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ABSTRACT

Metal-carbon composites (MCC) were produced by the dissolving of the Fe, Co and Ce nitrates in phenol–formaldehyde resin with further pyrolysis (under heating up to 800 °C). Concentrations of the metal compositions in final MCC were 2, 7 and 15 wt%. Phase composition of the final MCC samples was determined using XRD and Mössbauer spectroscopy. It was established phase separation in metallic compounds under pyrolysis process due to chemical interaction with phenol–formaldehyde decomposition products. The main phases for composites were: Fe₃O₄ (for MCC-Fe); Co (for MCC-Co) and CeO₂ (for MCC-Ce). Average crystal size for metalbased fillers was 28, 24–35 and 3.5 nm for Fe-; Co and Ce-based composites respectively. The electrodynamic properties of the MCCs in the Extremely High Frequency range (30–50 GHz) were studied as function of the filler concentration. The frequency dependences of the permittivity and permeability (real and imaginary parts) of the investigated composites were measured. The nature of the MCC electrodynamic properties was discussed in detail in terms of polarization losses.

1. Introduction

The rapid increase of the radio electronic devices requires development of the new composite materials with controllable electrodynamic properties [1–4]. Nowadays there are a lot of functional nanomaterials [5–7] and composites based on it [8–10] studied as materials with electromagnetic absorption properties for practical applications such as stealth-coatings [11,12], but not all of them have the satisfactory performance. Recently, "metal – carbon composites" or MCC have attracted much attention due to their microwave performances, chemical stability and corrosion resistance, high specific surface area [13–15]. MCC can be produced by the pyrolysis of the metal–organic solution at appropriate temperatures [16,17].

Functional materials can be divided on 3 main types in according with the mechanisms of the energy losses at high frequencies: 1st – materials with electrical losses; 2nd – materials with magnetic losses and 3rd – materials with multiple losses. First type materials are non-oxygen

ceramics [18,19], carbon based materials [20,21], metal oxides without magnetic properties [22,23] and polymer-based composites [24,25]. The electrical losses can be observed in materials due to conductivity losses and polarization losses [26,27]. The losses concerned with electrical conductivity are formed due to currents of charge carriers under the external electromagnetic radiation (EMR). In this case electrical energy transform to the thermal energy. The polarization losses can be divided on: ionic, electronic and dipoles polarization [28,29]. Materials with magnetic losses (second type) are ferro- and ferrimagnetic compounds: metals and alloys with magnetic transition elements [30,31], complex iron oxides [32,33] and composites based on it [34–36]. Especially great attention attracts materials with resonant absorption of the electromagnetic radiation (EMR) due to domain boundaries resonance [37] and natural ferromagnetic resonance [38–40]. Third type of materials are combination of the first one and second one.

The electrodynamic properties of the MCC are proven to be dependent both on the concentration of ferromagnetic particles in the

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composite and their size, as well as on the properties of the matrix. The synthesis of MCC can be carried out in one-pot if a common solvent is used for the precursors of nanoparticles and the matrix [41,42]. The Febased MCC were produced from iron nitrate and phenol–formaldehyde resin [43]. Co-based MCC were produced from Co and some organic compounds with further pyrolysis [44–46].

In this paper we present the novel synthetic route to carbon-based composites with Fe, Co and Ce nanoparticles and the results of investigation of their electrodynamic properties in the frequency band of 30–50 GHz.

2. Materials and methods

Phenol-formaldehyde resin of the novolac type (with 23 wt% mass fraction of hexamethylenetetramine), citrates of iron, cerium and cobalt, as well as 95 v% ethanol were used as raw materials for the synthesis of MCC.

Citrates were obtained by reacting FeCO₃, CoCO₃, or freshly precipitated CeO₂ with equimolar amounts of citric acid in a concentrated aqueous solution at 80 °C. After the completion of the reaction, the citrates were dried for 20 days at 40 °C. In this case, the citrates of cobalt and cerium formed a crystalline mass, while the iron citrate remained amorphous. The resulting iron-containing product was analyzed by Mössbauer spectroscopy. The Mössbauer spectra of iron citrate can be satisfactorily described by a superposition of three doublets, the isomer shifts of which correspond to iron ions in an octahedral oxygen environment in the oxidation states +3 (88 wt%) and +2 (12 wt %).

