromagnetic and ferroelectrics were obtained by self-propagating high-temperature synthesis (SHS). After SHS, the content of corresponding phase ranged from 30% to 65% depending on synthesis conditions. The subsequent sintering at T = 1180–1190ºC for 2 hours increased concentration of the corresponding phase to 85–92%. The resulting material was milled in a planetary ball mill to the appropriate particles dimensions. Several studies [11,12] shown that when the particle size is of 100–4000 nm the magnetic properties of materials are enhanced. The final product of the synthesis is ferrite powders with grain sizes from 30 nm to 42 nm and a particle size of 100–1000 nm. The ferroelectric materials have a grain size of about 100 nm and the particle size is not more than four microns.

Analysed carbon nanostructures (CNS) have a high degree of purity. They contain more than 90% nanostructures. The resulting product contains multi-walled nanotubes with a diameter of up to 50 nm, and more small-scale lamellar structure (Figure 2) [15].

X-ray phase analysis shows predominantly crystalline (90%) nature of the carbon product with coherent scattering region varying from 10 nm to 20 nm. Samples of material have specific surface area from 70 m^2/g to 170 m^2/g. This indicates the presence of structural elements with sizes of 10–20 nm. Ordered structure of carbon nanomaterial provides it with heat resistance up to 900ºC outdoors (for comparison: thermal stability of amorphous carbon is 450ºC and nanodiamonds is 600ºC). The structure and X-ray diffraction of composite carbon nanomaterials are presented below (Figure 3). The main peaks in the radiograph are responsible for different types of silicone structural components of the composite. The presence of carbon phase is weakly expressed on the background of the amorphous silicone component (the elevation in the beginning of the chart).

Figure 1 TEM images of the powders of $BaFe_{12}O_{19}$ (a), $Co_{0.6}Zn_{1.4}$-W+$CaTiO_3$ (b) and composites of hexaferrites $BaFe_{12}O_{19}$ (c), $Co_{0.6}Zn_{1.4}$-W+$CaTiO_3$ (d)

