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# Effect of Magnetic Field Treatment on the Electromagnetic Properties of Polymer Composite Based on Barium Hexaferrite at Microwave Frequencies

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**Abstract.** Polymer composite materials are used in widely different areas of science and industry. It is possible to change electromagnetic properties of composite materials by external treatments. The present work focuses on the change of electromagnetic characteristics of barium polymer composite, which is exposed to the external magnetic field with different strength. Composite materials, containing 65 wt. % concentrations of barium hexaferrite (Z-type) powder with a linear size of less than 80 μm as fillers and epoxy resin as matrix were prepared. Reflection coefficients were measured by coaxial method at frequency range of 0.01 – 18 GHz. It was revealed that reflection coefficients of barium hexaferrite and epoxy resin composite are very sensitive to the values of external magnetic field. There is nonlinear dependence of the reflection coefficients on the values of external magnetic field. The optimum value of the strength of the external magnetic field was shown to be equal 4 mT. The Cramers-Kronig relations were used to recover the real parts of the permeability and correct the imaginary parts of the permeability.

## INTRODUCTION

Nowadays, electromagnetic (EM) wave absorption polymer composite materials have received much attention due to their wide applications for many electromagnetic compatibility (EMC) intentions [1-8]. Polymer composite materials have more suitable mechanical properties then ceramic composite. The efficiency of EM wave absorption materials noticeably depends on electromagnetic parameters including complex magnetic permeability ($\mu^* = \mu' - i\mu''$) and dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$), which can influence the reflection and attenuation properties of such materials.

Hexagonal ferrites with a plane of easy magnetization are used extensively in microwave engineering. The most important characteristics of these materials are big values of magnetic permeability [9] and a narrow ferromagnetic resonance line as compared with single-crystal and polycrystalline hexaferrites [6, 10]. The dielectric permittivity of the majority of ferrites is related to the ionic mechanism of polarization and weakly varies in the microwave range. The frequency dependences of magnetic permeability are more complicated. It are consisted the volumetric resonance, the oscillations of domain boundaries, the natural ferromagnetic resonance, and the exchange resonance in the internal exchange field in the presence of two or more magnetic sublattices [11].

The methods of changes of electromagnetic properties of composite materials by external influences on their structure have been widely investigated. One way to change the internal structure of magnetic radiomaterials is magnetic texturing. This method for polycrystalline materials has been known for a long time [9, 10, 12]. However, this method concerning the production of polymer composite is insufficiently elucidated in literature [13]. High temperatures are used for the production of polycrystalline materials. Yet, it cannot be used for the polymer material.

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The aim of this work is to study the electromagnetic properties that are present in polymer composites obtained by the magnetic field treatment.

## METHODS AND MATERIALS

### Methods

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, X-ray diffraction is $2\theta=(20\div60)°$.

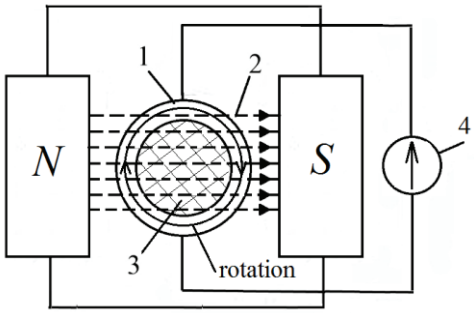
The structure of material was studied by optical microscope and by scanning electron microscopy. Electron-microscopic measurements were carried out with a scanning electron microscope with a focused ion beam QUANTA 3D.

The coaxial techniques were used for the evaluation of permeability of experimental samples at frequency range 0.01 – 18.0 GHz. The transmission and reflection coefficient were measured using a P4M-18 MICRAN Network Analyzer. Agilent's E4980A precision LCR meter was used to measure of resistance and inductance of experimental samples at frequency range 0.001 – 2.0 MHz.

### Apparatus for Texturing

A special device was used for magnetic polymer material texturing (Fig. 1) [14]. It consists of an electric magnet with the size of a field from 0.5 till 100 mT and an electric motor connected to a source constant tension 3V.

