Electromagnetic characteristics of light terahertz materials

Dorozhkin, Kirill, Suslyaev, Valentin, Kazmina, Olga, Semenova, Valeriya, Denisenko, V., et al.

Kirill V. Dorozhkin, Valentin I. Suslyaev, Olga V. Kazmina, Valeriya I. Semenova, V. Denisenko, Konstantin E. Matyskin, Artem V. Korshunov, "Electromagnetic characteristics of light terahertz materials," Proc. SPIE 11582, Fourth International Conference on Terahertz and Microwave Radiation: Generation, Detection, and Applications, 1158219 (17 November 2020); doi: 10.1117/12.2580645

Event: Fourth International Conference on Terahertz and Microwave Radiation: Generation, Detection, and Applications, 2020, Tomsk, Russian Federation

Electromagnetic characteristics of light terahertz materials

Kirill V. Dorozhkin[a], Valentin I. Suslyaev[a], Olga V. Kazmina[b], Valeriya I. Semenova[b], V. Denisenko[c], Konstantin E. Matyskin[c], Artem V. Korshunov[a]
[a]National Research Tomsk State University, 36 Lenina Ave., Tomsk, Russian Federation 634050; [b]National Research Tomsk Polytechnic University, 30 Lenina Ave., Tomsk, Russian Federation 634034; [c]Company «MK Electron», 43 Novosibirskaya St., Tomsk, Russian Federation 634063

ABSTRACT

Porous materials are promising for use in the terahertz range, when they have valuable properties: low weight, chemical inertia, thermal stability, and relatively low cost. These materials are required for effective shielding of electromagnetic radiation, attenuators, filters. Electromagnetic characteristics in the frequency range of 0.15 – 0.5 THz are considered. Samples are porous composite materials filled with carbonyl iron, waste from semiconductor production, and carbon nanostructures. Foamed polyurethane and foam glass material is used as a dielectric binder. The combination of high electromagnetic efficiency and the "green" origin of the constituent composites opens the way for successful practical use.

Keywords: Light materials, terahertz frequency range, carbonyl iron, MWCNTs

1. INTRODUCTION

Active development of terahertz (THz) band technology for solving various scientific problems: in medicine for diagnosing blood conditions [1], treating skin diseases [2]; quality control of medicines, in the study of works of art [3], to solve the problems of electromagnetic compatibility and shielding of electromagnetic emission [4], requires new hardware facilities. Also a different hardware components is needed for the creation of new specialized facilities, which would allowes to reduce the weight and size of devices, to reduce energy costs, complexity of maintenance and dangerous consequences for personnel [5, 6]. The development of the hardware components is impossible without materials with special electromagnetic properties. Over the past two decades progress has been made in the synthesis of various types of artificial media and materials with nanoscale structuring and properties that differ significantly from those of natural media. A great step has been taken to the creation of of materials, equipment and devices with new unique properties.

The creation of materials that absorb electromagnetic radiation in a wide frequency range occupies an important place among the current tasks [6-8]. At present, there is a great need to create small-sized anechoic chambers that can be installed next to the radio engineer's workplace or right at the workplace. Such chambers must have a relatively large working space without losing anechoic properties and broadband. It is impossible to solve the problem due to the widely used pyramidal structures, since they require a lot of space. Porous structures (3D structures) are promising materials for this purpose due to their unique properties: lightness, high electrical conductivity, chemical inertness, combined with low cost. From the point of view of electrodynamics, they are interesting because even flat porous materials are easy to match with free space over a wide frequency range.

To convert electromagnetic energy into thermal energy, active inclusions interacting with electromagnetic radiation are necessary: carbonyl iron, nitrogen carbide, ferrites, carbon materials, including nanosized ones [6 - 8]. Carbon nanomaterials (carbon nanotubes and nanofibers, graphite-nanoplates and graphene) are best suited for quality properties due to their superior properties such as light weight, high corrosion resistance, high electrical and thermal conductivity. Such a material can be obtained by foaming the carbon mass with a binder. In this case, a shielding device is obtained that provides a signal attenuation by 40 dB [9] due to almost complete reflection from the highly conductive surface of the shield. This method is not suitable for constructing anechoic chambers and other non-reflective devices.

