

## BT-30 CERAMIC ELECTROPHYSICAL PROPERTIES

N. A. Drokin,<sup>1,2</sup> V. S. Kiiiko,<sup>3,5</sup> A. V. Pavlov,<sup>4</sup> and A. I. Malkin<sup>3</sup>

Translated from *Novye Ogneupory*, No. 6, pp. 56 – 63, June, 2020.

*Original article submitted May 18, 2020.*

A total complex resistance (impedance) method is used to study the electrophysical characteristics of (BeO + TiO<sub>2</sub>)-ceramics modified with TiO<sub>2</sub> micro- and nanoparticles in an amount of 30 wt.% (BT-30). Dispersion of the actual  $\epsilon'$  and imaginary  $\epsilon''$  components of the dielectric permittivity component and specific conductivity in the frequency range from 100 Hz to 100 MHz from room temperature to the boiling point of liquid nitrogen are determined. High values of  $\epsilon'$  and  $\epsilon''$  in the low-frequency range are typical for structurally inhomogeneous materials due to the accumulation of electric charges at the surface and within microcrystals. Two dielectric relaxation processes associated with electrical conductivity within the body and at the surface of ceramics are detected for the first time. An increase in conductivity with an increase in the microwave field frequency above 1 MHz is explained by the appearance of a current relaxation component. The activation energy of the static resistance of ceramic specimens is determined as a function of the reciprocal temperature that depends little on the weight content of TiO<sub>2</sub> nanoparticles and varies in the range of 0.024 – 0.10 eV. This also confirms the existence of two independent conduction processes, weakly dependent on the nanoparticle content in the ceramic composition. With placement of ceramic in a high-frequency electric field, spatial charges are formed, the field of which contributes to creation of additional polarization and dielectric losses.

**Keywords:** (BeO + TiO<sub>2</sub>)-ceramic, electrophysical properties, electrical resistance activation energy.

### INTRODUCTION

Currently ceramic materials that are often used to replace metals and alloys exhibit not only heat resistance and high strength, but also special electrophysical properties [1, 2] that facilitate their extensive use in electronic engineering. Such a ceramic concerns beryllium oxide whose active dielectric permittivity  $\epsilon'$  is 6.9 – 7.5,  $\text{tg}\delta \approx 3 \times 10^{-4}$  at frequency  $f = 1$  MHz. With addition to the composition of micro- and nano-particles of TiO<sub>2</sub> the  $\epsilon'$  and electrical conductivity  $\sigma$  with suitable heat treatment in a reducing atmosphere may change significantly [2 – 8]. At the same time there is also a change in dielectric losses that opens up extensive possibilities for its use in wavelength radio- and

UHF-ranges [2 – 8]. There is special interest in BeO ceramic with addition to its composition of an optimum amount of BT-30 TiO<sub>2</sub> micro-powder (30 wt.%). Currently it is used in high power electronic engineering instruments as an absorbent material for dissipating UNF-radiation [2 – 8]. Physico-chemical interpretation of the existence of a conducting space within the volume of (BeO – TiO<sub>2</sub>)-ceramic and at an electrode – conductor boundary, in which charge carriers are moved and localized, and also the nature of conductivity, are so far unclear [9]. Detailed representation about processes of electrical polarization and specific relaxation of spatial charges, which are capable of accumulating at boundaries of individual micro-crystals, does not exist.

Work has been devoted to experimental study of the behavior of electrophysical properties of (BeO + TiO<sub>2</sub>)-ceramic modified with micro- and nano-particles of TiO<sub>2</sub> with a change in temperature and frequency. Studies were conducted in the range from +25 to –194°C in the electric field frequency range 100 Hz – 100 MHz and measuring total complex resistance ( $Z - Z' - iZ''$  (impedance)) of a measurement cell prepared in the form of a flat condenser filled with (BeO + TiO<sub>2</sub>)-ceramic. Measurement of impedance fre-

<sup>1</sup> FGBOU VO Academician M. F. Reshetnev Siberian Aerospace University, Krasnoyarsk, Russia.

<sup>2</sup> FGBUN Federal Research Center, Krasnoyarsk Scientific Center of the Siberian Section, Russian Academy of Sciences, Krasnoyarsk, Russia.

<sup>3</sup> FGAOU VO Ural Federal University, Ekaterinburg, Russia.

<sup>4</sup> FGAOU VO Siberian Federal University, Krasnoyarsk, Russia.

<sup>5</sup> v.kijko@mail.ru

quency relationships for specimens was conducted in an Agilent E5061B circuit analyzer.

### SPECIMEN PREPARATION

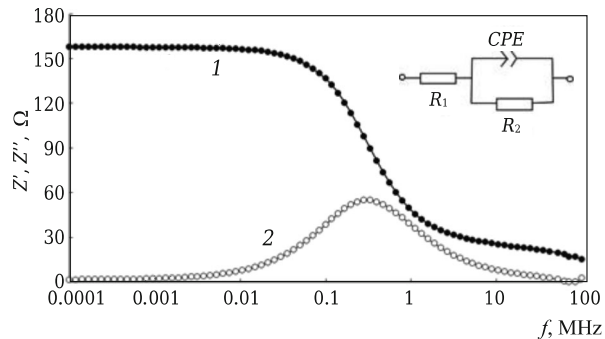
Specimens were prepared by sintering ceramic at 1530°C [2–6, 9] with subsequent reduction in a hydrogen atmosphere. It has been established by experiment that the optimum specimen heat treatment regime in hydrogen with addition of TiO<sub>2</sub> micro- and nano-powders is 800°C and a process duration of 1.0–1.5 h. After this treatment specimens acquire a dark gray color. Hydrogen consumption was 1200 ± 50 liters/h at a pressure of 30–50 mm of a water column. Specimens of (BeO + TiO<sub>2</sub>)-ceramic were prepared proceeding from the ratio: 70 wt.% BeO and 30 wt.% TiO<sub>2</sub> powders consisting of micro- and nano-powders. In this case addition of nano-powder was varied within the limits of 0.1–2.0 wt.%, and the res consisted of TiO<sub>2</sub> micro-powders (see Table 1) consisting of agglomerated particles with sizes from 5 to 45 nm.

