MICROSTRUCTURE AND ELECTRIC CONDUCTIVITY OF COMPOSITE (BeO + TiO₂) CERAMICS

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Specimens of composite (BeO + TiO₂) ceramics with TiO₂ added in an amount of 5, 10, 20, 30, and 40 mass% are obtained. The temperature dependence of the conductivity of the (BeO + 30 mass % TiO₂) ceramics is studied. Conduction is ensured by the titania additive present in the ceramics in a strongly reduced state. The maximum temperature (950 K) at which the (BeO + 30 mass % TiO₂) ceramics preserves its conductive properties in air for a long time and, possibly, the capacity to efficiently absorb microwave radiation is determined. Heating in air at a temperature exceeding 960 K is accompanied by the processes of oxidation of reduced TiO₂, which causes disordering of the structure and lowering of the conductivity. An electron microscope study is used to show that the distribution of TiO₂ in the BeO of the [BeO + (5, 10, and 30 mass %)) TiO₂] system is nonuniform; inclusions of large regions of grouped TiO₂ microcrystals are encountered. This affects the physicochemical properties of the ceramics, the thermal and electrical conductivities in particular. In order to ensure a uniform distribution of TiO₂ in the volume of the ceramics it is recommended to introduce the dioxide into the composition of the BeO powder from solutions (hydrochemical method).

INTRODUCTION

In addition to a high thermal conductivity (200 - 300 W/(m·K)) pure BeO ceramics possess a high electric resistivity that amounts to $1.0 \times 10^{15} - 1.1 \times 10^{15} \Omega$ ·cm at 300 K. The high thermal conductivity and electric resistivity of BeO ceramics makes them applicable in electronic engineering for dissipation of heat during operation of functional electronic devices [1, 2] and for making effective microwave insulators for vacuum electronic radiating tubes (traveling-wave tubes (TWT) and klystrons).

It is hard to modify the functional properties of BeO ceramics by directed alloying of the latter. The low isomorphic holding capacity of BeO with respect to impurities makes it virtually impossible to create such a concentration of impurity centers that would affect noticeably the physicochemical properties of BeO ceramics. For example, the content of typical impurities (Li, B, Al, Zn, Mg) that enter the crystal lattice of BeO in an isomorphic manner does not exceed background values ($10^{-4} - 10^{-3}$ mass %). Attempts to introduce higher amounts of other admixtures into BeO have shown that most of them do not enter the crystal lattice of BeO in an isomorphic manner but have the form of a second phase on the surface of BeO microcrystals or are located over the surface of micropores forming surface microstructures [2].

Among the heterogeneous systems mentioned the BeO ceramics with an additive of 5 - 40% TiO₂ possesses a number of unique properties, which explains its wide use in electronic engineering [2-5]. The introduction of various amounts of TiO₂ and its subsequent reduction make it possible to change the conductivity of ceramics composed of $BeO + TiO_2$ within a wide range (from 1×10^1 to $1 \times 10^{14} \Omega$ ·cm). The values of transmission and absorption of microwave radiation in such ceramics can be varied gradually in a wide frequency range, which makes it possible to use them in high-current microwave devices with a wide range of functional properties [2, 3, 5]. We have established that $(BeO + TiO_2)$ ceramics can be used as touchstones for assaying precious metals and subsequent electrochemical extraction of the metals from solutions after performing the operation of assay control [6].

In addition, the $(BeO + TiO_2)$ ceramics, which possess high conductivity and low work function of exoelectrons

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leaving the surface of BeO, present interest as a working substance (detector) on heat-stimulated exoemission and luminescent dosimeters [2, 4]. This makes it possible to remove the surface charges formed upon temperature changes (due to the pyroelectric effect) from BeO microcrystals and from the surface of the detector in the case of electron emission.

The introduction of various amounts of reduced TiO_2 into the composition of BeO ceramics permits smooth lowering of the intensity of x-ray and cathode luminescence of BeO (the peak in the region of 4.9 eV) [4]; the conductivity of (BeO + TiO₂) ceramics and its capacity to absorb microwave electromagnetic radiation can also be increased considerably [2, 3].