The MCC were prepared by heating or pyrolysis of a mixture of metal citrate and phenol–formaldehyde resin. To prepare composites with 15 wt% of metal (Fe, Co or Ce), 1.464 g of iron citrate, 1.451 g of cobalt citrate, or 0.669 g of cerium citrate were added to portions of 1.2 g of resin. A proportionally smaller mass of citrates was taken to produce carbon composites with 2 and 7 wt% of metal. For comparison, we also prepared a composite sample containing 7 wt% iron introduced into the resin in the form of $Fe(NO_3)_3*9H_2O$.

To increase the uniformity of the distribution of the components, the metal citrates were ground with resin to a homogeneous fine mass, and then a few drops of ethanol were added to it until a very viscous solution was formed. Heating was carried out in a muffle furnace without oxygen access when heated first for 20 h to 500 $^{\circ}$ C, then for 3 h to 800 $^{\circ}$ C, after which the furnace was switched off and cooled.

After heating, the morphology and composition of the samples were studied using a Jeol JSM-7001F scanning electron microscope with an attached Oxford INCA X-max 80 energy dispersive X-ray spectrometer (EDX). The phase composition was determined using a RigakuUltima IV powder X-ray diffractometer with $Cu_{K\alpha}$ radiation.

The Mössbauer absorption spectra were obtained on an MS1104EM express Mössbauer spectrometer manufactured by CJSC Cordon. The source of γ -radiation was ⁵⁷Co in a matrix of metallic rhodium with an activity of 47 mCi produced by RITVERTC GmbH. The spectra were recorded in an evacuated cryostat both at 77.6 \pm 0.3 K and at room temperature (296 \pm 3 K). The spectra were recorded in high resolution mode (1024 points) with a noise/signal ratio of less than 1%.

Mathematical processing of the Mössbauer spectra was performed using the SpectrRelax 2.4 software. The spectra were described by combinations of symmetric doublets and sextets with fixed ratios of intensity and widths of resonance lines. Chemical shift values were given relative to α -Fe.

Using an absorption measuring line, the S-parameters of powdered materials were determined. A WR-22 waveguide with dimensions of 5.7 \times 2.8 mm was used as a measuring line. The material sample was placed in a waveguide insert between two limiters made of material with parameters $\varepsilon \sim 1.1$ and $\mu \sim 1$. These limiters do not affect the measured parameters, since their influence was taken into account when calibrating the device. When measuring the S-parameters of a waveguide



Fig. 1. XRD patterns of MCC with 15 wt% of metals (MCC-Fe15; MCC-Co15 and MCC-Ce15).

Table 1
The results of quantitative full-profile Rietveld analysis of samples with 2, 7, and
15 wt% Fe.

Phase name	Chemical formula	2 wt% Fe	7 wt% Fe	15 wt% Fe			
Graphite	С	81(2)	83(2)	78(2)			
Magnetite	Fe ₃ O ₄	9.5(2)	9.5(3)	9.4(2)			
Cementite	Fe ₃ C	3.7(2)	5.4(3)	10.4(2)			
γ-Iron	Fe	2.4(2)	2.4(8)	1.9(2)			
α-Iron	Fe	3.5(2)	0.1(2)	0.6(2)			

transmission line with the investigated material as a dielectric, a twoport TRL calibration was used. For uniform filling of the waveguide insert with material, the measuring line was fixed vertically to reduce possible errors. The measurements were carried out in the frequency band of 30 to 50 GHz using an R&S®ZVA 50 vector network analyzer. The permittivity and permeability of the samples under study were calculated using the Nicolson-Ross-Weir method. For this, the frequency dependences of the S-parameters were measured [47,48].

3. Results and discussion

After heating, all samples form black carbon mass with a porosity of 40-80% and pore diameters of $5-1000 \ \mu\text{m}$. To study the morphology of the composites using a SEM, the samples were broken and then their fragments up to 3 mm in size were glued onto an electrically conductive substrate, with a fresh cleavage upwards. For X-ray phase analysis and Mössbauer spectroscopy, the samples were ground in a mortar.

