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Shielding properties of natural carbon-containing composites

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The results of an experimental study of the reflection coefficients R , transmission T , and absorption $R + A$ of natural carbon-containing composites ($2 \leq C \leq 97$ at.%) with a thickness of $8\text{--}20\ \mu\text{m}$ on laboratory tape in five frequency ranges from 7.8 GHz to 56 GHz. Frequency spectra of reflection and transmission coefficients are obtained. The dependences of R , T , $R + A$ on the carbon content at one of the frequencies for each studied range are given. It is shown that the shielding efficiency slightly depends on the frequency and varies more significantly depending on the carbon content. The influence of the structural characteristics and composition of natural carbon-containing composites on the shielding properties of the samples has been determined.

Keywords: natural disordered carbon, reflection and transmission coefficients, shielding properties.

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In recent years, there has been a significant increase in interest in natural disordered sp^2 carbon materials with a structure similar to synthetic glass carbon. Possibilities of application in various technological processes are developed for materials with a similar structure, for example, for the creation of batteries [1–3], temperature and electrochemical sensors [4,5]. Karelian shungites are the most promising natural materials [6]. Researchers are particularly interested in using disordered sp^2 carbon materials, including shungites, to shield microwave radiation [7–10]. It has been found that in certain microwave ranges, the shielding efficiency of ultrathin shungite plates can reach 100%, primarily due to the high reflection and absorption [10,11], which is directly related to the effect of the thickness of the shungite plate on the electrophysical properties [12]. Microwave reflecting, penetrating and shielding properties of ultrathin plates of naturally disordered sp^2 carbon with a thickness from 8 to $20\ \mu\text{m}$ in an extended and continuous frequency range from 7.8 to 56 GHz are studied in this paper.

For experimental studies, a series of shungite plates with a carbon content of C from 2 to 97 at.% were obtained. The samples were selected from several major occurrences of carbon-containing materials in Karelia: Maksovo (ShM1 — 96 at.%, ShM3 — 41 at.%, M25 — 17 at.%, M30 — 23 at.%, M58 — 53 at.%, Karan — 55 at.%), Shunga (ShSh1 — 97 at.%, ShSh2 — 73 at.%), Chebolaksha (ShCh3 — 34 at.%), Nigozero (ShN5 — 2 at.%), Tetyugino (Tetug — 54 at.%), Lebeschina (ShL2 — 49 at.%, ShL2a — 64 at.%), Zazhogino (ShZ3 — 47 at.%). Additionally, three samples of anthraxolites from the island of Novaya Zemlya from quartz-carbonate veins of the Perya ore occurrence (ANZPr — 96 at.%), the bitumen occurrence of Columbia

(Columb — 90 at.%) and the occurrence of Krasnaya Gora, Karelia (ShKG — 95 at.%). All samples were collected manually directly from the host rocks. Shungite plates with a thickness of 2–3 mm and dimensions of 2.5×1.5 cm are sawn from solid pieces of rock, glued with Canadian balsam onto standard laboratory glass with a thickness of 2.5 mm and sanded to a thickness of $8\text{--}20\ \mu\text{m}$. The thin shungite plate was removed from the glass using laboratory tape.

The microwave reflection coefficient R and transmission coefficient T (in power) of thin plates of disordered carbon were determined at normal wave incidence in a rectangular waveguide using panoramic VSWR meters in the frequency ranges: 8.24–12.05 GHz (P2-61), 12.05–17.44 GHz (P2-67), 17.44–25.86 GHz (P2-66), 25.86–37.50 GHz (P2-65), 37.50–53.57 GHz (P2-68). The method of measuring microwave reflection and transmission coefficients is described in more detail in Ref. [13]. To collect data from the VSWR meter, a four-channel 16-bit ADS1115 ADC was used, connected to a PC via an ATmega 328p microcontroller and a USB-Serial converter based on the CH340 chip. Two ADC channels were connected via current-limiting resistors $10\ \text{k}\Omega$ to the terminals X and Y of the „Recorder“ connector of VSWR meter. The received data was transmitted via a virtual COM port to a PC. Each measuring range was graded according to all marked divisions of the scale device. The data obtained were averaged using the weighted moving average method to eliminate the parasitic interference signal. The absorption coefficient of $A = 1 - R - T$ was calculated from the measured R and T .