Articles from an absorbing material with high thermal conductivity are required for powerful TWT amplifiers as interstage loads and for absorption of microwave electromagnetic radiation in order to eliminate the emergence of a back wave and the transition of the TWT from the amplification to the generation mode. At present TWT are primarily fabricated with the use of absorbing ceramics based on KT-30 aluminum oxide, which possesses low thermal conductivity (10 - 15 W/(m·K)). Therefore, at high thermal loads the material is heated strongly and its main functional characteristics (the damping factor and the standing-wave factor) worsen.

It is known that the thermal conductivity of TiO_2 is low compared to that of BeO and amounts to about 4.25 W/(m·K). In order to raise the thermal conductivity of composite (BeO + TiO₂) ceramics the amount of BeO in it should be increased as much as possible without lowering the high capacity of the material to absorb microwave radiation. In this connection the studies aimed at developing a process for fabricating (BeO + TiO₂) ceramics absorbing microwave radiation and articles from this ceramics are quite important.

The present work was performed with an aim of determining the structural and physicochemical properties of ceramics based of BeO and doped with reduced TiO_2 , to study the effect of the method of fabrication of the ceramics on its microstructure, electric conductivity, and phase composition, to work out recommendations for fabrication of (BeO + TiO_2) ceramics with stable absorption of microwave electromagnetic radiation, and to advance the process of their production.

Due to the high thermal conductivity of the BeO phase the composite (BeO + TiO₂) ceramics should remove heat at high heat loads more efficiently and should not be overheated and thus preserve the damping factor and the standing-wave factor and exhibit stably high absorption of microwave radiation. When used as ceramic current conductors or powerful microwave-absorbing components, the (BeO + TiO₂) ceramics should be characterized by uniform distribution of TiO₂ in the volume of the BeO ceramics. Nonuniform distribution of TiO₂ causes local temperature inhomogeneity inside the ceramics and additional overheating of the microwave-absorbing components.

SYNTHESIS OF SPECIMENS

In order to fabricate specimens of $(BeO + TiO_2)$ ceramics with different compositions we used beryllium oxide of grade kh. ch. and titania of grade os. ch. as the initial reagents. We prepared charges from BeO with additives of 5, 10, 20, 30, and 40 mass % TiO₂. The BeO powder was baked at 1470 K in order to ensure stable physicochemical properties. The TiO₂ powder was preliminarily heat treated at 1070 K. The articles were shaped using the method of slip casting with the use of an organic binder. The charge was prepared by wet mixing of the initial oxides taken in the required proportions in a ball mill for 4 – 5 h. Slip on a high-paraffin binder was prepared in a heated mixer at 348 – 358 K. The amount of the organic binder in the slip was 10 – 13 mass %. The organic binder was burnt from the articles at 1470 K for 4 h.

The articles were sintered by two methods, i.e.,

- in a vacuum-hydrogen electric furnace at 10-5 mm Hg^{*} and maximum temperature of 1830 K for 1 h; after the sintering the specimens were subjected to heat treatment at 1810 K in hydrogen;

- in a forevacuum furnace with graphite heaters in an atmosphere of carbon monoxide (in a graphite crucible or graphite filler, where the CO pressure was varied within $1 \times 10^{-2} - 5 \times 10^{-2}$ mm Hg) at maximum temperature of about 1810 K.

We obtained dense ceramics of a dark color with grayish tint; the specimens for the study were shaped as tubes and disks of various sizes.

After the sintering the specimens were subjected to x-ray diffraction analysis. We also determined the electric conductivity of the ceramics. For this purpose we deposited platinum electrodes on the end faces of preliminarily baked specimens with a brush and sintered the former.

PHYSICOCHEMICAL PROPERTIES, ELECTRIC CONDUCTIVITY, AND STRUCTURE OF SPECIMENS

We used pycnometers for measuring the apparent density of the sintered specimens (Table 1). It turned out that the method of fabrication of the specimens had no substantial effect on their apparent density, which was affected by the amount of titania introduced into the specimen.