It has been established that ceramic series 1–5 exhibited direct current electrical conductivity at room temperature. An exception was specimens of ceramic series 6 having dielectric properties. This fact is difficult to understand. It is planned to study this question in more detail subsequently.

### IMPEDANCE PROPERTIES OF CERAMIC WITH ADDED TiO<sub>2</sub> MICRO-POWDER

First we consider impedance and electrophysical properties of specimens of beryllium ceramic with addition of TiO<sub>2</sub> micro-powder alone in an amount of 30 wt.% (specimen series 1). Frequency dependences are shown in Fig. 1 for the actual and imaginary components of impedance at room temperature in the frequency range from 100 Hz to 100 MHz.

This form of impedance spectrum normally arises in dielectrics that may be first compared with a simple electric circuit containing capacitance  $C$  and in parallel with it a resistor  $R^2$  (see Fig. 1, insert). The resistor models the resistance of a specimens of series 1 and electrical losses. Numerical results of this modeling have established. This specimen



**Fig. 1.** Frequency dependences for the active (1) and imaginary (2) component of impedance  $Z'(f)$  and  $Z''(f)$  model of an equivalent electric circuit (insert) of series 1 specimens.

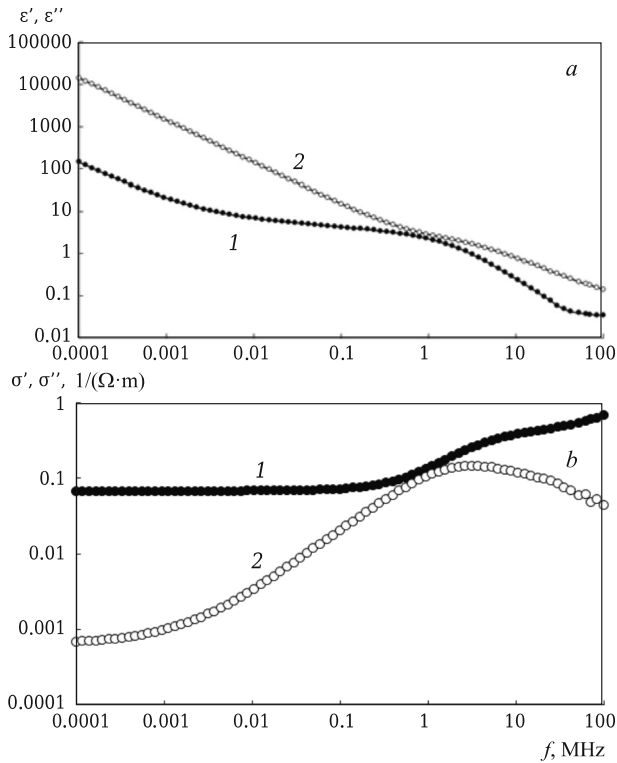
in a measurement cell exhibits resistance  $R_2$  160 Ω (taking account of contact resistance  $R_1$ ). The capacitance of a cell with specimen  $C = 3 \times 10^{-9}$  F. For these values the impedance relaxation time  $\tau = 4.8 \times 10^{-7}$  and relaxation frequency  $f = 3.26 \times 10^5$  Hz corresponds to the maximum in the frequency dependence  $Z''(f)$ .

A requirement arose for the specimens in question of introducing additional resistance  $R_1$  (15 Ω) that was included in the electrical circuit successively with the RC-circuit (see Fig. 1, insert). This resistance arises in the region between the metal electrode and a specimen surface. The values of resistance  $R_1$  depends on surface structure and cleanliness, presence of absorbed moisture or other contaminants, and on the amount of pressing or rolling on a contact of indium foil. It should be noted that transient resistance  $R_1$  in low-frequency regions only increases specimen static resistance a little, although in the high-frequency region, when reactive resistance of a specimen decreases considerably, the main drop in voltage occurs in resistance  $R_1$ . This leads to a reduction in phase angle, which may even change sign and lead to distortion of dielectric properties.