The PTFE hollow cylinders with different inner diameter are used for making of experimental samples.




1 – electric motor, 2 – constant magnetic field, 3 – form with mixture, 4 – DC source

**FIGURE 1.** Draft of device for texture

### Materials

The hexaferrite Z – type ($Ba_3Co_{2.4}Ti_{0.4}Fe_{23.2}O_{41}$) powders were prepared using standard solid state ceramic techniques [10, 11]. The initial materials for the synthesis were BaO, $TiO_2$, CoO, $Fe_2O$ powders. Prior to synthesis, the oxides powders were dried for 3 h at temperature of 200 °C. After that powders were weighed according to a stoichiometric ratio

$$3BaO + 2.4CoO + 0.4\ TiO_2 + 11.6\ Fe_2O_3 = Ba_3Co_{2.4}Ti_{0.4}Fe_{23.2}O_{41}.$$

Powders used for sintering experiments were ground for 4 h in a vibration mill. Powders were die-pressed at about 1000 atm. Solid samples were heated for 10–15 min to the sintering temperature (1150 °C), fired for 4 h and were cooled to room temperature. The chemical reactions in mixture of oxides were initiated at this stage. Solid state samples were of inhomogeneous structure at the end of this stage. There were Y, M, S, W and Z phases. After that samples were crushed. Powders were ground for 35 min in a vibration mill. Powders were die-pressed repeatedly at

about 1000 atm. Solid samples fired in oxygen for 6 h 1200 °C finally. Hexagonal ferrite solid solutions were obtained at the end of this stage. Figure 2 shows the microsection specimen of bulk ferrite. It is show the size and structure of crystallites into polycrystalline sample. The solid samples were contained 98% of Z phase. Then samples were ground once again. Finally, the powders were sifted by separator. The sizes of powders don't exceed 80 microns.

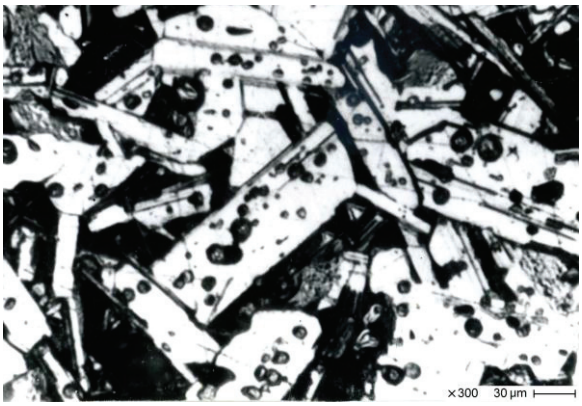



**FIGURE 2**. The microsection specimen of bulk ferrite $Ba_3Co_{2.4}Ti_{0.4}Fe_{23.2}O_{41}$

Basic characteristics of the resulting of the ferromagnetic material were measured and are given in Table 1. At room temperature, this material is characterized by magnetic anisotropy of "easy-plane" type.

**TABLE 1.** Characteristics of the powders

| Specification | Value |
|---|---|
| Contents of the Original Phase | > 95% |
| Average Size of Coherent Scattering Regions | ~ 82 nm |
| Size of the Ferrite Powder Particles | < 80 µm |
| The Content of the Spinel Phase | < 5.7 wt.% |
| True Bulk Density | 4.89 g/sm$^3$ |

For production of experimental samples polymer was used. It was epoxy resin EDP 20 (Gmbh «ChK FEM»). In the liquid state it has small viscosity. It allows a filler to move easily. Polyethylene-polyamine was used as the epoxy resin curing agent. For production of mix for experimental samples 65 wt. % of powders $Ba_3Co_{2.4}Ti_{0.4}Fe_{23.2}O_{41}$ was added to 35 wt. % of epoxy resin. Fillers and epoxy resin were weighed in the required proportions of mass on the scales Shimadzu AUX-320 (error ±0.5 mg), after that they were placed into the vessel and thoroughly mixed for 15 minutes until a homogeneous state. The composition of samples is given in Table 2.