Figure 1 shows examples of typical dependencies of reflection coefficients (Figure 1, *a*), transmission (Figure 1, *b*) and shielding (Figure 1, *c*) from the frequency of f

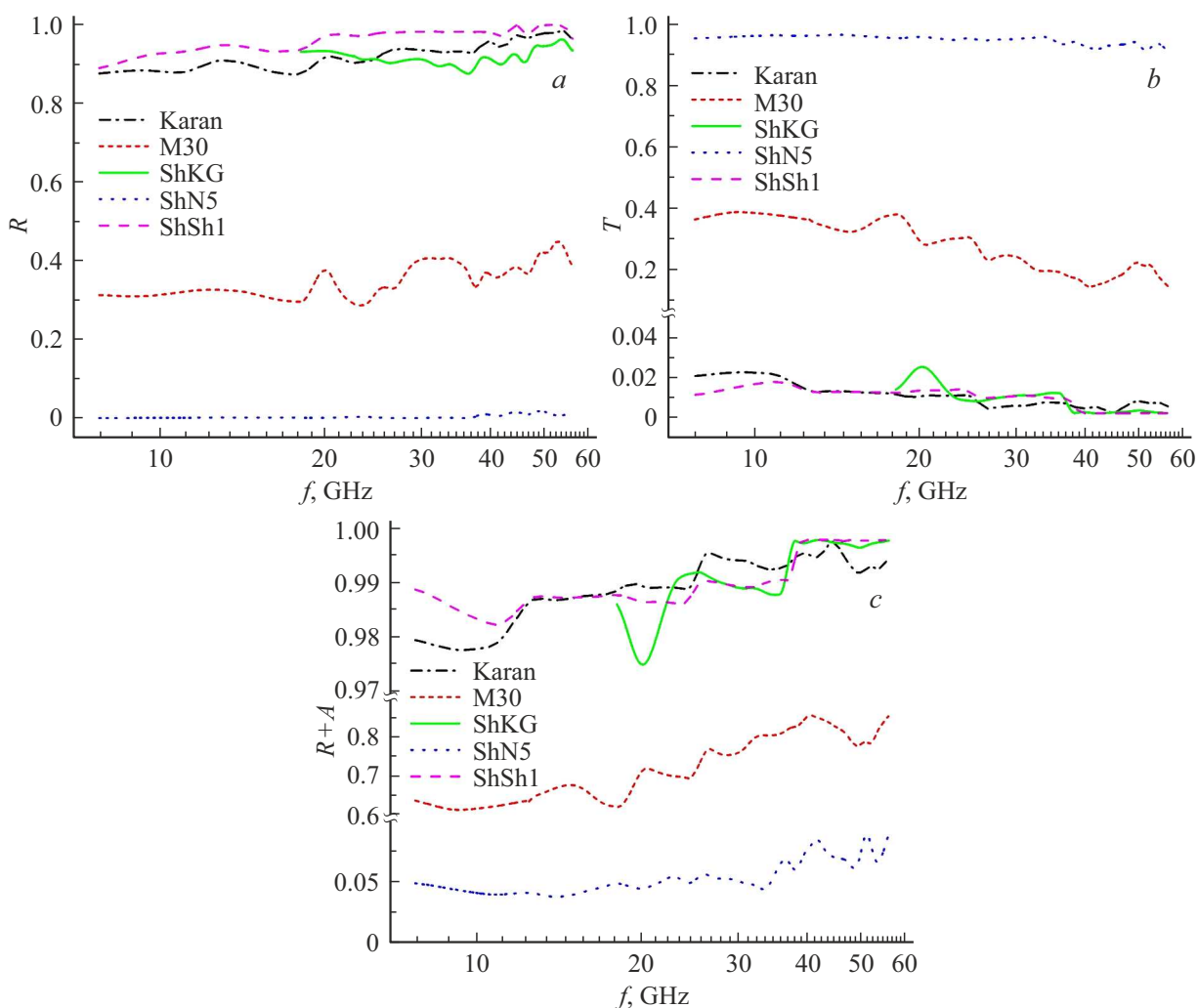


Figure 1. Dependencies of reflection coefficients (a), transmission (b) and shielding (c) from a frequency in the range of 7.8–56 GHz for four shungites and one anthraxolite.

electromagnetic radiation for four shungites in the range of 7.8–56 GHz and one anthraxolite (ShKG) in the range of 18–56 GHz. For anthraxolites, studies were carried out starting from the third frequency range (17.44–25.86 GHz) due to the fact that the sample sizes were smaller than the cross-section sizes of the waveguides of the first two ranges.

The research results showed for most shungite samples a gradual increase in the reflection coefficient and a decrease in the transmission coefficient depending on the frequency during the transition from one range to another, with a slight change of R and T within each range (the exception is the range 37.50–53.57 GHz, in which the oscillation amplitude R and T are significantly higher). Thus, for M30 shungites with a carbon content of 23 at.%, the microwave reflection coefficient was 0.31 at a frequency of 9 GHz, and it was 0.41 at a frequency of 55 GHz. It varied from 0.63 to 0.85 at similar frequencies for the Tetug sample (54 at.%) R .