A simple RC equivalent circuit normally only serves for preliminary analysis of specimens. For more precise approximation of an experiment a requirement often arises for using more complex equivalent circuits. For this specimen normal capacitance varies in a special frequency dependence (CPE1)

**TABLE 1.** Composition and Properties of BeO-Ceramic with Added TiO<sub>2</sub> Powder

Specimen series	Ceramic composition	Density, g/cm <sup>3</sup>	Presence of electrical conductivity
1	BeO + 30 wt.% TiO <sub>2</sub> (μm)	3.20	Conductor
2	BeO + 29.9 wt.% TiO <sub>2</sub> (μm) + 0.1 wt.% TiO <sub>2</sub> (nm)	3.18	Conductor
3	BeO + 29.5 wt.% TiO <sub>2</sub> (μm) + 0.5 wt.% TiO <sub>2</sub> (nm)	3.19	Conductor
4	BeO + 29.0 wt.% TiO <sub>2</sub> (μm) + 1.0 wt.% TiO <sub>2</sub> (nm)	3.21	Conductor
5	BeO + 28.5 wt.% TiO <sub>2</sub> (μm) + 1.5 wt.% TiO <sub>2</sub> (nm)	3.22	Conductor
6	BeO + 28.0 wt.% TiO <sub>2</sub> (μm) + 2.0 wt.% TiO <sub>2</sub> (nm)	3.20	Dielectric

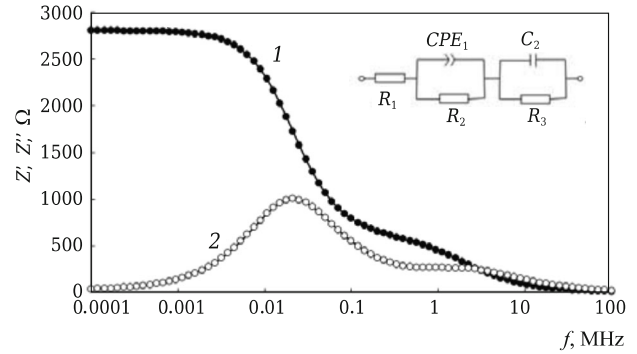


**Fig. 2.** Specimen series 1 dielectric dependences: a)  $\varepsilon'(f)$  (1) and  $\varepsilon''(f)$  (2); b)  $\sigma'(f)$  (1) and  $\sigma''(f)$  (2).

element with initial capacitance  $P_1 = 3.52 \times 10^{-8}$  F and its relative change with respect to frequency  $n_1 \approx 0.84$  (insert in Fig. 1). Since this capacitance exhibits frequency dependence, this means presence of  $\varepsilon$  dispersion. Frequency dependences of  $\varepsilon$  and specific  $\sigma$  for ceramic BeO + 30 wt.% TiO<sub>2</sub> ( $\mu\text{m}$ ) are shown in Fig. 2.

The actual and imaginary components of  $\varepsilon$  at low frequency increase anomalously, which is explained by accumulation of charges around electrodes or at micro-crystal boundaries. With an increase in frequency there is a nonuniform reduction of  $\varepsilon$  to values  $\varepsilon' = 34 - 35$  at frequency  $f = 100$  MHz. The imaginary component  $\varepsilon''$  also decreases with an increase in frequency, but remains quite high with respect to value ( $\varepsilon'' \geq 100$ ). Loss tangent  $\text{tg}\delta$  for this specimen at frequency 100 MHz does not fall below 2. An increase in  $\varepsilon'$  in the high-frequency region is normally connected either with presence of a jump in conductivity or with a delay of movement of the carrier charge within conducting structures. In this case additional active conductivity of a relaxation type arises.

A test specimen of series 1 with TiO<sub>2</sub> micro-particles exhibits quite high  $\varepsilon$  even at high frequencies and conductivity that probably arises within intercrystalline layers. This conductivity may be caused by volumetric valent electrons between existing titanium oxide phases. In this ceramic with TiO<sub>2</sub> micro-particles there may also be individual conducting



**Fig. 3.** Frequency dependences for the active  $Z'(f)$  (1) and imaginary  $Z''(f)$  (2) components of impedance and model of an equivalent electric circuit (insert) of series 1 specimens at  $-100^\circ\text{C}$ .

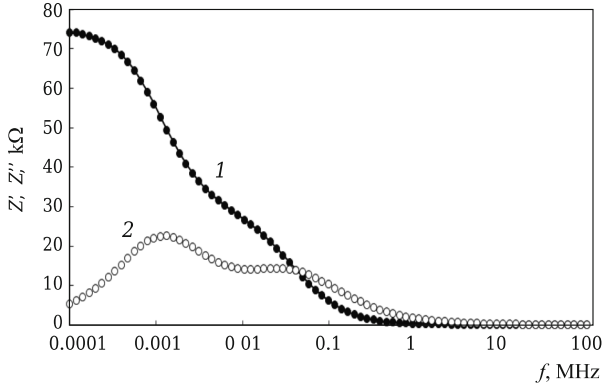
microscopic regions, alternating with dielectric sections. In this case the polarization that arises at boundaries of these regions may also be a source of an anomalous increase in electrical conductivity component, especially at low frequencies. This indicates that the jumpwise mechanism of conductivity, connected with exchange of electrons between localized states of ions  $\text{Ti}^{2+} \rightleftharpoons \text{Ti}^{3+} \rightleftharpoons \text{Ti}^{4+}$  is accomplished both within the volume of crystals and also within intercrystalline layers. The comparatively high values of dielectric permittivity component observed in the low-frequency region are caused by ceramic migration polarization connected with accumulation of charged particles at interfaces between crystallites and at existing defects of the polycrystalline structure [9].

