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Electrophysical Characteristics of *c*BN–NbN Composite Ceramics Doped with Al_2O_3, Si_3N_4 and SiC

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Different additives' influence on electric conductivity of 'dielectric/conductor'-type composites (namely, polycrystalline *c*BN-based composites contained *c*BN as a dielectric phase and NbN as a conductor phase) is investigated. Investigated samples are obtained by the application of HPHT (high pressure–high temperature) sintering ($P = 7.7$ GPa, $T = 2000$°C). Electrical-resistance dependences on the temperature and applied voltage are measured for all samples. Obtained results' analysis shows that all sintered samples have a semiconductor nature of conductivity. It is interesting that addition dielectrics (Al_2O_3, Si_3N_4) as well as semiconductor (SiC) leads to the electric-conductivity improve (drop in electrical resistance) for *c*BN–NbN composites in some degree (despite the lower electrical conductivity of these substances). Alumina whiskers' addition to *c*BN–NbN composites leads to a more significant drop in electrical resistance compared to powder particles' addition (from 1.85 to 0.72 Ohm·cm for samples with whiskers (Al_2O_3w) and from 1.35 to 0.17 Ohm·cm for samples with Al_2O_3 powder). Hence, as con-

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cluded, the sample electrical conductivity is affected by both the additive particles' morphology and the grain boundaries' state of the sintered polycrystalline ceramics.

Key words: dielectric, *c*BN, conductor, NbN, composite, additives, Al_2O_3, Si_3N_4, SiC, electrical resistance.

В роботі досліджено вплив різних добавок на електропровідність композитів типу «діелектрик/провідник» (полікристалічні зразки на основі *c*BN містили *c*BN в якості діелектричної фази та NbN — в якості провідної фази). Досліджувані зразки було одержано за допомогою спікання за високих тисків і температур (P = 7,7 ГПа, T = 2000°C). Залежність електричного опору від температури та прикладеної напруги було виміряно для всіх зразків. Аналіза одержаних результатів показала, що всі спечені зразки мають напівпровідниковий характер провідности. Цікавим є те, що додавання як діелектриків (Al_2O_3, Si_3N_4), так і напівпровідників (SiC) деякою мірою поліпшує електропровідність композиту *c*BN–NbN (незважаючи на меншу електропровідність цих речовин). Додавання вусів оксиду Алюмінію до композитів *c*BN–NbN приводить до більш значного пониження електричного опору порівняно з додаванням частинок порошку оксиду Алюмінію (від 1,85 до 0,72 Ом·см — для зразків з вусами (Al_2O_3w) та від 1,35 до 0,17 Ом·см — для зразків з порошком Al_2O_3). Зроблено висновок, що на електропровідність зразків впливає як морфологія частинок добавок, так і стан меж зерен спеченої кераміки.

Ключові слова: діелектрик, *c*BN, провідник, NbN, композит, добавки, Al_2O_3, Si_3N_4, SiC, електричний опір.

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1. INTRODUCTION

Modern electronics is steadily moving towards terahertz region of electromagnetic waves. This is putting ahead the electro-physical properties necessary to achieve a high circuits' electrons density with effective thermal management of its elements. One of the key problems is a decreasing of charge carrier's dissipation [1]. To lower the electron scattering on phonons we can use a high-thermal conductivity dielectric system in a thermal contact with a conductor/semiconductor [2]. Studies have been carried out of current propagation through the islet gold films on a surface of the high-thermal conductivity ceramic dielectrics like aluminium nitride (AlN, 120 W/(m·K)) [3] and cubic boron nitride (*c*BN, 160 W/(m·K)) [4], and through inclusions of metal-like refractory compounds: titanium nitride (TiN) in polycrystalline AlN [5] and niobium nitride (NbN) in polycrystalline *c*BN [6].

Materials with high thermal conductivity (diamond, GaN) and conductor/high-thermal conductive dielectric systems in thermal contact are most required for modern electronic applications. Experimental data's accumulation in the field of materials for electronics applications is critically important for electron processes' understanding in such systems.

This article devoted to the electrical properties' investigation of 'dielectric/conductor' composites, that contains dielectric (*c*BN) and conductor (NbN) phases. The aim of this work is to obtain the absolute values of electrical resistance and to investigate the charge's transfer character (metal, tunnel, semi-conductive).