It is theoretically predicted and experimentally confirmed [4, 10, 11] that the formation of an insulated conducting network is required to obtain a high efficiency of fillers. The electrical conductivity of composites with a conducting grid will be much lower (5–7 orders of magnitude) compared to the electrical conductivity of the original fillers, therefore,

Fourth International Conference on Terahertz and Microwave Radiation: Generation, Detection, and Applications, edited by Oleg A. Romanovskii, Yurii V. Kistenev, Proc. of SPIE Vol. 11582, 1158219 · © 2020 SPIE · CCC code: 0277-786X/20/$21 · doi: 10.1117/12.2580645

the composite will reflect electromagnetic radiation to a lesser extent. When interacting with a porous material, an electromagnetic wave is absorbed not only by the surface, but is also reflected many times inside the pores, which increases the length of the reflecting path and reduces the size of the absorber. The ability of a porous material to absorb electromagnetic radiation can be controlled by changing its macrostructure, forming pores that are optimal in shape and size [12-14]. The electromagnetic properties of composites have been studied to a lesser extent, in which silicon and gallium arsenide particles are used as fillers [15], which also have high absorbing properties. It is shown [16] that radioelectronic industry waste contains a large amount of such particles. Adding of waste into an absorbent coating allows you to solve two problems: to obtain an efficient screen and to dispose of waste without harming the environment. In this paper, the electromagnetic characteristics of porous materials are considered, in which carbon nanotubes and waste from the production of semiconductor materials are fillers.

2. SAMPLES

We used samples of two types: based on carbon nanotubes and polyurethane as a binder.

1. Preparation of samples based on carbon nanotubes was carried out in several stages. At the first stage, the activation of the surface of the TUBAL nanotubes (OCSiAl) was carried out to ensure the correct distribution in the matrix. After that, the preparation of a paste from nanotubes in water with the subsequent introduction of this paste into component A (polyol) was carried out. Then, carbonyl iron was encapsulated to prevent particle sticking and it was added to the mixture of component A and nanotubes. The fourth stage is the preparation of a compound from component A and component B (diphenylmethane diisocyate - MDI) and a blowing agent into a mold treated with an anti-adhesive. MDI was used to stiffen the resulting material. The elasticity and density of the polyurethane foam can be changed by adding TDI (toluene diisocyanate) or NDI (naphthylene diisocyanate).

The time for complete polymerization of the compound was 30 min. As a result of polymerization of the compound, the nanotubes are isolated inside the matrix, and microparticles of carbonyl iron are isolated in microcavities of the matrix and have free movement inside the closed volume. The density and thickness of the samples, the electromagnetic response of which was measured, are given in Table 1. Figure 1 shows photographs of the material obtained and samples cut from them for measurements.

Table 1. Description of samples

Name	The basis	Filler	Density, g / cm^3	Thickness, mm
Sample 1	Polyurethane	MCNT wt2,56%	0,07	3.85
Sample 2		Carbonyl iron P.100 wt38,46%	0,06	3.6
Sample 3		Carbonyl iron P.100 wt70%	0,06	2.8
Sample 4		Carbonyl iron P.100 wt39,5%; MCNT wt0,3%	0,097	3.6