Fig. 1 demonstrates XRD patterns of the MCC fixed concentration (15 wt%) of the different metals. The diffraction pattern of MCC-Fe15 (composite with 15 wt% Fe) represents a superposition of reflections of graphite, Fe₃O₄ and Fe₃C (Fig. 1, Table 1). The calculation of the crystal sizes (coherent scattering regions, CSR) of magnetite by the full-profile Rietveld analysis of the X-ray diffraction pattern leads to a value of 28 nm. This is consistent with the results of electron microscopy, which determined that the size of magnetite crystals is in the range from 10 to 200 nm (Fig. 2a). The mass ratio of the phases is shown in Table 1. Along with magnetite, there appears to be maggemite, having similar structure, the presence of the latter is indicated by weak reflections (for example, in the range of $10-25^{\circ}$ 20). X-ray phase analysis of the sample with iron nitrate [43] also revealed the phases of graphite (main peak near 26.3°), Fe₃O₄ and Fe₃C, with the average size of Fe₃O₄ crystals being 60–80 nm by the full-profile Rietveld analysis.

The Mössbauer spectra of composites, obtained both at room



Fig. 2. Morphology of composites with 7 wt% of metal: a) Fe - cleavage, b) Fe - surface of internal pore, c) Co - cleavage, d) Ce - cleavage.



Fig. 3. Mössbauer spectra of MCC-Fe at 77 K and its model description. From top to bottom: 2, 7 and 15 wt% Fe.

temperature and at the temperature of liquid nitrogen are a superposition of several sextets with large and medium magnitudes of magnetic splitting, differing in intensity depending on the iron content (Fig. 3). The spectra can be described satisfactorily within a single model of 7 at 296 K or 8 at 78 K symmetric sextets and one doublet (Table 2). All subspectra can be combined into four groups.

The first group of the sextets, including subspectra ## 1–3 at 296 K or ## 1–4 at 78 K (Table 2), describes weakly crystallized iron oxides with a spinel-type structure: γ -Fe₂O₃ and Fe₃O₄ [49] or a magnetite-maghemite non-stoichiometric solution Fe₃O_{4-δ} [50]. Sextets with the maximum values of magnetic splitting and minimum values of chemical

shifts (296 K, # 1, Table 2) correspond to iron atoms in the +3 oxidation state in tetrahedral spinel positions [51], while sextets with average values of magnetic splitting and high values of chemical shifts (296 K, # 2, Table 2) correspond to iron atoms in an intermediate oxidation state (from +2 to +3) in octahedral positions [51]. Considering that isomeric shifts of the subspectra in the samples with 7 and 15 wt% Fe reach 0.82 mm/s (296 K, # 2, Table 2), it can be assumed that most of the iron atoms in the indicated octahedral positions are in the +2 oxidation state. Sextets from this group with minimum values of magnetic splitting and maximum width of resonance lines (296 K, # 3, Table 2) describe the relaxation part of the spectrum of small-sized

Table 2

The results of processing the Mössbauer spectra obtained at 78 and 296 K for MCC-Fe samples with 2, 7, and 15 wt.% Fe δ is an isomer shift, $\Delta = 2\epsilon$ is a quadrupole splitting, Γ_{exp} is a line width, H_{eff} is a hyperfine magnetic field, and S# is a relative area of a subspectrum #.