Figure 2 shows the dependences of the reflection coefficients (Figure 2, a) and transmission (Figure 2, b) of shungites on the carbon content for frequencies 9, 15,

23, 32 and 55 GHz, representing all five frequency ranges under study. The graphs were approximated at frequencies 55 GHz for both dependencies Figure 2, at $f = 23$ GHz (Figure 2, a) and $f = 32$ GHz (Figure 2, b). As can be seen from Figure 2, with an increase in the carbon content, the decrease in the transmission coefficient is more pronounced than the increase in the reflection coefficient. Thus, for most samples with $C \geq 34$ at.%, the coefficient T practically ceases to change and does not exceed 0.10–0.15, starting from the frequency range 12.05–17.44 GHz (Figure 2, a), and with $C \geq 73$ at.% reaches 0.01 or less regardless of frequency. The coefficient R increases up to $C = 55$ at.% and is more than 0.90 (Figure 2, b). Therefore, it can be noted that the shielding properties of disordered carbon are primarily affected by the influence of the reflection coefficient (Figure 1, c). Figure 2 also shows a very noticeable spread of points in frequencies, which decreases significantly for R and T at $C \geq 55$ at.%.

Figure 3 shows the dependences of the coefficients of absorption A and shielding $R + A$ of shungites on the carbon