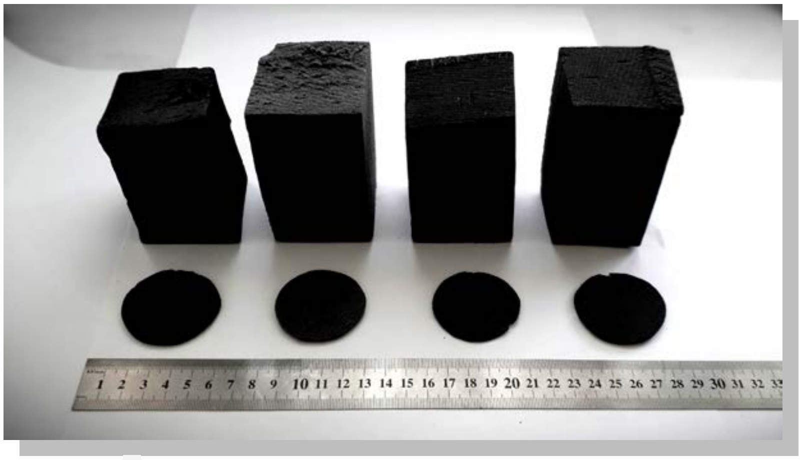


Figure 1. Photo of samples based on carbon nanotubes in a foam polyurethane matrix.

2. Obtaining a porous glass composite was carried out according to the developed low-temperature technology [16]. An industrial liquid glass with a silicate module 3 was selected as the matrix of the composite. The fillers of the composite are represented by such materials as expanded perlite, sodium hexafluorosilicate and semiconductor production waste. Perlite was used to reduce the density of the finished glass composite, the bulk density of expanded perlite is 80 kg / m3. Sodium hexafluorosilicate was added to the composition to solidify the water-insoluble state. The waste served as a modifying additive, increasing the ability of the glass composite to absorb electromagnetic radiation in the terahertz range. Waste is the sludge that is formed after grinding the plates on the silicon carbide wheels. In terms of particle size distribution, the waste is 90% represented by particles with a size of less than 5 microns. The chemical composition of the waste is represented by silicon carbide (38%) and gallium arsenide, the content of which is about 55%, the rest of the impurity in the form of gallium.

The method of obtaining a glass composite included the following technological operations. Stirring in a homogenizer for 3 minutes water glass in the amount of 65 - 74 wt. % and expanded perlite (7 - 9 wt.%), pre-moistened with water (3 wt.% by weight of pearlite). Adding a powdery waste to the composition in an amount of 7 wt. % and hardener (8 - 11 wt.%). The mixture was stirred and poured into split molds, followed by drying at room temperature. The dried samples were heated in a muffle furnace in air to 250 - 450 ° C for 30 minutes and cooled in the furnace. The amount of waste introduced into the composition of the material was 10, 20 and 30 wt%.

The description of the porous glass composite modified by waste presented in Table 2. It was found that with an increase in the composition of the waste, the apparent density of the material increases, which also leads to an increase in the mechanical strength of the material. According to the values of these indicators, the material meets the class of heat-insulating and structural materials. A higher waste amount leads to an increase in the density of the material. The appearance of the porous glass composite obtained by low-temperature technology is shown in Figure 2.