## TEMPERATURE DEPENDENCE OF CERAMIC SERIES 1 SPECIMEN IMPEDANCE

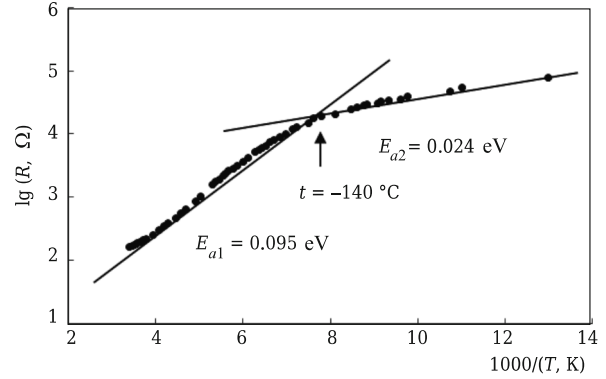
Electrophysical properties of the test ceramic depend strongly on temperature, on frequency, and during cooling there is a rapid increase ceramic electrical resistance [2, 3]. In order to determine activation processes of conductivity and dispersion of  $\varepsilon$  for specimens of ceramic BeO + 30 wt.% TiO<sub>2</sub> ( $\mu\text{m}$ ) measurements were made for the first time of impedance spectra in the range from  $+25$  to  $-194^\circ\text{C}$ . Frequency dependences of actual and imaginary components of impedance for the specimen of series 1 in question, obtained during cooling to  $-100^\circ\text{C}$  are shown in Fig. 3.

At this temperature  $Z'$  increased to 2.72 k $\Omega$ , but  $R_1$  was reduced 1  $\Omega$ , and  $f_1$  was reduced to a value  $2.5 \times 10^4$  Hz. For  $Z''$  there is clear appearance of a second region of dielectric relaxation at frequency  $f_1 = 3.7 \times 10^4$  Hz (see Fig. 3).

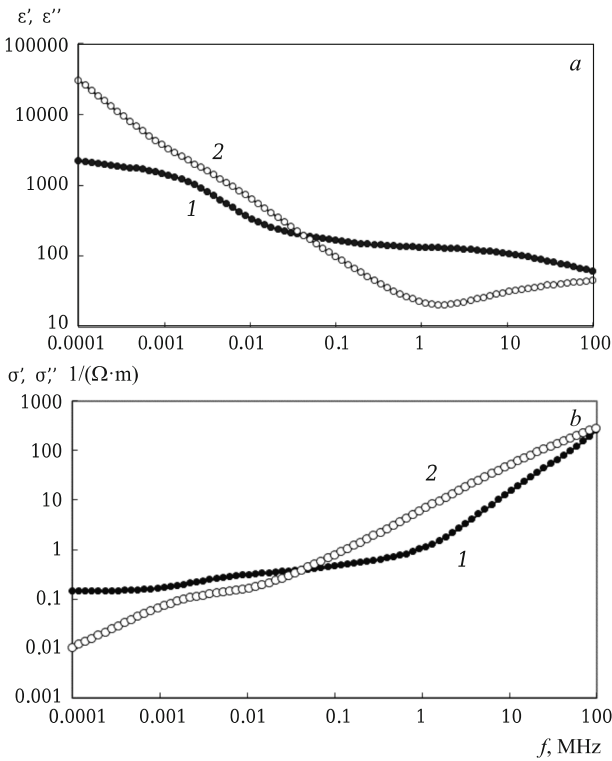
Schematic technical modeling of this behavior of impedance component in the case in question required complication of the equivalent electrical circuit. The most probable model of impedance at this temperature is shown in Fig. 3 (see insert). In order to model revelation of the two relaxation processes in an equivalent circuit, containing elements CPE1 and resistance  $R_2$ , a supplementary link was added



**Fig. 4.** Frequency dependences  $Z'(f)$  (1) and  $Z''(f)$  (2) components for series 1 specimen at  $-194^\circ\text{C}$ .



**Fig. 6.** Dependence of the logarithm of static resistance and activation energy for specimens of ceramic series 1 on inverse temperature.



**Fig. 5.** Specimen series 1 frequency dependences at  $-194^\circ\text{C}$ : a)  $\varepsilon'(f)$  (1) and  $\varepsilon''(f)$  (2); b)  $\sigma'(f)$  (1) and  $\sigma''(f)$  (2).

consisting of capacitance  $C_1 = 3.28 \times 10^{-10}$  F and resistance  $R_3$  included in parallel.

Contact transition resistance  $R_1 = 8 \Omega$  has a somewhat greater value compared with the value at room temperature, and resistances  $R_2$  and  $R_3$  in total exhibit overall ceramic resistance ( $\approx 2.7 \text{ k}\Omega$ ). Element CPE1 with exponent  $n = 0.79$  mainly corresponds to the frequency-dependent capacitance, and additional capacitance of the second link  $C_1 = 3.28 \times 10^{-10}$  F and resistor  $R_3$  determine the time of high-frequency relaxation  $\tau = C_1 \cdot R_3 = 6.87 \times 10^{-7}$  sec, which

corresponds to relaxation frequency  $f_1 = 3.7 \times 10^6$  Hz. With a further reduction in temperature to  $-194^\circ\text{C}$  both relaxation maxima shift uniformly into the low-frequency region (Fig. 4).

At this temperature  $Z'$  increased to 76 kΩ, but  $R_1$  remained unchanged ( $8 \Omega$ ). Both relaxation maxima shifted into the low-frequency region  $f_1 = 1.4 \times 10^3$  and  $f_2 = 5.5 \times 10^4$  Hz. Frequency dependences are shown in Fig. 5 for actual and imaginary components  $\varepsilon$  and  $\sigma$  obtained during specimen cooling to  $-194^\circ\text{C}$ .