**TABLE 2.** Composition of test samples

| No. | Ferrite Concentration, % | Epoxy Concentration, % | Magnetic Field, mT | Thickness, mm |
|---|---|---|---|---|
| 1 | 65 | 35 | 0.0 | 1.12 |
| 2 | 65 | 35 | 4.0 | 1.10 |
| 3 | 65 | 35 | 8.0 | 1.20 |

Barium hexaferrite and epoxy resin mixture was put into PTFE hollow cylindrical shapes with inner diameter of 7 mm and outer diameter of central core 3.04 mm. There were three identical shapes.

The first and second forms with mixture of epoxy resin and fillers were located on the electric motor. The electric motor was used to avoid exfoliation of the composite mixture. Electric motor was located between *N* and *S* poles of electric magnet. [14] The values of the strength of the external magnetic field were 4.0 and 8.0 mT, respectively. The duration of exposure by the magnetic field of the samples was 3 hours. The third form was located on desk without magnetic field. The polymerization process took place at room temperature. The final

polymerization was carried out within 2 days at the room temperature. The thicknesses of experimental samples are given in Table 2.

## Theory

It is well known that the wider the frequency range of measurements, the more adequate information is provided by Cramers – Kronig relations. The Cramers – Kronig relations are valid for the response functions of arbitrary linear systems. For the components of complex magnetic permeability they have the form [15]

$$\mu'(f)-1=\frac{2}{\pi}\int_0^{\infty}\frac{f_1\mu''(f_1)}{f_1^2-f^2}df_1, \tag{1}$$

$$\mu''(f)=-\frac{2f}{\pi}\int_0^{\infty}\frac{\mu'(f_1)}{f_1^2-f^2}df_1. \tag{2}$$

Notice that the integrals in (1) are evaluated in the sense of the Cauchy principal value.

In finding the spectrum $\mu'(f)$ by a known relation for $\mu''(f)$ (or vice versa), to simplify the calculations, it is possible to apply a piecewise linear approximation of the imaginary (real) component in the frequency band under consideration, which was proposed by Polivanov [16]. The entire frequency range of $\mu''(f)$ ($\mu'(f)$ is subdivided into intervals with coordinates $f_i$ ($i$ = 1, 2, …, $N$) in which the corresponding function can be approximated by linear expressions:

$$\mu_i''=k_if_1+d_i \quad \text{or} \quad \mu_i'=k_if_1+d_i. \tag{3}$$

Substituting (3) in (1) and (2) and evaluating the integrals, the authors [15] have obtained formulas (4) for recalculation of the permeabilities:

$$\mu'(f)=1+\frac{1}{\pi}\sum_{i=1}^{N}\left\{2(\mu_{i+1}''-\mu_i'')+k_if\ln\left|\frac{(f_{i+1}-f)(f_i+f)}{(f_{i+1}+f)(f_i-f)}\right|+d_i\ln\left|\frac{f_{i+1}^2-f^2}{f_i^2-f^2}\right|\right\},$$

$$\mu''(f)=-\frac{1}{\pi}\sum_{i=1}^{N}\left\{k_if\ln\left|\frac{f_{i+1}^2-f^2}{f_i^2-f^2}\right|+d_i\ln\left|\frac{(f_{i+1}-f)(f_i+f)}{(f_{i+1}+f)(f_i-f)}\right|\right\}. \tag{4}$$

The Cramers – Kronig relations (1), (2) are strictly fulfilled in an infinite interval of frequencies, which is unattainable in actual physical experiment. The results of calculations by the relations (4) involve an error related to the boundedness of the frequency interval in which approximation is performed. It is necessary to take advantage of the analytic properties of the function $\mu^*(f)$: (a) $\mu''(f)$ tends to zero as $f \to 0$ and $f \to \infty$ and the area bounded by the curve $\mu''(f)$ (it is proportional to the saturation magnetization) is finite and (b) $\mu'(f)$ is bounded: as $f \to 0$, $\mu'(f)$ tends to $\mu_0$, the static initial permeability, which is determined by independent experiments (it is also proportional to the saturation magnetization), and $\mu'(f) \to 1$ as $f \to \infty$.