Table 2. Physical and Mechanical Properties of the Composite

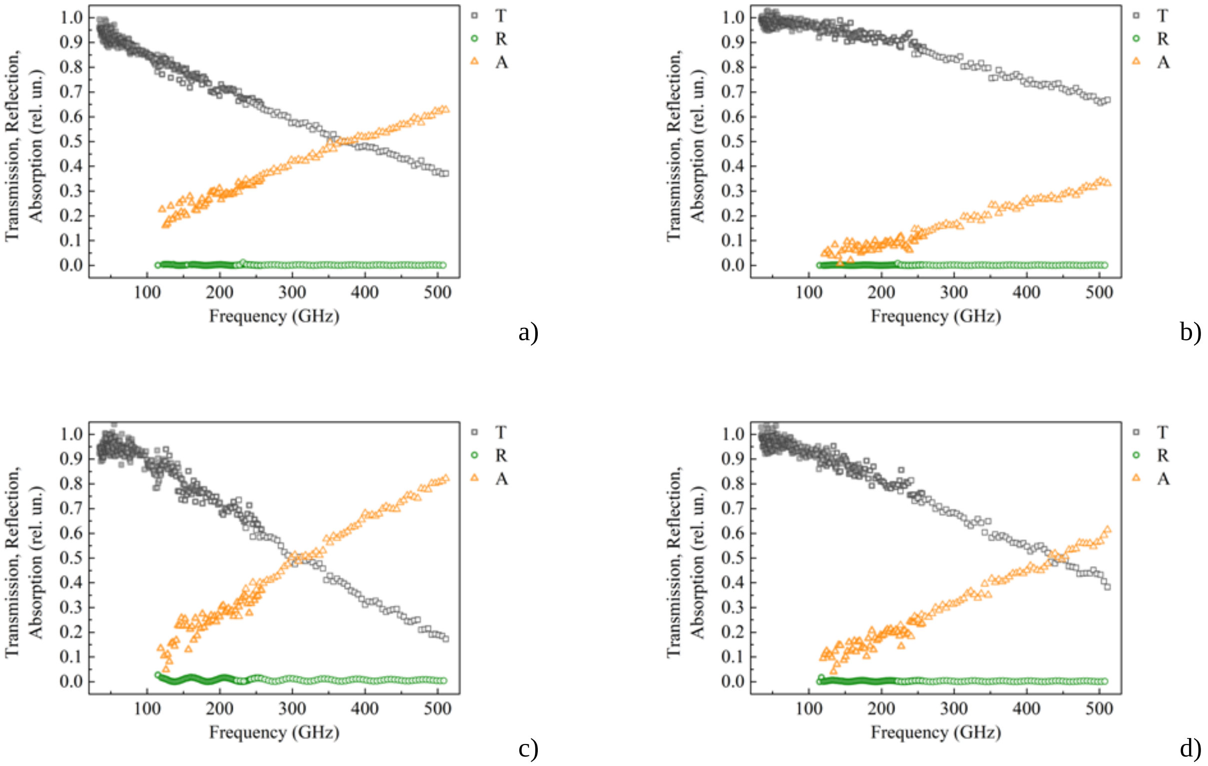
The amount of waste in the composite, wt. %	Apparent density, kg /m3	Compressive strength, MPa	The porosity of the composite, %
0	330	0,3	87
10	350	1,5	86
20	510	4,7	80
30	560	6,0	78

Figure 2. Photo of samples of porous glass composite obtained by low-temperature technology

3. MEASUREMENT RESULT AND DISCUSSION

Electromagnetic responses of samples were measured with an STD-21 BWT spectrometer. The STD-21 submillimeter-wave spectrometer is a laboratory setup combining high monochromaticity of radiation (Δν/ν ~ 10–5) The detection of signal transmitted through the sample is carried out acousto-optical converter (Golay cell)/

Frequency dependences of the electromagnetic properties (coefficients for reflection (*R*), transmission (*T*) and absorbption (*A*)) samples based on carbon nanotubes in a foam polyurethane matrix materials in teraherz frequency range 110–500 GHz by the method of free space were measured (Fig 3.).



a)

b)

c)

d)

Figure 3. Spectra of transmission, reflection and absorption coefficients for four samples 1 (a), sample 2 (b), sample 3 (c), sample 4 (d).

Figures 3 show that all samples practically do not reflect electromagnetic energy. In the low-frequency band, the small thickness of the samples leads to the absence of screening. In the high-frequency band, a sample containing 70 wt. % carbonyl iron has a higher absorption despite the fact that its thickness is almost a millimeter less than that of other samples. The addition of the relatively few of nanotubes to the carbonyl iron composite leading to a notable increase in absorption (Figs 3b and 3d). The values of the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ were calculated from the measured coefficients of the electromagnetic response (Figure 4). Figures 4 show that the electromagnetic parameters of the sample with the highest content of carbonyl iron have large values of the real and imaginary components. Shown as well is that the addition of carbon nanotubes led to an increase in both components of the dielectric constant due to the conductive properties of the carbon fillers, which formed isolated networks even at a relatively few content.