The x-ray diffraction study was performed at room temperature. We studied the phase composition of the specimens using a DRON-3M diffractometer and Cu K_{α} -radiation with wavelength $\lambda = 1.54178$ nm. In order to determine the phase composition of the (BeO + TiO₂) ceramics we studied specimens of (BeO + TiO₂) with 5, 10, 20, and 30 mass % TiO₂. Comparison of the diffractograms showed that independently of the content of TiO₂ there was no chemical interaction be-

^{*} 1 mm Hg = 133.322 Pa.

tween the components. In addition to the reflections typical for BeO we observed reflections from TiO_2 of a rutile modification. All the specimens exhibited diffraction peaks at a level of 1 - 2 rel.% (with respect to the 100% peak) that corresponded to a crystalline phase of titanium carbide.

Thus, it has been confirmed that $(BeO + TiO_2)$ ceramics are primarily represented by a mechanical mixture of BeO and TiO₂ oxides that weakly interact with each other chemically [2 - 4].

The main physicochemical properties of the BeO, TiO₂, and (BeO + 30 mass % TiO₂) ceramics are presented in Table 2. The stoichiometric TiO₂ (rutile) has a white color and possesses high dielectric properties [7]. The resistivity (specific resistance) R of rutile has been measured in [8] as a function of the temperature and of the degree of reduction. It has been shown that for colorless crystals of TiO₂ the value of *R* varies from 1×10^6 to $1 \times 10^7 \Omega$ ·cm.

The resistivity *R* of nonstoichiometric crystals having gray, dark-gray, and dark colors is equal to $4 \times 10^3 - 1 \times 10^4$, $5 \times 10^2 - 1 \times 10^3$, and $1 \times 10^{-1} - 1 \times 10^2 \Omega$ cm respectively.

Heat treatment of a mixture of $BeO + TiO_2$ in a reducing medium causes reduction of titania; the details of the mechanism of the process are still unknown. For example, in accordance with [9] rutile has defects in the form of vacancies in the oxygen sublattice on which electrons (F⁺ and F centers) can be localized upon irradiation; otherwise the electrons can be localized near Ti³⁺ ions. It is assumed in [10] that defects in rutile are titanium ions present in interstices of the crystal lattice. The disordering of the lattice is described by the formula $\text{TiO}_2 \rightleftharpoons \text{Ti}^{n+} + e^{-n} + \text{O}_2$. In accordance with the data of [11] the growth in the conductivity of TiO₂ is a result of the presence of a lower Ti₂O₃ oxide in its composition. In addition, it is known that titanium forms wide regions of α - and β-solid solutions with oxygen and many oxides, i.e., TiO, Ti_2O_3 , Ti_3O_5 , TiO_2 , and a Ti_nO_{2n-1} homologous series (Ti_4O_7 , Ti₅O₉, Ti₆O₁₁, Ti₇O₁₃, Ti₈O₁₅, Ti₉O₁₇, Ti₁₀O₁₉, and possibly other oxides) known as Magnelli phases [12 - 14].

We presume that when a mixture of $BeO + TiO_2$ is heat treated in a reducing medium, reduction of TiO_2 occurs when

2			
Number of specimen	Amount of introduced TiO ₂ , mass %	Apparent density of specimens, g/cm ³	
1	5	2.80	
2	10	2.88	
3	20	2.97	
4	30	3.20	

40

5

TABLE 1. Dependence of the Apparent Density of Specimens of $(BeO + TiO_2)$ Ceramics on the Amount of Introduced Titania

the valence of the cation ranges within $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti^{2+}$ upon growth in the number of its *d*-electrons. This explains the partial occupation of the zone including the 2*p*-atomic orbitals of oxygen and the atomic orbitals of titanium, which is vacant in stoichiometric TiO_2 . This results in an increase in the conductivity of TiO_2 and its darker coloring. Partially reduced TiO_2 is a semiconductor with electron type of conduction [2, 3]. It is mentioned in [7] that reduced TiO_2 has two conduction bands, i.e., an intrinsic one and an impurity one. In strongly reduced specimens the resistivity is a result of impurities, a carbon admixture in the first turn.