*c*BN is high-temperature dielectric material. The electrical resistivity of polycrystalline *c*BN-based materials obtained by sintering at high pressures and temperatures (even without activating additives' using) significantly depends on initial powders' purity and can vary over a wide range from 109 to 1013 Ω·cm. The electrical conductivity of *c*BN-based composite materials can be controlled by additives' introducing (usually electrically conductive additives use). Different refractory compounds that are stable at high temperatures should be added to initial composition. The most widely used additions are refractory compounds (nitrides, borides, and carbides of group IV transition metals (titanium, zirconium, and hafnium)). We decided to use NbN as a binder due to perfect properties' set of this material (that listed below). For instance, the superconducting nature of NbN has been exploited in low temperature superconducting electronics such as tunnel junctions [7] and nanostructured single photon detectors [8]. Good mechanical properties such as hardness and toughness make it a suitable material for wear protective coatings [9]. The chemical inertness of NbN makes it a good material for corrosion protective coating. In [8], NbN has also been studied as a possible cathode material in vacuum microelectronic devices. Furthermore, the chemical inertness, high melting point, and low resistivity are desired properties for a diffusion barrier in microelectronic devices [10].

Hence, in this work *c*BN-based (dielectric material) samples with NbN (semiconductor) using 5 vol.% Al (conductor) as a sintering aid and a getter of oxygen impurity. Dopants with different thermoelectrically properties and morphology were added to initial composition. For instance, dielectric dopants (Al_2O_3 and Si_3N_4) with different morphology (whiskers and powders) were added to the initial composition (*c*BN–NbN–Al). Samples with semiconductors' dopant (SiCw) were also sintered and investigated in the frame of this work. The investigations of microstructure and phase composition were done by the same way as in paper [11]. It should be taken into account that in the studied composites there is no phase interaction between *c*BN and NbN [11].

2. EXPERIMENTAL

The stand designed for electrical conductivity measuring of superhard

CMs was used to determine the samples' resistance. This stand allows to measure electrical conductivity in a wide temperatures and voltages ranges. The electrical circuit of the stand allows to work both in the current stabilization mode and in the voltage stabilization mode. The electrical circuit mounted on the basis of Agilent 4339B and B7Э-42 electrometers. The measuring cell's assembly is carried out using high-quality dielectric materials that meet the electrical measurements' requirements in high-resistance electrical circuits. The measuring electrodes have the form of flat parallel surfaces, between which the sample is clamped (at the same time, the volumetric characteristics of the sample are measured). Electrical contacts were applied to the opposite chemically cleaned surfaces of polycrystalline plates through a mask (it was done for contact resistance's reducing). Contacts have a shape of a circle with a diameter of 7 mm. The use of an electrometer provides a range of measured resistances $R \sim 10^{-6}$–10^{13} Ω. All measurements (the dependences of electrical resistance from applied voltage and their temperature) were carried out in a vacuum chamber at a pressure of $p = 10^{-3}$ Pa. This allows excluding external influences. Measurements carried out in the temperature stabilization mode in the wide temperature range (300–700 K).

The method of measuring the current and temperature dependence based on the registration of the voltage drop on the sample depending on the current (which passes through the sample in the temperature stabilization mode).

The magnitude of the voltage drop across the sample was measured using an NV724 nanovoltmeter.

3. RESULTS AND DISCUSSION

3.1. Discussion of the additions' influence on the *c*BN–NbN composites' electrical resistance

The influence of additions' chemical nature on electrical resistance was studied for *c*BN–NbN, *c*BN–NbN–SiCw, and *c*BN–NbN–Si_3N_4w systems by the help of methodics described before. The order of the specific electrical resistance absolute value (Fig. 1) points on semiconducting nature of conductivity for all samples. For all investigated samples there was a decrease in the electrical resistance value with temperature. This fact also evidences a semiconductor nature of electrical conductivity. It is well-known fact that in semiconductor systems when the temperature increases, the number of charge carriers' increases. Accordingly, at a constant voltage, the current increases that means that the value of the specific electrical resistance decreases (Table 1).