\

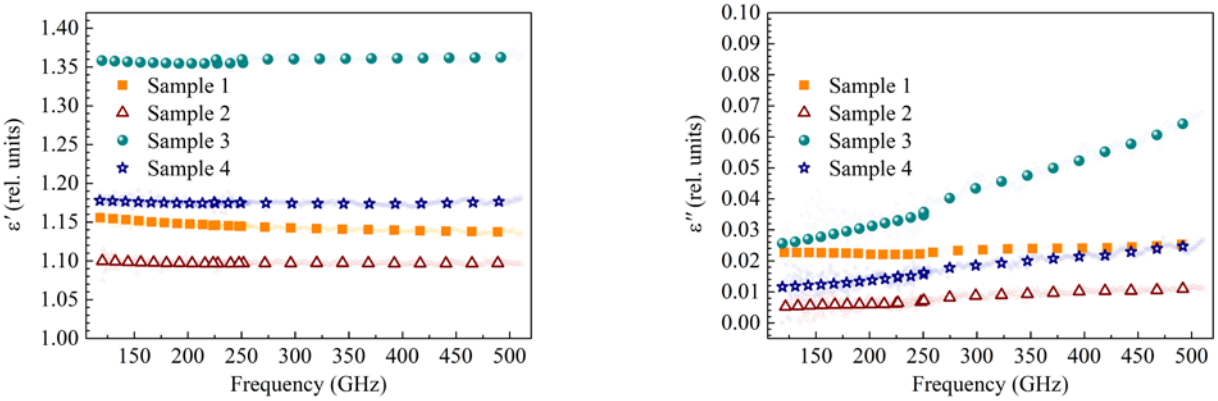


Figure 4Spectra of complex dielectric constant of foamed polyurethane samples with additions of carbonyl iron and carbon nanotubes (table 1)

The experimentally measured values of the absorption, reflection and transmission coefficients of electromagnetic emission for samples of porous glass composite with a filler in the form of radio-electronic industry waste in the production of semiconductors, and without it show that the value of reflection is also not observed (Fig. 5). In the absence of a filler, the low reflection coefficient is determined by the fact that the electromagnetic energy is distributed between the transmitted power and the absorbed one.

This indicates that the decrease in the intensity of electromagnetic emission behind the screen for these samples is determined by the absorption of the wave by the porous substance, and not by reflection. Due to the increased of filler from waste in the composite, the transmission coefficient gradually decreases and practically tends to zero at a filler content of 30 wt. %. The maximum absorption coefficient is equal to 100% for the sample with the maximum filler content at a frequency of 240 GHz (Fig. 4). The value of the transmission coefficient for a sample with 30% filler in comparison with a sample without a filler decreases 15 times at 120 GHz, and 33 times at 240 GHz. Thus, the composition of the initial mixture, including up to 30 wt. % filler in the form of waste from semiconductor production, containing silicon carbide and gallium arsenide, makes it possible to obtain a composite that absorbs electromagnetic emission in the extremely high frequency band of 30 - 300 GHz. The proposed method for obtaining a lightweight composite material allows us to solve the problem of recycling waste from semiconductor production.

4. CONCLUSION

It is shown that a relatively small addition of carbon nanotubes (9.3 wt%) to the foamed polyurethane composite with carbonyl iron noticeably increases the values of the real and imaginary components of the dielectric constant, which leads to a greater screening of electromagnetic radiation.

It has been established that with an increase in the amount of waste in the material from 10 to 30%, the apparent density of the material increases from 350 kg / m3 to 560 kg / m3 and the compressive strength from 1.5 MPa to 6 MPa. At the same time, the efficiency of absorption of electromagnetic radiation increases, which is determined by the effect of silicon carbide and gallium arsenide on the processes of polarization and conductivity in the composite when absorbing the energy of electromagnetic radiation. It is shown that by creating a composite based on a foam glass material, it is possible to obtain new elements of radio-electronic equipment (absorbers, matched loads, elements of anechoic chambers), while utilizing waste from the production of semiconductor devices.