The conductivity σ of the (BeO + TiO₂) specimens was determined at room temperature. It should be noted that the value of σ was affected considerably not only by the amount of TiO₂ but also by the method of sintering of the specimens. Sintering of ceramics in vacuum at 10⁻⁵ – 10⁻⁴ Pa in a BeO crucible without carbon filling did not result in considerable growth in σ . The conductivity of the BeO ceramics without introduced admixtures, which had been fabricated by a similar process at 300 K, amounted to $1.0 \times 10^{-11} - 1.0 \times 10^{-13} \Omega^{-1} \cdot \text{cm}^{-1}$. Further studies showed that the growth in σ of the specimens of (BeO + TiO₂) ceramics compared to the specimens of pure BeO depended on the amount of the introduced TiO₂ and on the degree of its reduction.

It turned out that the $(BeO + TiO_2)$ ceramics (especially those sintered in carbon filler) contained (according to the data of x-ray diffractometry) a certain fraction of titanium

Physicochemical properties	BeO	TiO ₂ (rutile)	(BeO + 30 mass % TiO ₂) ceramics
Temperature, K, of:			
melting	2823	1830 - 2100	_
boiling	4393	3200	-
Thermal conductivity at 300 K, W/(m·K)	220 - 260	4.25	60
Apparent density, g/cm ³	2.85 - 2.98	4.1	3.2
Bulk resistivity at 300 K, Ω·cm	1×10^{15}	$1 imes 10^2 - 1 imes 10^7$	5×10^2
Tangent of the dielectric loss angle tan δ at 300 K (at a frequency $f = 1 \times 10^{10}$ Hz)	5×10^{-4}	$6.0\times 10^{-5} - 0.5\times 10^{-2*}$	0.2
Dielectric constant \sum at 300 K (at a frequency $f = 1 \times 10^{10}$ Hz)	7.2	80 - 100	20
Water absorption, %, at most	0.2	_	0.3

TABLE 2. Physicochemical Properties of BeO, TiO₂, and (BeO + 30 mass % TiO₂) Ceramics

* Depending on the degree of reduction of the rutile modification of TiO2.

3.32



Fig. 1. Logarithm of electrical conductivity σ of specimens of (BeO + 30 mass % TiO₂) ceramics as a function of reciprocal temperature: *1*, specimen heat treated in hydrogen; *2*, specimen sintered in carbon monoxide.

carbide. The admixtures of other elements, i.e., Si, Al, Ca, and Fe, present in the composition of the initial BeO powder in a total amount of $1.0 \times 10^{-2} - 5.0 \times 10^{-2}$ mass% could form titanates with titania and a low amount of liquid phase located on boundaries of BeO single crystals and pores. The liquid phase concentrated over boundaries of BeO grains delayed the recrystallization of beryllium oxide and promoted sintering of the ceramics.

Figure 1 presents the conductivity of specimens bearing 30 mass % TiO_2 as a function of the reciprocal temperature. It can be seen that the dependences for the compounds studied have a rather complex nature. For specimens obtained by different methods the dependences of the conductivity on the temperature are similar at 680 - 960 K. At a temperature exceeding 960 K and up to 1230 K the dependences have special features due to the change in the nature of conduction, because in this range the semiconductor type is transformed into a metallic type of conduction. Then the conductivity falls or decreases, which is explainable by the start of the processes of oxidation of reduced titania. This is typical for the temperature range of 1300 – 1450 K. The specimens of (BeO + 30 mass % TiO_2) ceramics heat treated in hydrogen possess a higher conductivity than the specimens sintered in CO (see Fig. 1), which is a sign of higher degree of reduction of titania in them.