Temperature, K	#	Phase	Iron content, wt. %														
			2				7				15						
			δ	$\Delta=2\epsilon$	Γ_{exp}	H _{eff}	S#	δ	$\Delta=2\epsilon$	Γ_{exp}	H _{eff}	S#	δ	$\Delta=2\epsilon$	Γ_{exp}	$\mathbf{H}_{\mathrm{eff}}$	S#
			mm/s			kOe	%	mm/s			kOe	%	mm/s			kOe	%
296	1	$Fe_{3-\delta}O_4$	0.31	-0.02	0.59	495.9	53	0.28	-0.04	0.56	491.7	30	0.27	-0.06	0.52	490.2	25
	2		0.62	0.53	0.26	478.4	2	0.82	0.19	0.42	471.5	5	0.80	0.18	0.43	470.5	6
	3		0.53	-0.07	1.01	434.2	7	0.51	-0.15	2.07	437	12	0.53	-0.22	1.9	429	9
	4	α-Fe											0.01	0.02	0.36	331.4	2
	5	θ-Fe ₃ C	0.20	0.04	0.21	211.2	8	0.19	0.04	0.24	211.7	14	0.19	0.05	0.22	212.3	12
	6		0.18	0.01	0.41	204.3	25	0.19	0.00	0.38	203.8	30	0.19	0.01	0.36	204.6	35
	7	χ-Fe ₅ C ₂						0.23	-0.28	0.40	111.8	3	0.23	-0.31	0.38	110.8	3
	8	Fe ⁺³	0.27	0.98	0.58		5	0.24	0.95	0.55		6	0.26	0.96	0.56		7
78	1	$Fe_{3-\delta}O_4$	0.46	-0.00	0.56	527.2	35	0.46	-0.01	0.59	524.4	25	0.46	-0.02	0.53	525.9	16
	2		0.37	-0.02	0.47	511.6	16	0.36	-0.04	0.41	509.3	7	0.37	-0.02	0.47	506.4	10
	3		0.44	0.03	0.43	483.6	4	0.43	0.08	0.57	486.8	6	0.61	-0.12	1.57	477	17
	4		0.88	-0.40	1.43	439	7	0.76	-0.34	1.61	449	10					
	5	α-Fe						0.14	-0.07	0.61	342	1	0.14	-0.07	0.39	339.6	4
	6	θ-Fe ₃ C	0.32	0.03	0.24	252.7	11	0.32	0.03	0.23	252.7	12	0.32	0.05	0.24	252.4	14
	7		0.30	-0.03	0.37	244.0	22	0.30	-0.02	0.39	244.1	34	0.30	-0.02	0.37	244.1	34
	8	χ-Fe ₅ C ₂						0.40	-0.23	0.28	148.1	3	0.44	-0.20	0.25	143.4	3
	9	Fe ⁺³	0.41	1.25	0.97		5	0.36	1.26	0.39		3	0.35	1.22	0.30		2



Fig. 4. Frequency dependences of the permittivity of MCC-Ce: a) real part; b) imaginary part.

particles of non-stoichiometric iron oxide [52]. The subspectrum # 4 at 296 K (# 5, Table 2, at 78 K) corresponds to metallic iron α -Fe [53] and is reliably recorded for a sample with 15 wt% Fe. In a sample with 7 wt% Fe, the corresponding subspectrum with low intensity and strongly broadened resonance lines can be observed only at low temperatures. The third group of subspectra includes sextets with medium values of magnetic splitting, describing iron atoms in iron carbides. The subspectra ## 5, 6 at 276 K (## 6, 7 at 78 K) [54–56] describe θ-Fe₃C. The subspectrum # 7 at 276 K with an effective magnetic field of 111 kOe (at 78 K – # 8–145 kOe), corresponds to the internal sextet of χ -Fe₅C₂ (the other two sextets of χ -Fe₅C₂ fall into the range with θ -Fe₃C and are masked by it) [57]. The last group is a paramagnetic doublet of iron in the oxidation state +3 [12] (# 8 or # 9 at 296 or 78 K, respectively), which can have a dual nature: on the one hand, it can describe the superparamagnetic state of iron atoms in highly dispersed oxocompounds; on the other hand, it may include subspectra of amorphous forms of iron carbides [58]. In general, the data of the quantitative analysis of the phases containing iron, according to the Mössbauer spectra and diffraction patterns, agree well (Tables 1, 2). In particular, with an increase in the total iron content, the fraction of cementite increases.

The effect of iron citrate (or iron nitrate) on the formation of graphite (main reflection is near 26.3°) from phenol-formaldehyde resin is probably associated with the dissolution of iron citrate and its participation in the ordering of the resin melt prior to its solidification and cross-linking. Similarly, a much weaker effect of Co citrate on the formation of weakly crystallized graphite from phenol-formaldehyde resin was detected. Ce does not cause graphitization even to a small extent. Interestingly, the more Fe citrate put in the resin, the more graphite formed, so that mass ratio of graphite to iron containing crystalline phases is almost constant, with 78–83 wt% graphite regardless of 2, 7 or 15 wt% Fe in composite (Table 1).

It can be noted that on the surfaces of the inner pores of the composite samples with 2 and 7 wt% Fe, electron microscopy revealed areas inside pores covered with relatively straight carbon nanotubes with a diameter of 70–140 nm and a length of 5–10 μ m (Fig. 4b). At the free ends of the carbon nanotubes there are well faceted crystals of iron oxide (confirmed by the EDX mapping), the size of which is proportional to the diameter of the nanotubes. Most likely, during the growth of the nanotubes, these particles were metallic Fe [59], but after crashing the composite, they were oxidized in the air. According to the analysis of SEM images, the mass fraction of nanotubes does not exceed 1 wt% of



Fig. 5. Frequency dependences of the permittivity of MCC-Co: a) real part; b) imaginary part.

the sample.