The real component  $\varepsilon'$  at low frequencies, and also at room temperature, reaches enormous values, but at high frequencies  $\varepsilon'$  decreases to 60 (see Fig. 5a). In this case the real and imaginary components of conductivity do not increase uniformly with an increase in frequency (see Fig. 5b). At low frequency  $f = 100$  Hz with a reduction in temperature from room to  $-194^\circ\text{C}$  the value of real conductivity components  $\sigma'$  decreases compared with the value at room temperature by approximately a factor of three. A temperature dependence is shown in Fig. 6 measured at room temperature for static resistance  $R$  of this ceramic on logarithmic coordinates in relation to inverse temperature and the change in activation energy  $E_0$  has been determined.

At temperatures in the range  $+25$  to  $-196^\circ\text{C}$  activation energy changes from 0.095 to 0.024 eV. This points to existence in this ceramic of two mechanisms of transfer of charge carriers, one of which may be connected with volumetric valent electrons between clusters with titanium oxide phases, and the other is an activation process of charge transfer may occur for example over a specimen surface. In spite of the fact that with a reduction in temperature impedance frequency dependences vary considerably, they are approximated by a two-link electric circuit. The nonuniform polycrystalline structure in ceramic, exhibiting as a rule different defects, has a marked effect not only on frequency dependence of complex dielectric permittivity, but also the frequency dependence of complex specific electrical conductivity.

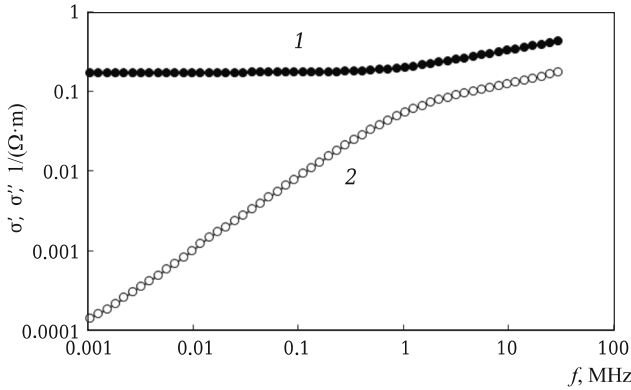


Fig. 7. Frequency dependence  $\sigma'$  (1) and  $\sigma''$  (2) for series 2 specimen.

### EFFECT OF ADDING TiO<sub>2</sub> NANO-PARTICLES ON CERAMIC BT30 IMPEDANCE SPECTRA

We consider the electrophysical properties of beryllium ceramic to which TiO<sub>2</sub> micro- and nano-particles have been added, comprising in total 30 wt.% (specimens of series 2 – 6). Preliminary measurements of ceramic specimen impedance using not only indium, but also other metal contacts, showed that the electrical conductivity of specimens varied during changes of both direct and alternating currents. In order to remove moisture adsorbed at a metal surface specimens were held at elevated temperature (50 – 60°C). Specimen activation in an electric field and surface cleaning with micro-powder was also conducted. It has been established that specimens surface resistance may vary in relation to many factors: type of metal contact and application method to a surface, preparation technology, nonuniformity of reducing phase TiO<sub>2</sub> addition and distribution of BeO and TiO<sub>2</sub> micro-crystals having different sizes. The resistance of specimens of series 2 – 5 varied with exposure in air at room temperature, which may be connected with adsorption at their surface of polar molecules and radicals caused by presence for BeO and TiO<sub>2</sub> of piezo- and pyro-electric properties. An exception is specimens of series 6 whose resistance conversely increased. After different manipulation the resistance of specimens series 2 – 5 was found within the limits of 50 – 100 Ω. Results of measuring frequency dependency of resistance in a specimen of series 2 is shown in Fig. 7.

The active component of conductivity  $\sigma'(f)$  is hardly dispersed and only increases a little at frequency  $f > 1$  MHz. Approximately the same conductivity frequency dependences have been established for specimens of series 4 and 5. Their dielectric permittivity was distorted by comparatively high conductivity. Specimens of series 3 remained relatively low-ohmic (about 800 Ω).

Results of impedance measurements for specimens of series 5 containing 2.0 wt.% TiO<sub>2</sub> nano-powder are shown in

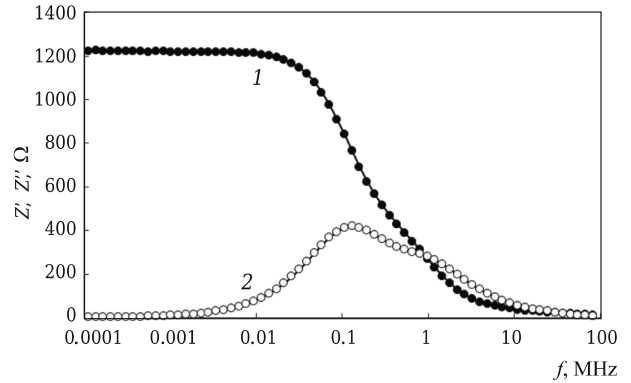


Fig. 8. Frequency dependence  $Z'(f)$  (1) and  $Z''(f)$  (2) for specimen series 6 at +25°C.

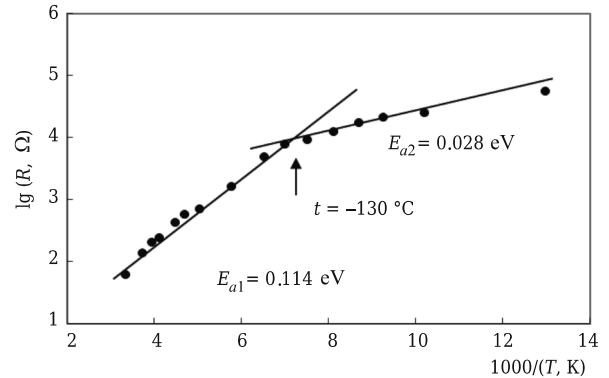


Fig. 9. Dependence of logarithm of static resistance and activation energy for series 6 specimen on inverse temperature.