We determined the activation energy E_a for ceramic specimens fabricated by different methods. The values of E_a at 680 – 960 K amounted to about 0.05 eV for both kinds. In the range of 960 – 1225 K the values of E_a differed; for the specimen treated in hydrogen $E_a = 0.13$ eV whereas for the specimen sintered in CO it was 0.05 eV.

At 1225 - 1450 K the conductivity fell due to the rapid process of oxidation of reduced TiO in the specimens. In accordance with the temperature dependence of σ , the maximum temperature at which the (BeO + TiO₂) ceramics preserve their conductive properties in air for a long time as well as, probably, the capacity to efficiently absorb microwave radiation, is 950 – 960 K. Heating in air at a temperature above 960 K is gives rise to the processes of oxidation of reduced titania, which causes disordering of its structure. This is reflected on the conductivity curves. This feature is the most typical for specimens of $(BeO + 30 \text{ mass }\% \text{ TiO}_2)$ ceramics obtained with heat treatment in hydrogen and is the least manifested in specimens sintered in CO.

We used an electron probe of type JEOL JSM-5900 LV to study the microstructure of specimens of $(BeO + TiO_2)$ ceramics with 5, 10, and 30 mass % TiO₂.

The results obtained (Fig. 2) show that the distribution of TiO_2 in BeO in the (BeO + 5 mass % TiO_2) system is nonuniform; inclusions of regions of grouped TiO_2 crystals $150 - 200 \ \mu m$ in size are encountered. This affects primarily the physicochemical properties of the specimens, their conductivity, and the capacity to absorb microwave electromagnetic radiation.

In the specimens of (BeO + 10 mass % TiO₂) ceramics (see Fig. 2) and in the specimens with 5 mass % TiO₂ the distribution of TiO₂ over the volume is nonuniform. Often, regions of grouped TiO₂ microcrystals with a mean length of $50 - 70 \mu m$ and a mean width of $30 - 50 \mu m$ can be observed. The microcrystals of TiO₂ are chiefly located individually and do not form closed nets, which is responsible for the low conductivity of the ceramics.

In contrast to the specimens bearing 5 and 10 mass % TiO_2 the specimens with 30% TiO_2 are characterized both by a nonuniform distribution of TiO_2 over the volume and by the presence of large groups of TiO_2 microcrystals adhered to each other (Fig. 3). These formations are 200 – 250 µm long and 100 – 150 µm wide.

The structure of the (BeO + 30 mass % TiO₂) ceramics is characterized by formation of bridges between microcrystals of reduced TiO₂, which should result in changes in the conductivity. Measurements of the conductivity at 300 K gave $3 \times 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$.

The mean sizes of microcrystals and pores evaluated from micrographs of regions with uniform distribution of BeO and TiO₂ microcrystals are presented in Table 3. Analysis of the microstructure shows that when the content of TiO₂ increases, the mean size of the BeO grains in the ceramics decreases. The mean size of the TiO₂ crystals (uniformly distributed over the volume) changes insignificantly. It should be noted that the number and the mean size of the pores decrease upon increase in the content of TiO₂ in the composition, i.e., the (BeO + 30 mass % TiO₂) ceramics becomes denser.

In addition, analysis showed that in all the specimens of $BeO + TiO_2$ the TiO_2 additive was distributed nonuniformly over the volume, which indicated imperfection of the process of production of the ceramics, i.e., mixing of BeO and TiO_2 powders in a ball mill for 4.5 h did not ensure homogeneity of the mixture. In order to obtain a uniform distribution of the TiO₂ additive for ensuring high conductivity and absorption of microwave radiation the amount of the introduced TiO_2 should have been decreased (from 30 mass % to, possibly, 20 - 25 mass %) for formation of closed conducting chains.



Fig. 2. Microstructure of ceramic specimens: 1 - 3, BeO + 5 mass % TiO₂ (1, × 55; 2, × 200; 3, × 1000); 4 - 6, BeO + 10 mass % TiO₂ (4, × 200; 5, × 400; 6, × 1000).