X-ray diffraction pattern of a sample with 15 wt% Co represent a superposition of a wide halo from amorphous glassy carbon, a weak graphite reflection, and reflections corresponding to a nanocrystalline Co (Fig. 1). According to a full-profile Rietveld analysis, crystalline part of composite consists of 41 wt% graphite, 47 wt.% Co in a form of a high-temperature face-centered cubic β -modification with a CSR size of 24 nm, and 12 wt% in the form of a hexagonal α -Co with a CSR size of 35 nm. This is consistent with the results of the study of morphology using scanning electron microscopy, which determined that the size of cobalt crystals is in the range from 20 to 800 nm. It is known that β -cobalt is formed when cobalt oxide is calcined in hydrogen flow [60].

X-ray diffraction pattern of a sample with 15 wt% of Ce citrate confirms the formation of X-ray amorphous glassy carbon and nanocrystalline CeO₂ (Fig. 1). Calculation of the CSR size of cerium oxide by the full-profile Rietveld analysis gives a value of 3.5 nm. This is consistent with the results of studying the morphology of ceriumcontaining samples using scanning electron microscopy, which determined that the grain size of cerium oxide in them does not exceed 20 nm.

X-ray diffraction patterns of samples with lower concentrations of metal citrates generally coincide with those shown in Fig. 1, but have a lower intensity of reflections of the corresponding metal compounds and graphite.



Fig. 6. Frequency dependence of the permittivity of MCC-Fe: a) real part; b) imaginary part.

The use of iron citrate resulted in the formation of the finest and most uniformly distributed particles in the form of magnetite (Fig. 2a). Slightly larger particles of metallic cobalt were formed from cobalt citrate (Fig. 2c). Particles of cerium oxide formed from cerium citrate have a nanometer size; however, they are unevenly distributed in the matrix (Fig. 2d). This morphology may be related to the difference in the solubility of citrates in the ethanolic resin solution. Iron citrate is highly soluble in this solution, cobalt citrate is much less soluble, and cerium citrate is almost insoluble.

Figs. 4-6 represent frequency dependences of real and imaginary parts of permittivity for MCCs. Dipole polarization, which determines the value of ε , is associated with the orientation of dipoles in an external electric field and is caused by losses on overcoming the chemical bond forces.

The dipole moment (*Mq*) is found by the formula:

$$M_q = e \cdot r \tag{1}$$

where *e* is the value of the dipole charge;

r is the radius-vector directed from the center of gravity of a negative electric charge to the center of gravity of a positive charge.

Due to the different shape and polarizability of the s- and f-orbitals, the center of gravity of the dipole moment is shifted towards oxygen by the value r, which causes the appearance of an additional, so-called



Fig. 7. Frequency dependences of permeability of MCC-Ce: a) real part; b) imaginary part.

homeopolar dipole moment. Due to this, an increase in the concentration of cerium oxide in the MCC significantly increases the real part of the dielectric constant e^{i} in the entire frequency band (Fig. 4a).

Dielectric losses are determined by the imaginary part of the dielectric constant ε . At lower frequencies, when dipole polarization prevails, these losses are very large, since in the composite with cerium oxide, the value of ε is comparable in modulus with ε (Fig. 4b). With increasing frequency, there is a transition from dipole to ion-relaxation polarization. As this transition proceeds, the losses decrease, which is expressed in a decrease in the absolute value of ε (Fig. 4b).

A decrease in the value of ε' in the MCC-Ce in the 30–36 GHz band is also due to the transition from dipole to ion-relaxation polarization (Fig. 4a). This transition from one type of polarization to another is clearly visible as a minimum of ε' at a frequency of 36 GHz. Since the number of electrons in a cerium atom is twice as large as in iron and cobalt, the polarizability of a cerium atom is much higher and an increase in the amount of cerium oxide in the composite leads to a significant increase in the real part of the dielectric constant. In contrast to MCC-Ce, for MCC-Fe or MCC-Co, the real part of the dielectric constant decreases with an increase in their content, and the frequency dependence changes more monotonically (Fig. 5a, 6a). This is due to the fact that the dipole moment with an increase in the amount of cerium increases faster compared with that for iron and cobalt.