Fig. 8. After cleaning, drying, and other manipulations at the surface the resistance did not fall below 1.2 kΩ.

Even at room temperature  $Z''(f)$  for specimens of series 6 has two clearly defined maxima at frequencies  $f_1 = 1.5 \times 10^5$  and  $f_2 = 2 \times 10^6$  Hz, which also points to existence of two conductivity processes for this specimen.

A temperature dependence is shown in Fig. 9 at a frequency of 100 Hz for static resistance  $R$  of specimens of series 6 on logarithmic coordinates in relation to inverse temperature, and the change in activation energy has also been determined.

Values of activation energy obtained are close to those for specimens of series 1, in which TiO<sub>2</sub> in amount of 30 wt.% consisted entirely of micro-powder. A change in activation energy also occurred at about  $-130^\circ\text{C}$ . Nano-particles of TiO<sub>2</sub> cannot participate directly in conductivity, but they stimulate or conversely suppress electron exchange between titanium ions differing in valency. Approximately the same value of electrical resistance activation energy is also exhibited by more conducting specimens of series 3 – 5.

**CONNECTION OF ELECTRODYNAMIC PROPERTIES OF (BeO + TiO<sub>2</sub>)-CERAMIC WITH PHYSICO-CHEMICAL PROPERTIES OF BeO AND TiO<sub>2</sub> OXIDES**

(BeO + TiO<sub>2</sub>)-ceramic is currently used in electronic engineering as a material for absorbing scattered UHF-electromagnetic radiation. In order to absorb radiation and occurrence of electrical-conducting phases within ceramic there is reduction firing [2–9]. In this case the reduction process is accomplished under non-equilibrium conditions in a vacuum, and in a reducing atmosphere including CO and H<sub>2</sub> gases. Titanium ions during heat treatment of (BeO + TiO<sub>2</sub>)-ceramic may probably be in bi-, tri-, and quadri-valent conditions. This facilitates occurrence of electron exchange between localized states of Ti<sup>2+</sup> ⇌ Ti<sup>3+</sup> ⇌ Ti<sup>4+</sup> ions. As is well known, in the Ti-O system the main condensed phases are five oxides, the most refractory of which is TiO<sub>2</sub> with a melting temperature of 1912°C. For the rest of the oxides it comprises 1837 (Ti<sub>2</sub>O<sub>3</sub>), 1777 (Ti<sub>3</sub>O<sub>3</sub>), 1757 (TiO), and 1687°C (Ti<sub>4</sub>O<sub>7</sub>). During sintering at 1530°C and treatment in a reducing atmosphere within (BeO + TiO<sub>2</sub>)-ceramic there may be formation of solid solutions (TiO<sub>2</sub> + TiO + Ti<sub>3</sub>O<sub>5</sub> + Ti<sub>2</sub>O<sub>3</sub>, etc.) represented by condensed, liquid, and gaseous phases on TiO<sub>2</sub>, and probably BeO. The weight fraction of the most thermally stable TiO<sub>2</sub> in ceramic over the whole temperature range remains predominant.

In (BeO + TiO<sub>2</sub>)-ceramic by means of an electron microscope existence of TiO<sub>2</sub> solid phase and liquid solution [2–6, 9] flowing at a certain temperature over the BeO of micro-crystals has been detected that is probably represented by a mixture of oxides Ti<sub>4</sub>O<sub>7</sub> + TiO + Ti<sub>3</sub>O<sub>5</sub> + Ti<sub>2</sub>O<sub>3</sub> as solution components. Therefore, a condensed medium formed during heating TiO<sub>2</sub> in a reducing atmosphere is not the only original TiO<sub>2</sub> oxide in solid or liquid conditions. Currently details have not been established for chemical transformations proceeding under conditions of high-temperature synthesis for (BeO + TiO<sub>2</sub>)-ceramic, and also compositions of condensed media and gas phase during heating of BeO + TiO<sub>2</sub> in a reducing atmosphere.

It has been established by x-ray phase method that in specimens alongside reflections from the BeO crystal structure diffraction peaks for TiO<sub>2</sub> were recorded, corresponding to crystalline modifications of rutile and anatase, and also a background in the region of low angles pointing to some amount of amorphous phase. Presence of a high-temperature modification of TiO<sub>2</sub> after heat treatment of ceramic specimens above 900°C is probably connected with formation of solid solutions based on TiO<sub>2</sub> having a structure similar to an anatase modification. In addition, weak reflections have been recorded corresponding probably to titanium carbide and other phases that it has not so far been possible to identify.

In an optical microscope within the (BeO + TiO<sub>2</sub>)-ceramic composition some phases have been recorded relating to crystalline modifications of beryllium oxide, titanium di-

oxide and carbide, glass, and also an unknown phase in a comparatively small amount [2, 3].