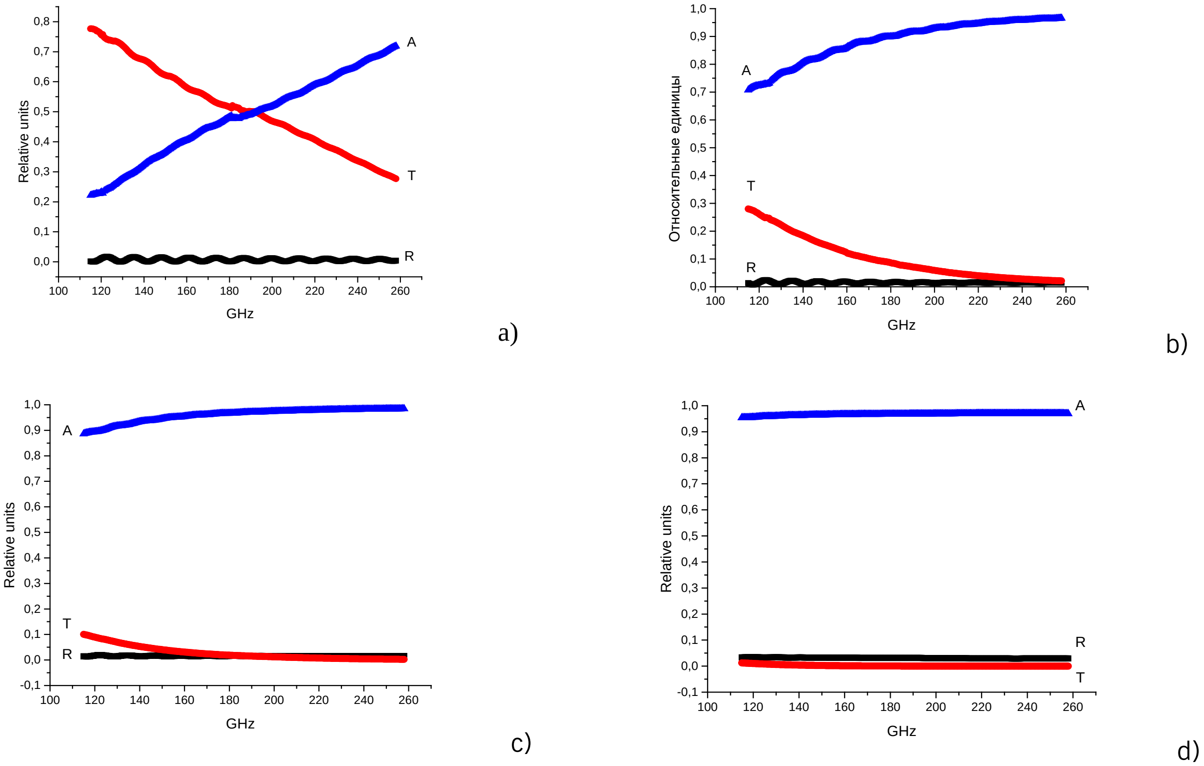


Figure 5. The dependence of the absorption, reflection and transmission coefficients of the frequency 120 - 260 GHz for the sample without waste (a) and with a waste 10wt.% (b), 20 wt%(c), 30 wt % (d)

ACKNOWLEDGMENT

The reported study was funded by RFBR, project number 19-32-90150.

REFERENCES

[1] Deng, Jianwei Li, Jin Wang, Ningning Huang, (…), Jianguo Tian Shikc Liu «Measurement of the refractive index of whole blood and its components for a continuous spectra! region»,. Biomed. Opt. 24(3), 035003 doi: 10.1117/1JBO.24.3.035003 (2019).

