Temperature-frequency dependences of conductivity and impedance of disordered carbon in shungites

© E.A. Golubev[1], I.V. Antonets[2], R.I. Korolev[1]

[1] Institute of Geology of the Komi Scientific Research Center of the Ural Branch of the Russian Academy of Sciences, Syktyvkar, Russia
[2] Syktyvkar State University, Syktyvkar, Russia

E-mail: yevgenygolubev74@mail.ru

Received May 11, 2023
Revised September 3, 2023
Accepted October 30, 2023

The temperature-frequency properties of samples of natural disordered carbon were studied in the frequency range 50 kHz — 10 MHz and temperatures 120−420 K. A consistent increase in conductivity with increasing temperature and an exponential decrease in conductivity with increasing frequency were found. The revealed temperature-frequency properties are compared with various structural models of the structure of natural disordered carbon.

Keywords: natural disordered carbon, conductivity, impedance, temperature-frequency properties.

DOI: 10.61011/PSS.2023.12.57654.5136k

In recent years, there has been a growing number of reports on the successful use of disordered sp^2 carbon materials with a glassy carbon structure in various technological processes [1], for example, in the creation of materials that shield microwave radiation, of rechargeable batteries [2]. It is known that the industrial production of such materials involves environmentally hazardous processes. At the same time, in nature, disordered graphite-like carbon in „ready-made“ form is common, easily extractable, and its technological application will be more economically profitable and environmentally cleaner than of synthetic analogues. One of the most in-demand properties of disordered graphite-like carbon (DGC) is high electrical conductivity, which, combined with thermal and chemical stability, provides good prospects in the industry. The most promising in terms of the amount of recoverable reserves and physical properties is shungite carbon from Karelia [2]. Shungites are natural carbon-mineral composites with carbon content in various cases from 2 to 97 at.% [3–9]. Structurally, shungite carbon is similar to low-temperature (1500−1800°C) glassy carbon. In addition to shungites, numerous manifestations of DGC of similar structure are worldwide distributed, which makes it relevant to study the properties of such substances using different samples, taking into account the variability of formation conditions in a natural laboratory. Electrophysical properties serve as the key both to understanding the structural features of DGC and to the search for new technological applications. The available information on the influence of high and low temperatures on the electrical conductivity of DGC is contradictory [2], and information on frequency-temperature dependences was not found in available sources. In this paper, we determined the temperature (range 120−420 K) dependences of impedance and conductivity, and temperature-frequency dependences in the frequency range 50 kHz−10 MHz for natural DGC on the example of shungite and similar natural substances.

Three samples of shungite with a carbon content of 27% (Maxovo sample), 56% (Tetug), 82% (Shunga) and two samples of shungite-like carbon with C = 97% (manifestations Perya (ANZPr) and Pavlovo (ANZPa), Novaya Zemlya) were studied. The samples were made in the form of plates of dimensions $6.0 \times 6.0 \times 1.5$ mm with polished faces. The opposite faces of the plates were coated with a thin layer of gold using magnetron sputtering in a vacuum. Impedance and phase angle were measured using E7-29 immittance meter using a four-wire circuit. The temperature of the samples was controlled in a thermostat in a nitrogen atmosphere. Temperature was measured using a thin-film platinum thermal resistance and V7-23 universal voltmeter. The sample was heated by the temperature increasing of the nitrogen atmosphere with electric heater through a PID-controlled evaporator. The sample was cooled by supplying liquid nitrogen to the thermostat.

Based on the measurement results, a weak (maximum by three times) increase in the conductivity of shungites with temperature increasing was determined; the main increase occurs at temperatures starting from 300−310 K for different samples (a typical example of the dependence is shown in Figure 1, *a*). This distinguishes shungites from synthetic nanostructures (nanotubes, nano-onions), where conductivity often changes by tens of times, and from natural shungite-like samples, where an increase in conductivity in the studied temperature range by more than an order of magnitude was detected (Figure 1, *a*). Conductivity jumps, which were reported in the paper [10], were not detected. In the graphs of the temperature dependence of conductivity