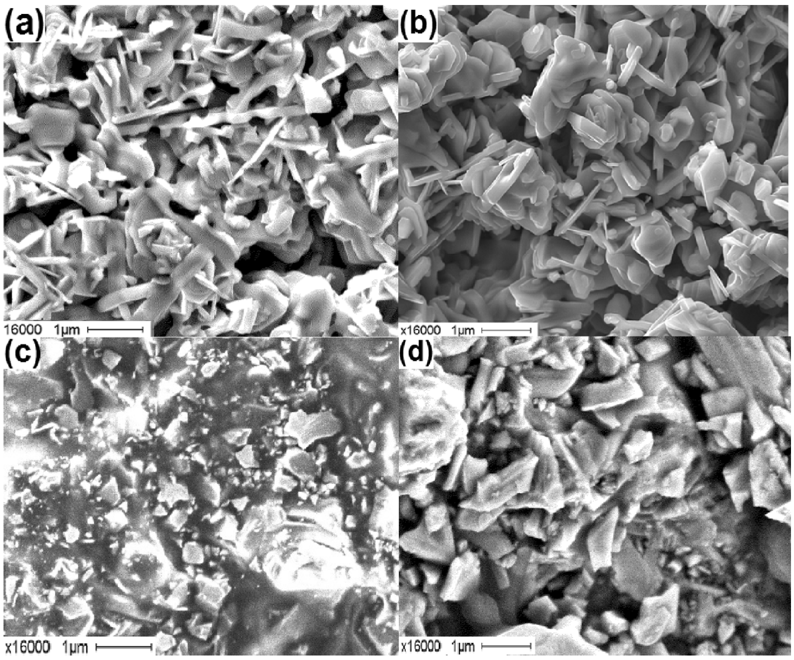


Figure 2 TEM images of the carbon nanostructures

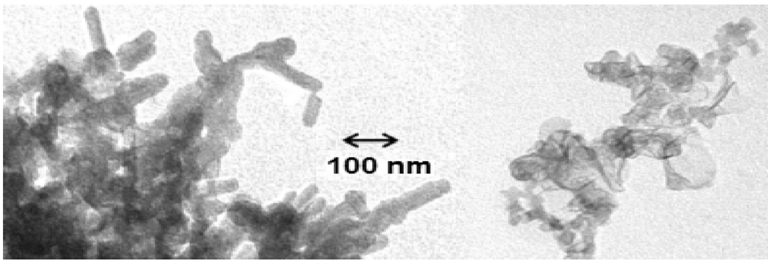
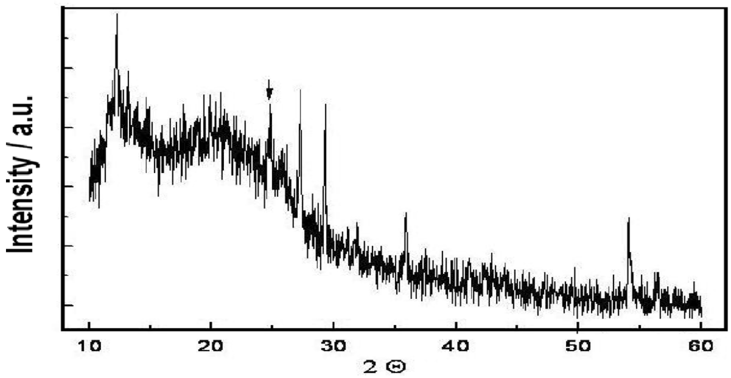


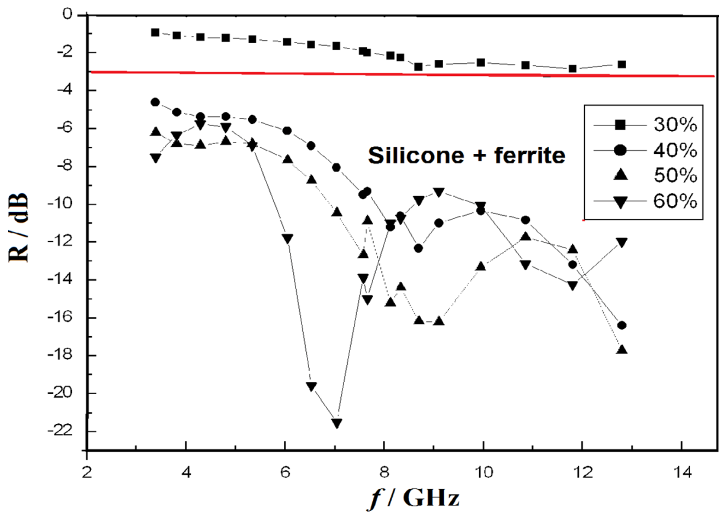
Figure 3 X-ray diffraction of a composite materials based on carbon nanostructures



3 Means of measurement

The results of reflectance coefficient calculation of composite materials on the metal surface are presented in this section. Frequency dependence of the reflectance on different concentrations of ferrite filler BaM is shown in Figure 4. For each concentration, optimum layer thickness was selected (calculated): 30 wt. % – 8.2 mm, 40% – 5.1 mm, 50 wt. % – 5.1 mm, 60 wt. % – 5.3 mm. It is seen that R > –3 dB of a composite with 30 wt. % in the whole range. At the same time, R < –3 dB at a composite concentration of 40–60 wt. %. This implies that the composites with 30 wt. % BaM can be used as a material for reflecting microwave power, and others – for absorption.

Figure 4 The dependence of the reflection coefficient on frequency for composites: silicone and ferrite $BaFe_{12}O_{19}$ (see online version for colours)



The reflection coefficients of composites with nanostructure fillers obtained by microwave plasmatron are shown in Figure 5. Just as in the first case, we selected the optimum thickness of the absorbing layer: for CNS (grinding) – 23 mm, CNS (annealing)

– 13 mm and CNS – 4.8 mm. Therefore, we can see that original CNS composites have R < –3 dB in the range of 7.3–9 GHz. In composites containing powder obtained by grinding the solid fraction of carbon nanostructures or by annealing CNS, R > –3 dB. Moreover, by varying the concentration of filler in the composite, we can change the characteristics of the protective coating.