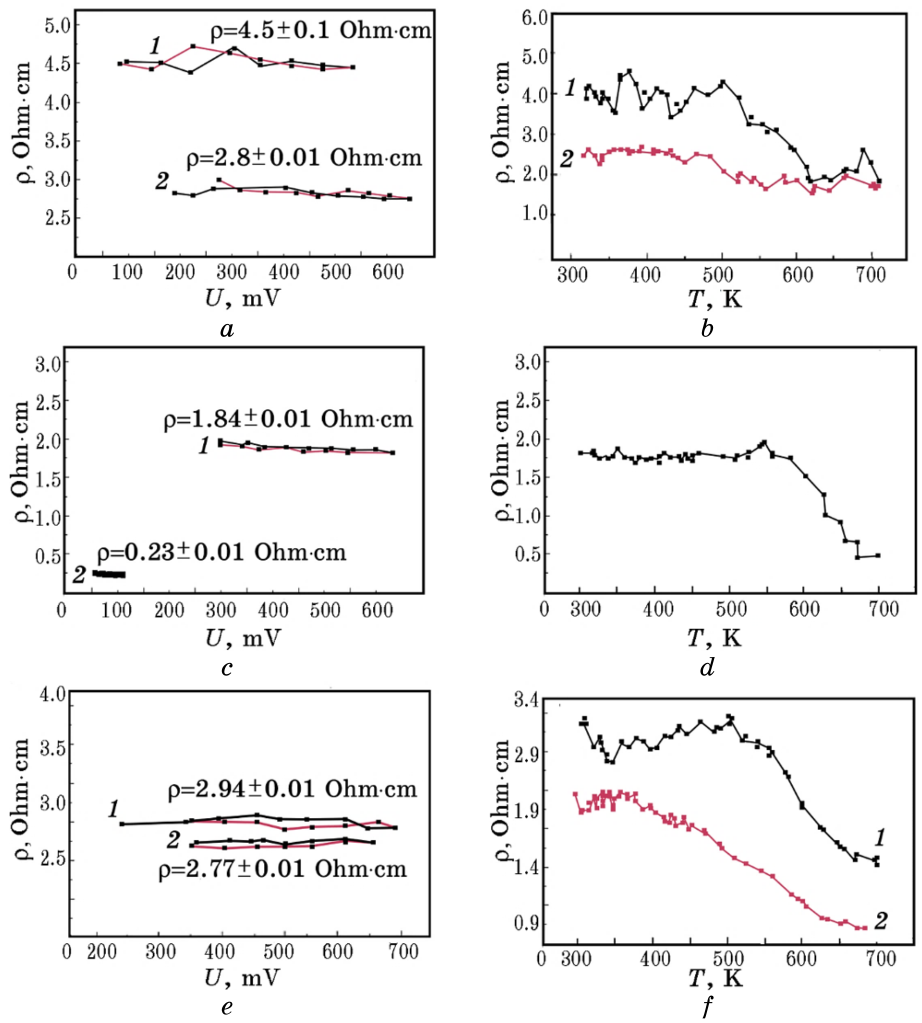


Fig. 1. The dependence of electrical resistance on applied voltage (*a*, *c*) and heating temperature (*a*, *c*, *e*) for samples: *c*BN–35 vol.% NbN (*a*, *b*); *c*BN–25 vol.% NbN–10 vol.% SiCw (*c*, *d*); *c*BN–25 vol.% NbN–10 vol.% Si_3N_4w (*e*, *f*) before (*1*) and after (*2*) heating up to 400°C.

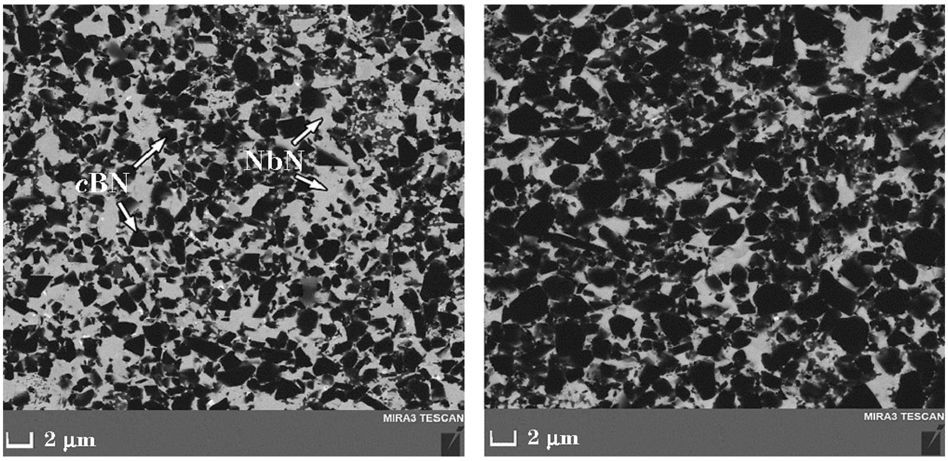
The complex nature of specific electrical resistance dependence from the temperature (Fig. 2) should be explained by the additives' influence (because their introduction leads to the impurity levels' creation in forbidden zone). After all, it is known that intrinsic conductivity and impurity conductivity can determine the electrical resistance of a doped semiconductor in different temperature ranges. For instance, temperature dependence of specific electrical resistance for aluminium

