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Physical and Chemical Processes of Structure Formation of (BeO+TiO$_2$)-Ceramics with the Addition of TiO$_2$ Nanoparticles

This paper describes in detail the solid-phase sintering mechanism of BeO + $\mathrm{TiO}_2^{\mathrm{\mu m}}$ + $\mathrm{TiO}_2^{\mathrm{nano}}$ ceramics in the 1520–1550 °C temperature range. It is shown that the structural elements are formed due to the processes of pore disappearance and grain growth in the process of ceramic shrinkage during sintering. It is found that under the influence of TiO2 nanoparticles it is possible to increase the sintering temperature of such ceramics by 30 °C, which promotes the transformation of the crystal structure of TiO2 into a more conductive Ti3O5 with an orthorhombic structure. The mechanism of the slowing down of the grain boundary movement by the second phase impurity as the segregation of nano impurities on the grain boundary is described. The calculation of binding energy of spontaneous chemical reactions during sintering of ceramics is performed, chemical elements and compounds related to conductive phase in ceramics of BeO + $\mathrm{TiO}_2^{\mathrm{\mu m}}$ + $\mathrm{TiO}_2^{\mathrm{nano}}$ composition at sintering temperature 1550 °C are determined. It is shown that the specific conductivity of the synthesized nanocomposite material increases in comparison with the ceramics consisting of micropowders in the frequency range of 100 Hz–100 MHz, at a sintering temperature of 1550 °C.

Keywords: (BeO+TiO2)-ceramics, nanoparticles, solid-phase sintering, microstructure, mechanical mixture, specific conductivity, phase diagram.

Introduction

At present, due to the wide development of radio-electronic equipment, devices, and wireless communication equipment, much attention is paid to the creation of small-sized receiving and transmitting devices, containing in composition shielding and absorbing bulk materials that retain their properties in a wide range of frequencies and temperatures [1]. One of the most perspective materials for the creation of absorbers of microwave energy is ceramics based on BeO with the addition of TiO$_2$ to 30 wt.% [2]. Electrophysical and other properties of such ceramics can be essentially improved by introducing into structure of micro-and nano-powders TiO$_2$ [3]. Because sintering of ceramics is a physical and chemical process of production of dense workpieces under the influence of heat treatment, the study of the processes occurring at this is the most relevant task [4]. In particular, in the semiconductor industry, many products are produced by sintering: capacitors, resistors, substrates, bulk microwave energy absorbers, ferroelectrics, etc. [5].

The possibility of increasing the sintering temperature of BeO-based ceramics with the addition of TiO$_2$ micro-powders by adding a small amount of TiO$_2$ nanoparticles is one of the directions of research to improve the electrodynamic properties of such ceramics [6]. Theoretically, it will allow for achieving an increase in the density of ceramic samples and, consequently, higher values of electrophysical and absorption characteristics of the investigated material [7].

Information about the change in the electrophysical characteristics of ceramics based on BeO with the addition of micro-and nano-powder TiO$_2$ at a change in sintering temperature in the literature at the present time is absent. In this scientific article, the studies of physical and chemical processes occurring during the formation of the structure of ceramics based on (BeO+TiO$_2$)$_{\mathrm{\mu m}}$ with the addition of nanoparticles TiO$_2$, under the influence of temperature are presented.

Experimental

Microstructure, granulometric composition, and phase analysis of powders and sintered samples were studied on a scanning electron microscope with energy dispersive microanalysis attachment JSM-6390LV, 2007, with resolution in high vacuum until 3nm and the ability to image in secondary and reflected electrons. The microscope has a magnification from 5x to 300,000x at accelerating voltages from 0.5 kV to 30 kV.

Evaluation of the primary data on the powder material and the sintered product crystal size, analysis, and measurement of micropores, cracks, inclusions, and other defects were performed using an optical microscope MBS-10, at 16x magnification, with a measuring scale with a division value of 0.05 mm.

The AgilentE5061B Spectrum Analyzer technique is designed to measure the total complex resistance (impedance) of composite samples in the frequency range 1 Hz–100 MHz. The “frequency variation” method allows measuring the frequency dependence of such electrophysical characteristics as complex conductivity, dielectric permittivity, and contact resistance.

The essence of the method is to determine the electro-physical characteristics of composite materials depending on the frequency of the alternating voltage applied to the electrodes mounted on the sample, based on Ohm’s law to determine the instantaneous values of alternating current and measure the phase shift between current and voltage. As a result, the total complex resistance (impedance modulus |Z|) is calculated as the ratio of the effective alternating voltage to the effective alternating current.

Results and Discussion

Beryllium oxide in relation to TiO_2 is an inert compound, that is, there is no chemical potential of interaction between them. Figure 1 shows phase diagram of beryllium oxide interaction with titanium dioxide.