For MCC-Fe, a weak minimum of about 35 GHz can be distinguished on the frequency dependence of ε only for a sample with 2 wt% Fe,



Fig. 8. Frequency dependences of permeability of MCC-Co: a) real part; b) imaginary part.

while for samples with 7 and 15 wt% Fe and all samples with cobalt, there is no pronounced minimum.

Since the loss in all substances usually decreases during the transition to ion-relaxation polarization, the values of the imaginary parts of the dielectric constant ε ["] in modulus generally decrease in all MCCs (Fig. 4b, 5b, 6b). When an electromagnetic wave affects an ion of an element with higher weight, it shifts more weakly from its equilibrium position in the crystal lattice. Due to this, as the frequency increases, the losses for the composite with cerium oxide decrease much more significantly than for the composites with iron and cobalt (Fig. 4b, 5b, 6b). This indirectly confirms the above conclusion about the observed transition from dipole to ion-relaxation polarization.

When the frequency increases, the orientation of the dipoles does not have time to change in accordance with the frequency of the applied field. As a result, the dipole polarization transforms into ion-relaxation polarization. Ion-relaxation polarization is caused by the displacement of ions at the sites of the crystal lattice.

The permeability of composites has its features in the same frequency band as the permittivity. Figs. 7-9 represent frequency dependences of real and imaginary parts of permeability for MCCs. In the material, the spin and magnetic moments are balanced so that each atom of the magnetic moment is compensated. In the magnetic field inside the atom, weak induction currents are generated according to Faraday's law of electromagnetic induction. According to Lenz's law, the magnetic flux created by induction currents is counter-directed to the external



Fig. 9. Frequency dependences of permeability of MCC-Fe: a) real part; b) imaginary part.

magnetic field.

All samples of the substance under study behave like paramagnets. For such materials, $\mu \leq 1$. The variation of permeability with frequency can be explained using Larmor's theorem. In a quiescent state, samples of the substance have their own magnetic moments of low values, which do not significantly affect the overall value of the magnetic permeability of the composite. According to Larmor's theorem, in the substance placed into the external variable magnetic field, electron magnetic moment precession begins. Since the magnetic moment of the lattice is compensated, the main contribution to the overall permeability will be made by the magnetic moments of the atomic cores of cerium, cobalt, and iron.

For cerium, which has a larger number of electrons, the precession of the magnetic moment of the electrons increases with increasing frequency and, as a consequence, the real part of the permeability μ' grows. Due to the small magnetic moment of cerium itself, when its concentration increases, this slightly affects the overall value of μ' . Cobalt has a smaller number of electrons compared to cerium and with an increase in the concentration of cobalt, the total precession of the magnetic moments of the electrons slightly increases the real part of the permeability μ' . For iron, the total precession of the magnetic moments of the electrons practically does not affect the total value of μ' .

The increase in absolute value of the imaginary part of the magnetic permeability μ' with increasing concentration can be explained as follows. An increase in frequency leads to an increase in the precession of

the electron magnetic moment and an increase in the energy needed to maintain the precession, i.e., losses.

4. Conclusion

The proposed synthesis method allows one-pot preparation of MCC with Fe, Co and Ce (2, 7 and 15 wt%). The electrodynamic properties of the MCC under study were considered. The values of real and imaginary parts of permittivity and permeability were measured using Nicolson-Ross-Weir method in the bandwidth of 30–50 GHz. Frequency dependences of real and imaginary parts of permittivity and permeability were obtained and presented in the paper.

It was established the influence of different polarizations on the electrodynamic parameters of the MCC and proposed the mechanism of that influence in the frequency band studied. It was shown that the main contribution to the value of the parameters in the frequency range 30–40 GHz was made by dipole polarization. At frequencies above 40 GHz, the orientation of the dipoles does not have time to change in accordance with the frequency of the applied field. As a result, the dipole polarization becomes ion-relaxation polarization. The influence of the precession of the electron magnetic moments on the values of the real and imaginary parts of the permeability in the frequency band was analyzed. MCC with Fe or Co exhibited radar absorbing properties in the gigahertz band, in contrast to composites with cerium oxide.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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D.S. Klygach et al.

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