Using an electronic paramagnetic resonance (EPR) method within the composition of (BeO + TiO<sub>2</sub>)-ceramic after treatment in a reducing atmosphere at –196°C without x-ray radiation an electronic signal has been recorded corresponding to the Ti<sup>3+</sup> ion with the following Hamiltonian spine parameters:  $g = 1,940-0,05$  and  $dH = (115 \pm 0.5)$  G [2, 3, 10]. Ions of Ti<sup>2+</sup> and Ti<sup>4+</sup> are not recorded by the EPR method. On holding ceramic specimens in the region from –196 to ~ –140°C the EPR signal disappeared. Broad and intense EPR signals from Ti<sup>3+</sup> ions at –196°C for specimens of BeO + 30 wt.% TiO<sub>2</sub> (μm) are probably connected with formation at the BeO surface and TiO<sub>2</sub> grains of Ti<sup>3+</sup>-O<sub>2</sub>-Ti<sup>3+</sup> clusters for which there is strong exchange interaction Ti<sup>3+</sup> ions. Also possible is formation of clusters of the Ti<sup>3+</sup>-O<sub>2</sub>-Ti<sup>4+</sup> type, where volumetric interaction is somewhat lower. Disappearance of EPR signals from Ti<sup>3+</sup> ions at approximately –140°C coincided with a change in electrical resistance activation energy during heating specimens of ceramic in the range from –196°C to +25°C (see Figs. 6, 9). A break in dependences for electrical resistance activation energy on temperature approximately at –140°C is probably connected with disordering of the (BeO + TiO<sub>2</sub>)-ceramic structure accompanied by presence of a concealed phase transformation [2, 10–12]. Additional calcining in air (at 1100°C) led to a reduction in EPR signal intensity and to broadening ( $\Delta N$  to 170 G). The process of TiO<sub>2</sub> reduction (when valency varies in the series Ti<sup>4+</sup> → Ti<sup>3+</sup> → Ti<sup>2+</sup>) is accompanied by an increase in electrical conductivity and coloring of (BeO + TiO<sub>2</sub>)-ceramic to a darker shade [2, 3].

The degree of TiO<sub>2</sub> reduction in BeO-ceramic is connected with the dielectric loss value. Deviation of TiO<sub>2</sub> from stoichiometric composition leads to a sharp change in electrophysical properties (see Fig. 1–5, 7–9). In the range from –196°C to +25°C the temperature dependence of electrical conductivity for specimens of BeO + 30 wt.% TiO<sub>2</sub> (μm) was studied. This dependence is typical for semiconducting (with *n*-type conductivity) reduced TiO<sub>2</sub>. At close to room temperature electrical resistance of BeO + 30 wt.% TiO<sub>2</sub> (μm) ceramic decreases significantly (by about a factor of 1000) compared with the electrical resistance at –196°C [2, 3].

The method of x-ray photoelectric spectroscopy (XPES) in BeO + 30 wt.% TiO<sub>2</sub> (μm) ceramic with uncontrolled carbon impurity after heat treatment in a reducing atmosphere detected microscopic areas the differed strongly with respect to surface recharging value [11]. Analysis of photoelectron spectra of BeO + 30 wt.% TiO<sub>2</sub> (μm) ceramic showed that in spectra there are two component electron peaks Be1s, C1s, and Ti2p shifted on the energy scale with respect to each other by approximately 3.8 eV. These components relate to the same chemical forms of Be, C, and Ti, but they are located at different parts of the surface of BeO and TiO<sub>2</sub> crystals with an individual charge. One form of Be, C, and Ti

concerns the surface of micro-crystals with good conductivity, and other areas exhibit good dielectric properties. Therefore, (BeO + TiO<sub>2</sub>)-ceramic exhibits considerable disordering of the structure. It has been established that in areas of ceramic with increased conductivity the Ti content is considerably higher than for Be. According to XPES data approximately half the Ti atoms in the form of oxide enter into the composition of a conducting phase that also includes about 10–20 at.% Be in the form of BeO. Typical for BeO + 30 wt.% TiO<sub>2</sub> (μm) ceramic is formation of conducting regions at the surface of BeO and TiO<sub>2</sub> micro-crystals exhibiting dielectric properties at which there is probably a layer of reduced TiO<sub>2</sub> forming an electrical conducting surface. Presence of these phases leads to a change in the nature of BeO + 30 wt.% TiO<sub>2</sub> (μm) conductivity [2, 3, 9, 11]. An external electric field with movement of electrical charges within ceramic may lead to their accumulation at structural defects, boundaries, inclusions, inhomogeneities, dislocations, impurities, layers of reduced oxides, ion vacancies, and clusters at the surface BeO and TiO<sub>2</sub> micro-crystals. This is probably accompanied by occurrence volumetric-charge polarization, typical for layered dielectrics or those containing different dielectric inclusions. In (BeO + TiO<sub>2</sub>)-ceramic migration polarization may also arise, which is observed in nonuniform dielectrics having conducting inclusions with different electrical conductivity [1]. An indication of this is the existence of an anomalously high increase in real and imaginary components of dielectric permittivity observed in the low-frequency region (see Figs. 2, 5). With an increase in frequency above 1 MHz the dielectric permittivity values for specimens of (BeO + TiO<sub>2</sub>)-ceramic with addition of TiO<sub>2</sub> powder, having both micro- and nano-sizes, is reduced. In this case dielectric permittivity of ceramic is mainly due to polarization of its crystalline structure. In this case the value of specific conductivity in this frequency range is conversely significantly reduced (see Figs. 2, 5, 7).