TABLE 1. Electrical resistance of *c*BN-based samples with different whiskers before and after heating.

Sample	*c*BN –35 vol.% NbN	*c*BN –25 vol.%. NbN –10 vol.%. SiCw	*c*BN –25 vol.%. NbN –10 vol.%. Si_3N_4w
Electric resistance before heating, Ohm·cm	4.5 ± 0.1	1.84 ± 0.01	2.94 ± 0.01
Electric resistance after heating up to 400°C, Ohm·cm	2.8 ± 0.01	0.23 ± 0.01	2.77 ± 0.01

nitride has two clearly defined regions with different inclination's angles to the abscissa axis. This fact explained by the change in the conductivity's type (from intrinsic to impurity type of conductivity) [12, 13].

One of the additives in the studied composites, namely wurtzite (hexagonal) modification of silicon nitride Si_3N_4w (it is also designated as β–Si_3N_4). β–Si_3N_4 is a good insulator (wide-band semiconductor with 5.18 eV bandgap). This addition couldn't change the overall electrical system resistance, because differing little in this physical quantity from the *c*BN matrix phase. On the other hand, the SiC addition (narrow-band semiconductor) has low electrical resistance. This addition can significantly affect the overall electrical resistance of the studied *c*BN-based samples.



a *b*

Fig. 2. The microstructure of non-reinforced (*a*) and whisker-reinforced (*b*) samples.

Niobium nitride is the main electrically conductive inclusion in the studied system. The addition of NbN, together with others, brings the composite with the *c*BN matrix phase into an integral electrically conductive state. In addition, in the obtained *c*BN-based composites, when refractory compounds are introduced into the structure of the microfibers, there is a sharp increase in the area of the interphase boundaries, which can serve as charge transfer channels, *i.e.*, additionally increase the flow of electric current through the sample.

Obtained composites' microphotographs show that the electrically conductive phases form a continuous grid, hence, also serve as a charge transfer channel (Fig. 2). It causes a decrease in the total electrical resistance to the units (Table 1).

It can be concluded that in the studied *c*BN–NbN, *c*BN–NbN–SiCw, and *c*BN–NbN–Si_3N_4w systems the electrically conductive additives' content was equal to (or greater) than 30 vol. %. It means that the percolation threshold has been exceeded in these samples. *i.e.*, they became conductive for electric current.

Since it is known that the percolation threshold for three-dimensional systems is approximately 17 vol. %, then the data we obtained for *c*BN-based composites don't contradict the general laws of electric current flow in three-dimensional systems dielectric matrix—conductive inclusions.

For instance, *c*BN-based composites with electrically conductive inclusions of titanium nitride (TiN) also had similar electrical resistance's behaviour [14]: the introduction of 30 vol. % TiN into the *c*BN matrix led to specific electrical resistance decreasing of material by 10 magnitude's orders (the electrical resistance of these composites was 12 Ω·cm).

3.1. Discussion of the additions' morphology influence on the *c*BN–NbN composites' electrical resistance

Samples with the Al_2O_3 additions also have a characteristic semiconducting nature of conductivity (this is evidenced by the order of magnitude of the electrical resistance) (Table 2).

The experimental results' analysis showed that the samples' specific resistance both before and after heating the samples is almost independent of temperature (Fig. 3, *a* and *c*). This fact indicates the homogeneity of the material structure of the studied samples, and may be caused by a tunnel mechanism of a current. With the addition Al_2O_3w, a more significant drop in electrical resistance is observed (Fig. 3, *b* and *d*) than with the addition of aluminium oxide. It is explained by a more significant increase in the area of interphase boundaries when adding whiskers than when adding powder, and therefore, improving the flow of electric current through the sample.