Fig. 3. Microstructure of a specimen of (BeO + 30 mass % TiO₂) ceramics under 50-fold (1), 200-fold (2), and 1000-fold (3) magnification.

TABLE 3. Mean Sizes of Microcrystals of BeO, TiO_2 , and Pores in Specimens of (BeO + TiO_2) Ceramics

Content of TiO_2 in (BeO + TiO_2) ceramics, mass %	Width, µm		Length, µm			
	of micro	ocrystals	ofmonoo	of microcrystals		ofmonos
	TiO ₂	BeO	or pores	TiO ₂	BeO	- or pores
5	3.3	15.8	2.4	5.7	19.3	2.8
10	3.5	11.5	2.4	6.0	17.1	3.5
30	3.6	9.5	1.1	7.1	16.6	1.2

This would have increased somewhat the thermal conductivity of the composite ceramics, which is a very important characteristic for materials used in high-current devices of the microwave range. For this reason it is expedient to introduce the TiO_2 additive into the composition of the charge from a solution (hydrochemical method), which would ensure its homogeneous distribution over the volume of the ceramics.

CONCLUSIONS

We have obtained specimens of composite (BeO + +(5-40) mass % TiO₂) ceramics and studied their phase composition. In accordance with the data of x-ray diffraction analysis the specimens of BeO + (5, 10, and 30) mass % TiO₂ are represented by a mechanical mixture of oxides weakly interacting with each other.

The (BeO + TiO₂) ceramics (especially those sintered in graphite filler) exhibit diffraction lines of a small amount of titanium carbide. The admixtures of other impurities (Si, Al, Ca, and Fe present in a total amount of $1.0 \times 10^{-2} - 5.0 \times 10^{-2}$ mass %) contained in the initial BeO powder can form titanates with TiO₂ and a low amount of liquid phase located on the boundaries of BeO microcrystals and pores. The liquid phase concentrated on the boundaries of BeO microcrystals delays the recrystallization of BeO and promotes sintering of the ceramics.

The specimens of the ceramics heat treated in hydrogen possess a higher electrical conductivity than the specimens sintered in CO. Marked growth in the electric conductivity of $(BeO + TiO_2)$ ceramics can be ensured by introducing such amount of reduced TiO₂ (up to 30 mass %) that causes formation of a closed net of titania microcrystals.

In accordance with the temperature dependence of the conductivity, the maximum temperature at which the $(BeO + 30 \text{ mass }\% \text{ TiO}_2)$ ceramics preserves its conducting properties in air and, probably, the capacity to efficiently absorb microwave radiation is 950 K. Heating in air at a temperature exceeding 960 K stimulates processes of oxidation of reduced titania.

As a result of electron microscope studies we established that the distribution of TiO_2 in BeO in the system of BeO + (5, 10, and 30) mass % TiO_2 is nonuniform; the structure contains inclusions of large regions of grouped TiO_2 microcrystals. This affects the physicochemical properties of the ceramics and especially their thermal and electric conductivities and the capacity to absorb microwave radiation. For a uniform distribution of titania it is expedient to introduce it into the composition of the BeO powder from a solution (by the hydrochemical method), which should ensure its uniform distribution in the volume of the ceramics.

It follows from the analysis of the microstructure that as the content of TiO_2 in the (BeO + TiO₂) composition increases, the mean size of the BeO grains becomes smaller. In our opinion this is connected with the higher amount of liquid phase formed in the composition of the ceramics upon growth in the content of TiO₂. The mean grain size of TiO₂ (which is uniformly distributed over the volume) changes insignificantly. It should be noted that the mean size of the pores also decreases with growth in the content of TiO₂, i.e., the (BeO + TiO₂) ceramics become denser.

Introduction of different amounts of reduced TiO_2 into BeO ceramics has made it possible to change the electric conductivity, which makes the ceramics applicable in various devices and processes where it is necessary to have chemically stable materials with a wide range of electric conductivity.

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