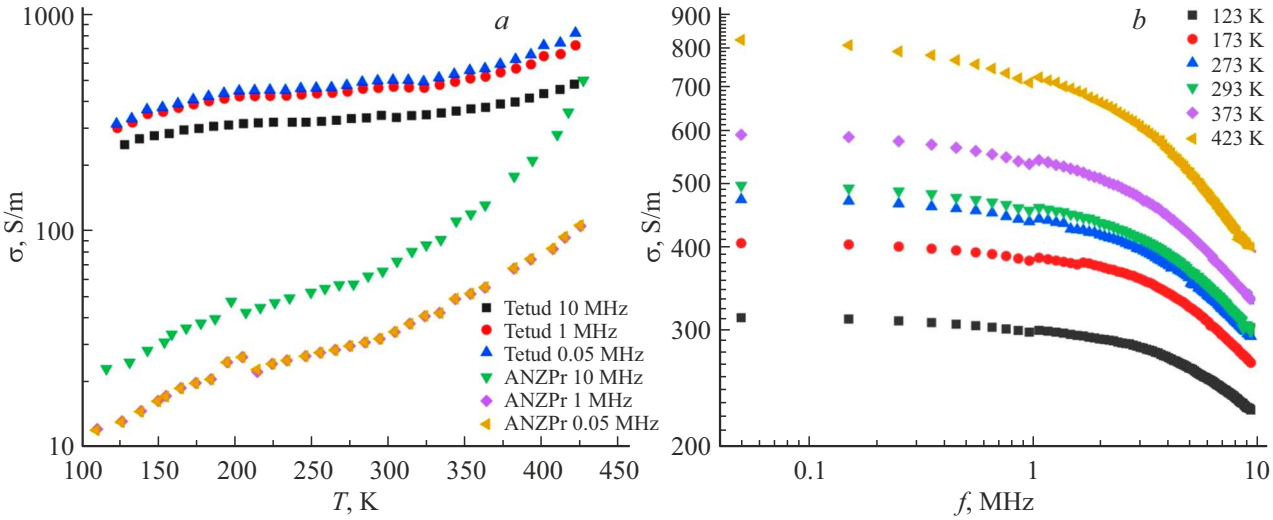

Figure 1. Typical temperature-frequency dependences of the electrical conductivity of shungite (Tetug sample) and shungite-like carbon (ANZPr sample) (*a*) and frequency-temperature dependences of shungite (Tetug sample) (*b*). The dependences for ANZPr sample at frequencies 1 MHz and 0.05 MHz coincide.

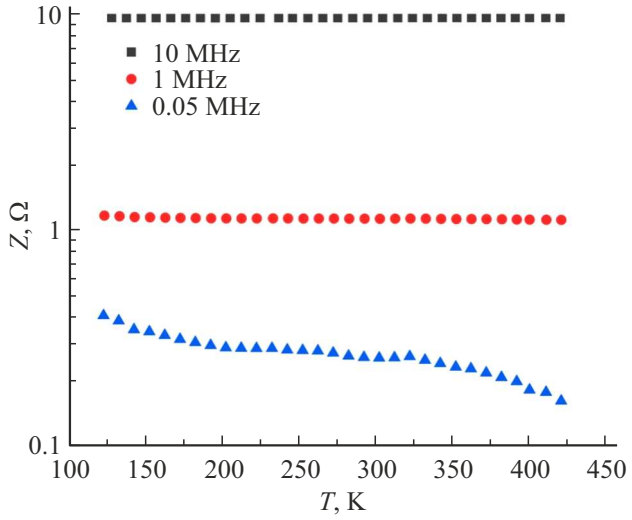

Figure 2. Typical temperature-frequency dependence of shungite impedance (Maxovo sample).

in each sample two linear sections with different slope angles can be distinguished (Figure 1, *a*), which indicates the presence of at least two different dominant mechanisms of electrical conductivity. The frequency properties of the samples practically do not change with changes in temperature (example in Figure 1, *b*). The curves behave identically over the entire temperature range: a decrease in conductivity occurs that increases with frequency increasing, and the steepness of the decrease with the temperature increasing is proportional to the intrinsic conductivity value.

The complex resistance (impedance Z) in all samples at low frequencies decreases with temperature increasing. As the frequency increases, the absolute value of the impedance increases, and the temperature dependence decreases until it is completely absent at frequencies above 1 MHz (example in Figure 2). This is due to the fact that in shungites in this frequency range active resistance dominates, which practically does not depend on frequency, and determines the type of complex resistance. The reactance turns on at frequencies above 1 MHz and changes the conductivity by maximum two times at frequency of 15 MHz.

The change in the slope of the conductivity dependence on temperature indicates the presence of different conduction mechanisms. Using Mayer–Neldel rule [11], the activation energies of the studied samples were approximately estimated. For shungite samples the activation energies do not depend on carbon content and are 0.003–0.005 eV in the conventionally low-temperature (up to 300 K) region and 0.04–0.06 eV in the high-temperature (above 300 K) areas. For non-shungite samples the activation energy is significantly higher: 0.01–0.03 and 0.1–0.3 eV respectively.