We also measured reflection coefficients of the composite layer containing soot multiferroic systems $Co_{0.6}Zn_{1.4}W+CaTiO_3$.

For obtaining multilayer absorber, we used layers with 60 wt. % ferrite BaM, 1 wt. % CNS and 50 wt. % multiferroic. The total thickness of the absorber was 8 mm. Calculation for the composite material is shown in Figure 6.

Figure 5 The dependence of the reflection coefficient on frequency for composites: silicone + carbon nanostructures (see online version for colours)

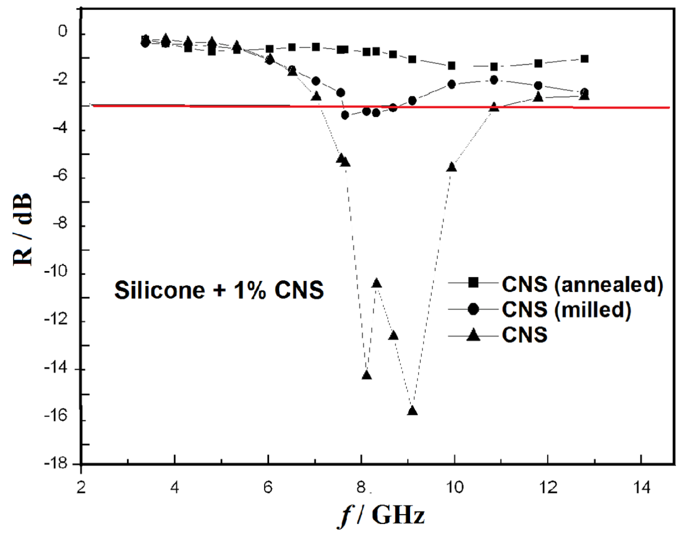
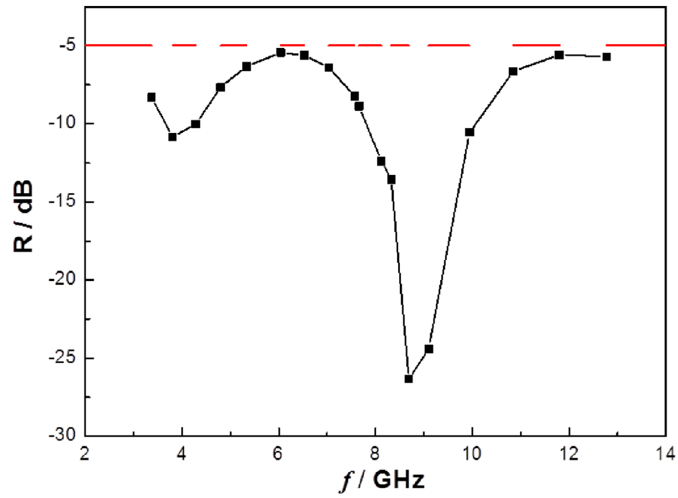


Figure 6 The dependence of the reflection coefficient on frequency for a multilayer composite silicone-based ferrite, multiferroic and CNS (see online version for colours)



Adding this material leads to possibility of using a multilayer absorber throughout the frequency range from 3 GHz to 13 GHz – with level of reflectance R < –5 dB.

The dependence curve in Figure 6 shows that it is possible to extrapolate the obtained data to the low-frequency region. One can assume that in the range of up to 2 GHz value of R < –5 dB.

4 Conclusion

This study shows the possibility of using nanosized powders of hexaferrite, multiferroics and carbon nanostructures as an active phase of composite radio materials interacting with high-frequency electromagnetic radiation. They can be used for electromagnetic compatibility of radio electronic facilities, for protection of biological objects from the influence of microwave radio emissions produced by scientific and household appliances, etc.

As a result of the work, the multi-layer coating was made and it reduces the electromagnetic radiation.

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