## RESULTS AND DISCUSSION

The texturing process was observed by macrograph. For this purpose, we put the mixture into PTFE hollow cylindrical shapes with inner diameter of 30 mm. When the external magnetic field was zero, the surface coating particles are randomly disposed (Fig. 3,a). When the strength of external magnetic field was not equal to zero, the filler particles rotated. Figure 3,b shows the magnetic field lines. Similar results obtained in [17]. The external magnetic field was equal to 0.64 T. The authors [17] studied a mixture with nanotubes and ferrite fillers.

After this cylindrical shapes with a mixture rotated. The external magnetic field was equal to 4 mT and magnetic field lines are seen on the entire surface of the sample (Fig. 4,a).


(a) (b)

**FIGURE 3.** The photomacrography of ferrite powder in the liquid epoxy matrix: a) without magnetic field; b) magnetic field of equal to 4 mT

It was shown that particles stick to the walls of shapes when exposed by the increased external magnetic field (Fig. 4,b). The surface coating is about 2 mm. The surface coating particles are randomly disposed. The distance between outer and inner radius of shapes is equal to 1.96 mm. Thus, if the strength of external magnetic field is equal to 8 mT, then the particles at volume of shapes is randomly arranged.


(a) (b)

**FIGURE 4.** The photomacrography of ferrite powder in the liquid epoxy matrix under a constant magnetic field: a) magnetic field of equal to 4 mT; b) magnetic field of equal to 8 mT.

The results of measurement of reflection coefficients are shown in Fig. 5. The spectra show that reflection coefficients for texture and nontexture composite materials are different. Figure 5 shows that there is the greatest change of the reflection coefficients for the field of equal to 4 mT. It is the optimum value of the strength of external magnetic field. The electromagnetic properties of experimental sample No. 3 are poorer as opposed to other samples (Fig. 5). Sample No. 3 has a worse absorbing characteristic.

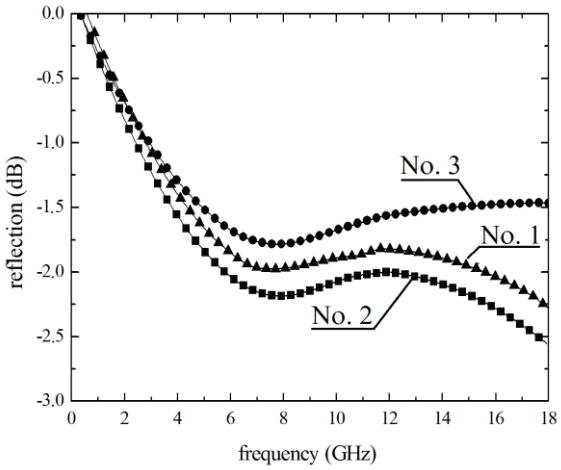



**FIGURE 5.** Reflection coefficients. Samples with different value of the strength of external magnetic field treatment (numbers description can be found in Table 2)

Sample No. 2 is a better for engineering of microwave absorbing material because it has a minimum value of reflection coefficient. Thus, the effect of magnetic field treatment on composite mixture contained magnetic fillers is shown. It is necessary to further studying of this effect.