[2] Anna Kochnev, Noa Betzalel, Paul Ben Ishai and Yuri Feldman «Human sweat ducts as helical antennas in the sub-THz frequency range-an overview», Terahertz Science and Technology.Vol.11. No.2. P.43-56 (2018).

[3] Menshikova Elena «Terahertz for painting: how research by scientists from Russia and France helps to restore art objects», Electronic resource URL: https://www.rfbr.ru/rffi/ru/press_about/o_2092033. Date of treatment July 19, (2019).

[4] Ludmila Vovchenko, Ludmila Matzui, Viktor Oliynyk (…) and Polina Kuzhir «Polyethylene Composites with Segregated Carbon Nanotubes Network: Low Frequency Plasmons and High Electromagnetic Interference Shielding Efficiency» Materials, 13, 1118, 14 p, (2020).

[5] Cao, M.-S.; Wang, X.-X.; Cao, W.-Q.; Yuan, J. «Temperature dependent microwave absorption of ultrathin graphene composites». J. Mater. Chem. C, 3, 10017–10022 (2015).

[6] Kolanowska, A., Janas, D., Herman, A.P., (...), Giżewski, T., Boncel, S., «From blackness to invisibility – Carbon nanotubes role in the attenuation of and shielding from radio waves for stealth technology», Carbon, 126, 31-52 (2018).

[7] Wei, Y., Yue, J., Tang, X.-Z., Du, Z., Huang, X., «Enhanced magnetic and microwave absorption properties of FeCo-SiO2 nanogranular film functionalized carbon fibers fabricated with the radio frequency magnetron method», Applied Surface Science, 428, 296-303 (2018).

[8] Volski V., Vandenbosch G.A.E., «Full-wave electromagnetic modelling of fabrics and composites», Compos Sci Technol, 69, 161–168 (2009).

[9] Kuzhir, P.P., Letellier, M. Bychanok, D.S.,(…) , Fierro, V., Celzard, A. «Electrical Properties of Carbon Foam in the Microwave Range», Russian Physics Journal V.59,№10, Pages Pages 1703-1709 (2017)

[10] Wu, D.; Gao, X.; Sun, J.; Wu, D.; Liu, Y.; Kormakov, S.; Zheng, X.; Wu, L.; Huang, Y.; Guo, Z. «Spatial confining forced network assembly for preparation of high-performance conductive polymeric composites», Compos. Part A, 102, 88–95. (2017).

[11] Deng, H.; Lin, L.; Ji, M.A.; Zhang, S.; Yang, M.; Fu, Q. «Progress on the morphological control of conductive network in conductive polymer composites and the use as electroactive multifunctional materials,. Prog.Polym. Sci., 39, 627–655. (2014).

[12] González, M., Crespo, M., Baselga, J., Pozuelo, J., «Carbon nanotube scaffolds with controlled porosity as electromagnetic absorbing materials in the gigahertz range», Nanoscale, 8 (20), 10724-10730 (2016).

[13] Zakharychev E. A., Ryabov S. A., Zefirov V. L., Semchikov Y. D., Belov M. S., Kirpichev D. V. and Zuev A. A., «Development of polymer radio-absorbing materials with carbon nanotubes for extremely high frequency range», Inorganic Materials: Applied Research, 4 (5), 405 – 409 (2013)

[14] Ren, F., Yu, H., Wang, L., Tian, Z., Ren, P., «Current progress on the modification of carbon nanotubes and their application in electromagnetic wave absorption», RSC Advances, 4 (28), 14419-14431 (2014)

[15] Stebeneva V. I., Kazmina O. V., «Method of processing waste containing gallium arsenide»", Collection of selected articles. Conference materials "National Development", Saint Petersburg, 176 -178 (2018)

[16] Kazmina O, Semenova V, Suslyaev V, Dorozhkin K. «Composition and method of obtaining a material that absorbs electromagnetic radiation». Patent RU № 2707656, registration date 28.11.(2019)