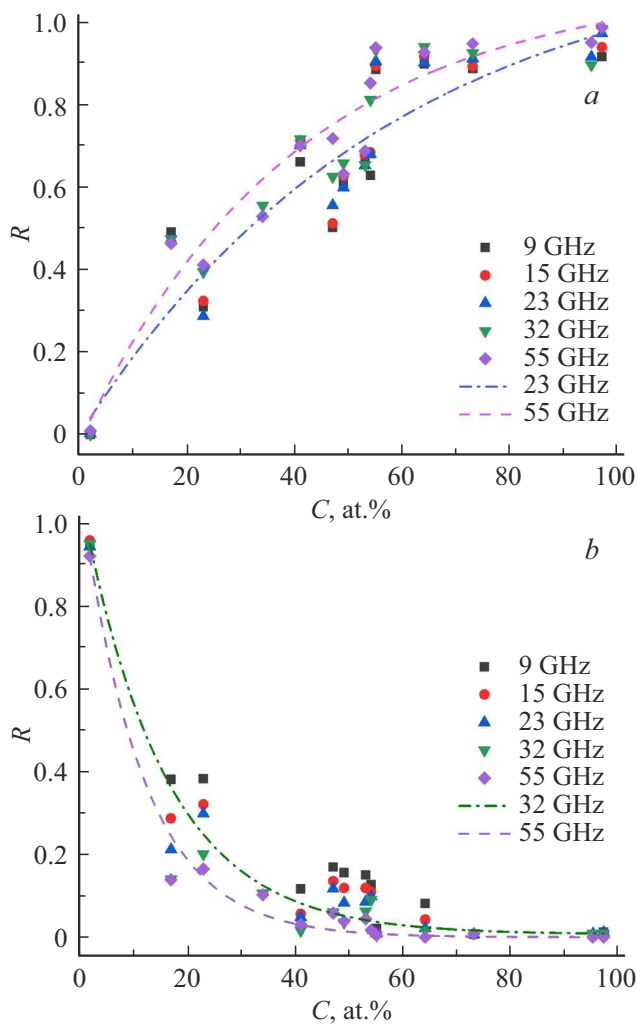


Figure 2. Dependences of the reflection coefficients (a) and transmission (b) of shungites on the carbon content for different frequencies. Symbols — experimental data, lines — approximation.

content C for various frequencies. It can be seen from Figure 3, a that shungite samples with a carbon content of 17–49 at.% have the highest absorption from 30 to 45%. For the M30 sample, individual stretching in the absorption coefficient can exceed 45%, especially at frequencies above 30 GHz. This coincides with the results of Ref. [10].

The results of this study showed that the shielding efficiency increases with the transition from a lower frequency range to a higher one due to increasing reflection, and for most samples the maximum efficiency is achieved in the frequency ranges 25.86–37.5 GHz and 37.5–53.57 GHz (Figure 1, c). This is due to a significant increase in the dynamic conductivity of disordered carbon with an increase in the frequency [11,13]. The weakest shielding properties are shown by the sample with the lowest carbon content of ShN5 (4–7 at.%) and anthraxolite Columb (20–22 at.%). The shielding efficiency of shungites with a carbon content from 17 to 34 at.% can range from 61% in the first

frequency range of 8.24–12.05 GHz to 89% in the last frequency range of 37.5–53.57 GHz. Anthraxolite ANZPr (82–85 at.%) can be attributed to the same group. All other studied samples, from $C \geq 41$ at.%, have a shielding efficiency of 82% at frequencies of 8.24–12.05 GHz to 91% and higher, starting from the frequency range of 25.86–37.50 GHz (Figure 3, b). Karan, ShSh1, ShSh2, ShM1 shungites and ShKG anthraxolite have the maximum shielding efficiency of 97.5–99.8% regardless of the studied frequency range. Tetug and ShL2 samples have similar properties in the two highest frequency ranges.

The system under study consists of disordered sp^2 carbon with good and isotropic (unlike crystalline graphite) conductivity (~ 1000 S/m) and embedded in carbon nano- and micro-sized grains of minerals, mainly quartz and pyrite. Carbon creates a conductive matrix in which a non-conductive mineral phase is evenly distributed as a filler. Traditional carbon-based shielding systems are predominantly designed according to a different princi-