Oxides of Be and Ti that are classified as ferro-pyroelectric exhibit spontaneous polarization and are characterized by presence within them of a domain structure [2, 3, 10, 12]. In the case of a ceramic nonuniform structure there may be occurrence of charge accumulation and redistribution of an electric field at BeO and TiO<sub>2</sub> grain interfaces. Therefore, (BeO + TiO<sub>2</sub>)-ceramic is a nonuniform dielectric containing polar and charged groups or semiconducting layers within their structure. On placing this ceramic in a high-frequency electric field free charges and clusters are displaced and concentrated in boundary layers of BeO and TiO<sub>2</sub> micro-crystals, forming spatial charges, whose field facilitates formation of different forms of polarization phenomena.

## CONCLUSION

Specimens of BT-30 ceramic have been prepared with addition of micro- and nano-particles of TiO<sub>2</sub> (30 wt.% in total). The content of nano-powder in (BeO + TiO<sub>2</sub>)-ceramic was varied from 0.1 to 2.0 wt.%. Dispersion sensitivity and the imaginary component of dielectric permittivity and specific conductivity in the frequency range from 100 Hz to 100 MHz, and temperature from room to the liquid nitrogen temperature have been determined. The cluster structure of (BeO + TiO<sub>2</sub>)-ceramic is reflected in values of frequency characteristics  $\epsilon$  and  $\sigma$ . High value of  $\epsilon'$  and  $\epsilon''$  in the low-frequency region are typical for structurally inhomogeneous materials due to accumulation of electrical charges at the surface and within micro-crystals. This feature is connected with polarization of conducting micro- and nano-clusters present within ceramic. An increase in conductivity with an increase in UHF-field frequency above 1 MHz is explained by development of a current relaxation component. Ceramic impedance spectra have been modelled by a corresponding equivalent circuit, as a basis for which probable electrical polarization and conductivity mechanisms are discussed. For the first time two processes of dielectric relaxation have been detected, connected with electrical conductivity within the volume of ceramic and over a surface. Static electrical resistance activation energy  $E_a$  has been determined for ceramic specimens, which also depends little on the weight content of TiO<sub>2</sub> nano-particles and varies within limits depending on temperature in the range from 0.24 to 0.10 eV. This is also confirmed by the existence of two independent conductivity processes, depending weakly on nano-particle content within the ceramic composition. It has been established that during preparation of specimens for measurement a marked role is played by surface condition. Exposure of the surface of specimens of series 2–5 in air at room temperature showed that their electrical conductivity increased. This may be connected with adsorption at the ceramic surface of polar molecules and radicals caused by presence for BeO and TiO<sub>2</sub> piezo- and pyro-electric properties.

## REFERENCES

1. B. A. Belyaev, N. A. Drokin, and V. A. Poluboyarinov, "Study of electrophysical properties of cation-substitution ceramic of barium hexa-aluminate by impedance spectroscopy," *FTT*, **60**(2), 266–275 (2018).
2. V. S. Kiiko, Yu. N. Makurin, and A. L. Ivanovskii, *Ceramics Based on Beryllium Oxide: Preparation, Physicochemical Properties, and Application* [in Russian], UrO RAN, Ekaterinburg (2006).
3. V. S. Kiiko, S. N. Shabunin, and Yu. N. Makurin, "Preparation, physicochemical properties and UHF-radiation transmission by ceramic based BeO," *Ogneuproy tekhn. Keram.*, No. 10, 8–17 (2004).
4. V. S. Kiiko, M. A. Gorbunova, Yu. N. Makurin, et al., "Microstructure and electric conductivity of composite (BeO + TiO<sub>2</sub>) ceramics," *Refract. Ind. Ceram.*, **48**(6), 429–434 (2007).

5. V. S. Kiiko and A. V. Pavlov, "Composite (BeO + TiO<sub>2</sub>)-ceramic for electronic engineering and other fields of technology," *Refract. Ind. Ceram.*, **57**(6), 423 – 426 (2018).
6. V. S. Kiiko, A. V. Pavlov, and V. A. Bykov, "Production and thermophysical properties of BeO-ceramics with the addition of nanocrystalline titanium dioxide," *Refract. Ind. Ceram.*, **59**(6), 616 – 622 (2019).
7. V. Ya. Vaispapir and V. S. Kiiko, "Beryllium ceramic for contemporary fields of engineering," *Vestn. Vozd.-Kosm. Oborony*, No. 1(17), 59 – 69 (2018).
8. V. S. Kiiko and V. Ya. Vaispapir, "Thermal Conductivity and Prospects for Application of BeO Ceramic in Electronics," *Glass Ceram.*, **71**(11 – 12), 387 – 391 (2001).
9. A. A. Lipeshev, A. V. Pavlov, N. A. Drokin, et al., "Features of the preparation and study of electrophysical characteristics (BeO + TiO<sub>2</sub>)-ceramics by impedance spectroscopy," *Refract. Ind. Ceram.*, **60**(3), 309 – 317 (2020).
10. V. S. Kiiko, "Anomalous properties of BeO and ceramics based upon it," *Neorgan. Materialy*, **37**(11), 13 – 1401 (2001).
11. V. S. Kiiko, M. V. Kuznetsov, and A. L. Ivanovskii, "x-ray photon-electron spectroscopy of complex oxide ceramic BeO–TiO<sub>2</sub>–C," *Steklo Keramika*, No. 10, 16 – 21 (2010).
12. V. G. Mazurenko, "Lattice dynamics and anomalous physical properties of beryllium oxide," Author's Abstr. Diss. Cand Phys. Mat. Sci., UPI, Sverdlovsk (1981).