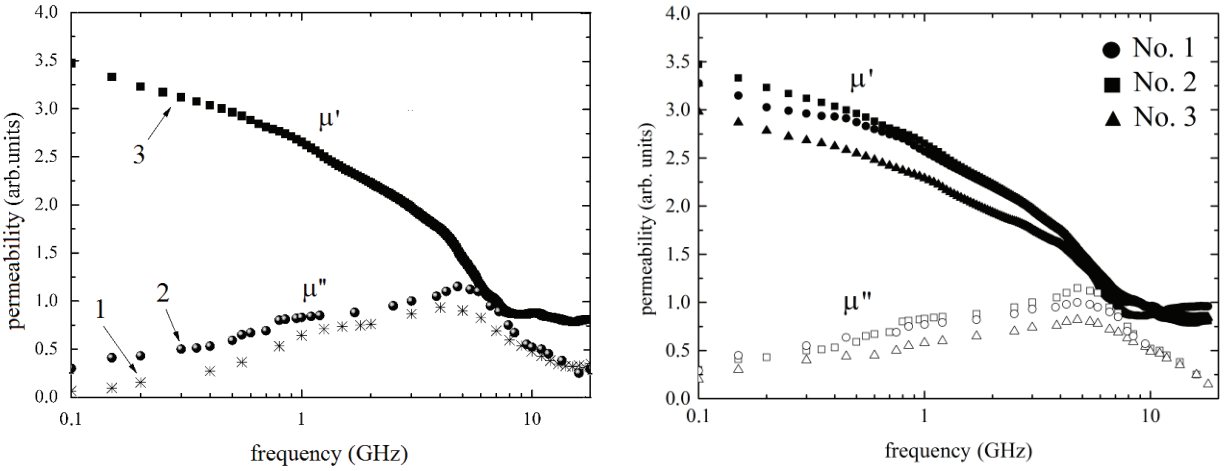
The electromagnetic (EM) parameters (ε′, ε″, μ′, μ″) were calculated by the materials measurement software. So, the imaginary permeability was calculated by formulas [18]:

$$\mu'' = \frac{15(1-K_r)}{\pi f h(1+K_r)}, \tag{5}$$

where $h$ is the thickness of sample, $f$ is the frequency, $K_r$ is the reflection coefficients.

To the application of formulas (4) to processing experimental data, we shall consider the permeability spectra of sample No. 2 given in Fig. 6,a (line 1). The initial permeability was measured by Agilent's E4980A precision LCR meter and calculated by the materials measurement software. The piecewise linear interpolation of the corresponding characteristics in the measurement range, necessary for calculations by formulas (4), was performed immediately over the experimental points.

According to the Cramers – Kronig relations (4) the real and imaginary parts of the permeability were recovered. Figure 6,a shows the $\mu''(f)$ spectra of measured samples No. 2 (star points). The square points in Fig. 6,a represent the real parts of the permeability restored by the experimental spectra $\mu''(f)$ and the circle points represent the imaginary parts calculated by the relations $\mu'(f)$.




1 – experimental points, 2, 3 – calculation
The strength of the external magnetic field 4 mT
(a)

Samples with different value of the strength of external magnetic field treatment
(numbers description can be found in Table 2)
(b)

**FIGURE 6.** Frequency dependence of the real and the imaginary parts of the permeability

As shown in Fig. 6,a, the real parts of the permeability decrease from 3.5 to 0.75 with increasing frequency from 0.1 to 18 GHz. The frequency dependences of the imaginary part of the permeability have one maximum. It is region around 4 GHz. It is considered to be related to natural ferrimagnetic resonance. There is flatness in region around 1 GHz. It is treated by the authors of [9] to be caused by the processes of displacement of domain boundaries.

Cramers-Kronig relations were used to recover of permeability of all samples. All charts are similar (Fig. 6,b). As shown in Fig. 6,b, the values of the real $\mu'(f)$ and imaginary $\mu''(f)$ parts permeability of sample No. 2 are more than the other samples. This result agrees with the measurement of the reflection coefficients.

## CONCLUSIONS

The Z-type hexaferrites were synthesized using a ceramic technique. The composite has been prepared using epoxy as a matrix with 65 wt% the Z-type hexaferrite fillers concentration. Electromagnetic characteristics are measured in range of 0.01 – 18.0 GHz.

There is nonlinear dependence of the reflection coefficients with the value of an external magnetic field. Thus changing the texture of composite materials can change the working range of the radioelectronic devices.

Analysis of the spectra by using the Cramers – Kronig relations enables one to select the most reliable experimental results.

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