Structural representations about natural DGC are reduced to a set of nanoscale fullerene-like structures, multilayer curved ribbons and packs of misoriented graphene layers (Figure 3) [2–5]. It is difficult to assess the quantitative relationships between these structures in a specific sample, as well as to assess the conditions of contact between them. However, it is possible to consider the influence of each of these elements. In a constant electric field, electrons move along graphene layers and between layers, across the boundaries of packs and ribbons. The basis of DGC molecular structure is a nanoscale graphene layer, within which the local conductivity is high and close to metallic. However, the graphene layers in the packs are terminated by a necklace of heteroatoms [4], which leads to dipole losses at the boundaries and the need to overcome high-energy barriers. This structure gives the electrical conductivity

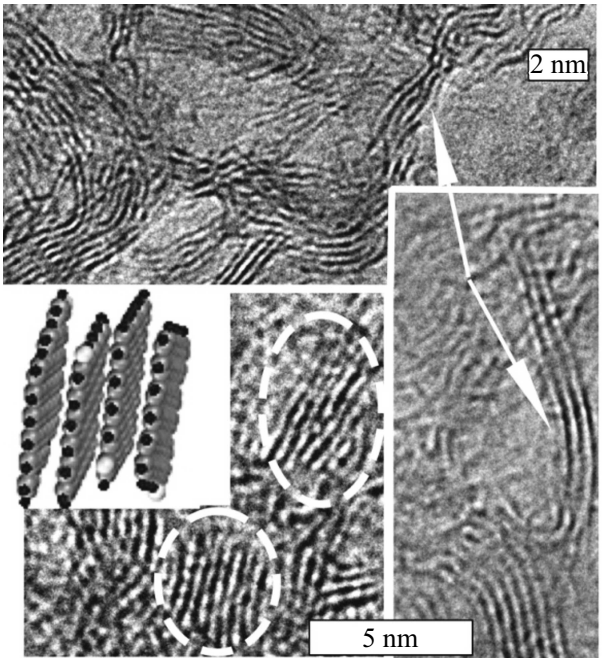

Figure 3. Electron microscopic images of the structural elements of natural DGC: packs of graphene layers (dashed areas) and multilayer ribbons (marked with arrows). Insert: model [2] of pack of graphene layers (gray balls — carbon) with a necklace of heteroatoms along the edges (black balls — hydrogen, white balls — oxygen).

of DGC a semiconductor nature. A significantly sharper dependence of conductivity on temperature for shungite-like DGC samples indicates a comparatively worse quality of contacts between packs of graphene layers and ribbons.

A significant increase in reactance with a frequency above 1–2 MHz in shungite and shungite-like samples with a high carbon content indicates the inductive nature of conductivity and indicates a significant content of ribbon structures. Numerous inclusions of minerals up to several micrometers in size, fragmentarily coated with a thin film of graphitic carbon [12], were identified. Along with multilayer carbon ribbons, such structures can act as inductors.

Funding

The study was supported by RSF grant 21-47-00019.

Conflict of interest

The authors declare that there was no conflict of interest.

References

[1] L.S. Vieira. Carbon **186**, 282 (2022).
[2] Ye.A. Golubev, I.V. Antonets. Nanomaterials **12**, *21*, 3797, (2022).
[3] J. Jehlička, J.-N. Rouzaud. Carbon **30**, 1133 (1992).
[4] Ye.A. Golubev, N.N. Rozhkova, Ye.N. Kabachkov, Yu.M. Shulga, K. Natkaniec-Holderna, I. Natkaniec, I.V. Antonets, B.A. Makeev, N.A. Popova, V.A. Popova, E.F. Sheka. J. Non-Cryst. Solids 524 (2019).
[5] V.V. Kovalevski, P.R. Buseck, J.M. Cowley. Carbon **39**, 243 (2001).
[6] L.M. Lyn'kov, T.V. Borbot'ko, E.A. Krishtopova. Tech. Phys. Lett. **35**, 410 (2009).
[7] I.A. Moshnikov, V.V. Kovalevski. Nanosyst. Phys. Chem. Math. **1**, 214 (2016).
[8] M.A. Augustyniak-Jabłokow, Y.V. Yablokov, B. Andrzejewski, W. Kempiński, S. Łoś, K. Tadyszak, M.Y. Yablokov, Zhikharev. Phys. Chem. Miner. **37**, 237 (2010).
[9] Ye.A. Golubev, I.V. Antonets, V.I. Shcheglov. Mater. Chem. Phys. **226**, 195 (2019).
[10] L.S. Parfen'eva, I.A. Smirnova, A.Z. Zaidenberg, N.N. Rozhkova, G.B. Stefanovich. Phys. Solid State **36**, 129, (1994).
[11] J.C. Wang, Y.F. Chen. Appl. Phys. Lett. **73**, 948 (1998).
[12] I.V. Antonets, Ye.A. Golubev, V.I. Shcheglov, A.S. Prikhodko, Borgardt. J. Phys. Chem. Solids **171**, 110994, (2022).

Translated by I.Mazurov