TABLE 2. Electrical resistance of *c*BN-based samples with Al_2O_3 additions with different morphology before and after heating.

Sample	*c*BN –35 vol.% NbN	*c*BN –25 vol.%. NbN –10 vol.%. Al_2O_3	*c*BN –25 vol.%. NbN –10 vol.%. Al_2O_3
Electric resistance before heating, Ohm·cm	4.5 ± 0.1	1.85 ± 0.007	1.35 ± 0.05
Electric resistance after heating up to 400°C, Ohm·cm	2.8 ± 0.01	0.72 ± 0.002	0.17 ± 0.006

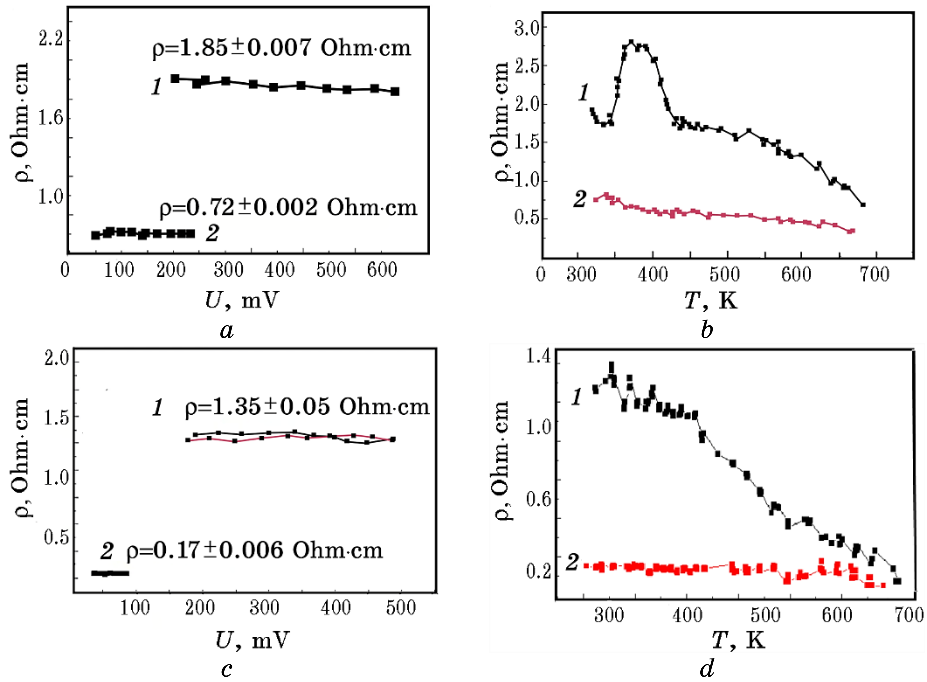


Fig. 3. Electrical resistance's dependence on applied voltage (*a*, *c*) and heating temperature (*b*, *d*) for the samples: *c*BN–25 vol.% NbN–10 vol.% Al_2O_3w (*a*, *b*); *c*BN–25 vol% NbN–10 vol.% Al_2O_3 (*c*, *d*) before (*1*) and after (*2*) heating up to 400°C.

4. CONCLUSIONS

It is established that all investigated samples of dielectric/conductor composites *c*BN–Al_2O_3–Si_3N_4/NbN–SiC both by the order of the absolute value of the specific electrical resistance and by the nature of the temperature dependence (decrease in the value of the electrical resistance with temperature) are semiconductors. The impurity morphology's influence on the electrical conductivity of sintered samples has been shown: the addition alumina's whiskers lead to a greater drop in electrical resistance than the addition of alumina powders. It's occurs due to a greater increase of the interface area between the grains (when the whiskers added), and thus an improved flow of electric current through the sample. Authors expects that obtained results should be also helpful for deepen understanding of electrical conductivity's nature of multiphase *c*BN-based composites. Moreover, the ability of the developed ceramic composites to conduct an electric current is important from the point of their application in different industries. For instance, for obtaining parts of a complex shape by the method of electric spark cutting. It's also point on the perceptiveness of their application in the nuclear industry (due to their good mechanical properties, oxidation resistivity [11] and electrical properties' level at the same time (described in this work).

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