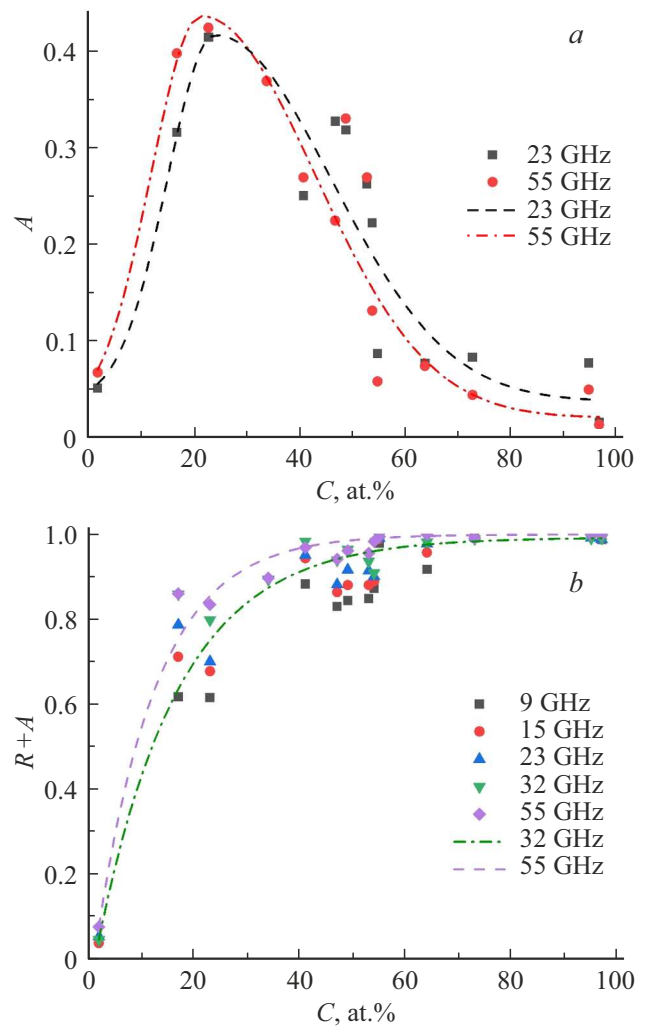


Figure 3. Dependences of absorption coefficients A (a) and shielding $R+A$ (b) of shungites on the carbon content. Symbols — experimental data, lines — approximation.

ple [7–9] — a conductive filler consisting of nano- and micro-sized particles (graphenes, nanotubes, fullerenes) is introduced into a non-conductive, usually polymer, matrix. In this case, a significant thickness of the shielding material (several millimeters) and a high concentration of conductive filler are required. In our case, the natural system effectively shields even at ultra-small (units and the first ten micrometers) coating thickness due to the high conductivity of the matrix. Moreover, even with a low carbon content (17–23 at.%), shungite plates show high reflection and absorption efficiency. The shielding efficiency is determined by the sum of reflection and absorption of electromagnetic radiation. As the carbon content increases, the reflective properties begin to dominate, and the shielding efficiency tends to 100%. With high reflection, a significant proportion of electromagnetic radiation does not penetrate deep into the sample and, consequently, conditions for its absorption do not arise. At a carbon content of 17–37 at.%, reflection becomes weaker, so absorption begins to play an essential role in shielding. The absorption mechanisms are primarily related to the porosity of carbon itself, since shungite carbon has a nanoscale porosity [14–16], as well as to micro-sized mineral weakly or non-conductive inclusions.

Thus, the shielding properties of natural carbon-containing composites in the frequency range of 7.8–56 GHz have been studied. The screening efficiency of the samples increases slightly with increasing frequency and increases significantly with increasing carbon content. The shielding mechanisms are determined by the conductivity of carbon, its porosity, and micro-sized mineral inclusions. The practical significance of shungite disordered carbon materials is due to solving technical problems in materials science, primarily related to the needs of communications, flexible micro- and nanoelectronics, monitoring the state of construction infrastructure, as well as the problems of extensive growth of electromagnetic pollution that disrupts the operation of surrounding electrical equipment. The most important advantage over alternative shielding coatings is the extremely small thickness of the studied samples ($\sim 8\text{--}20\ \mu\text{m}$).

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Conflict of interest

The authors declare no conflict of interest.

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