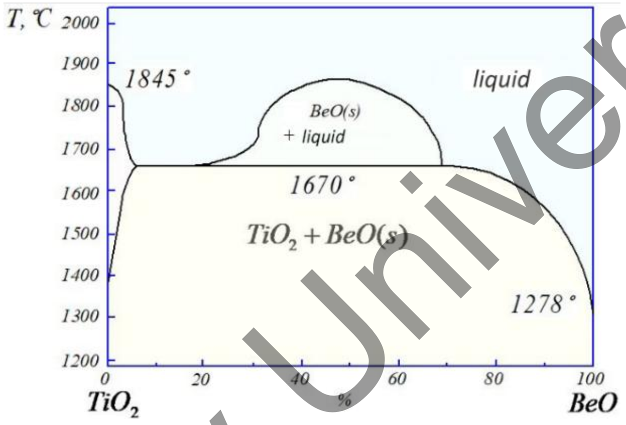

Figure 1. Phase diagram of TiO_2 — BeO interaction [8]

As can be seen from Figure 1, the content of titanium dioxide is from 20 to 70 mol. %wt., above the temperature of 1670 °C, titanium dioxide passes into the liquid phase. Therefore, in order not to “lose” mechanical properties due to crystal growth, the sintering temperature of (BeO+TiO_2)-ceramics should not exceed this temperature. In turn, the optimum sintering temperature for serial ceramics (BeO + 30 wt% $TiO_2^{\mu m}$) is 1520–1530 ºC, above this temperature starts crystal growth, the sample loses density, mechanical strength, geometric parameters (bloated).

Depending on the sintering mechanism, the microstructure of the ceramic is also determined. In the case of the solid-phase sintering mechanism, individual grains are formed due to the pore disappearance and grain growth processes. Both of these processes are accompanied by a change in the shape of the crystals, which tend to take the form of polyhedrons capable of filling the existing volume of the sample (Figure 2).

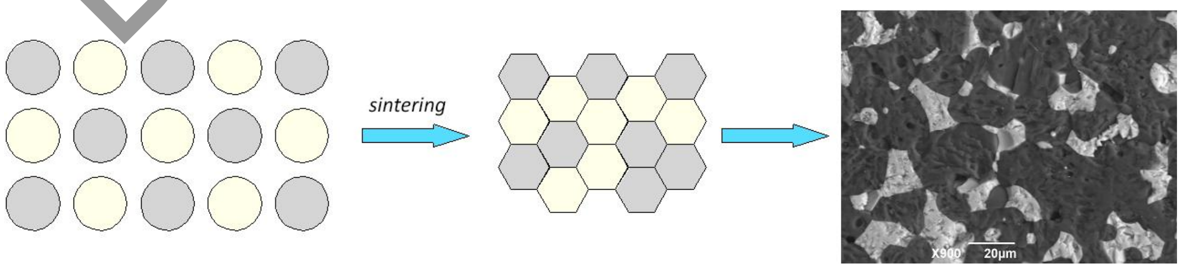

Figure 2. Solid-phase sintering mechanism of ceramics. In the inset on the right microstructure of ceramics of BeO + 29.0 wt% $TiO_2^{\mu m}$+ 1.0 wt% TiO_2^{nano} sintered at T = 1550 °C

The free energy in this sintering mechanism changes because of changes in the total surface area of all grains and changes in the specific surface energy when the solid-gas interface is replaced by a solid-solid interface. These changes can be represented as summations:

$$dG = \gamma dA + Ad\gamma$$

where A — area; γ — surface energy. These two summands are also expressed accordingly in the change in the microstructure of ceramics during sintering (Figure 3).

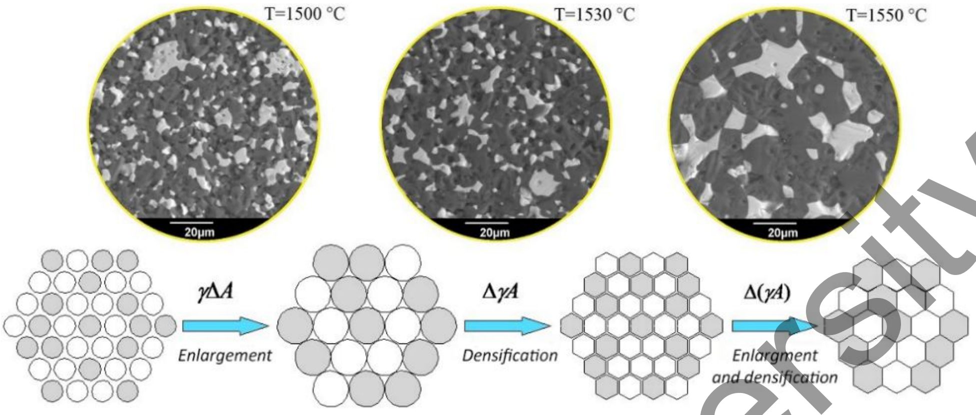

Figure 3. Scheme of mechanisms of enlargment and densification of ceramic structure during sintering. On the inserts on top the microstructure of ceramics of composition BeO + 28,5 wt% $TiO_2^{\mu m}$+ 1,5 wt% TiO_2^{nano}

In practice, during the sintering of ceramics the processes occur simultaneously — "enlargement of particles", accompanied by reduction of the total surface area of grains, and compaction, as a result of which the grain-gas interface is replaced by the grain-grain interface. This replacement can be accompanied by a decrease in the specific surface energy.

In turn, the chemical potential of the phase depends on the curvature of the surface, since the properties of the atoms on the surface of the particle are different from the properties of the atoms inside it.

The intergranular boundary is formed as a result of particle sintering, on which the change of direction of crystallographic grain axes takes place, characterized by the value of specific surface energy γ_b. In the case of two-phase ceramic composition (BeO, TiO_2) at the grain boundary with the second phase, a region is formed, which is represented in Figure 4.

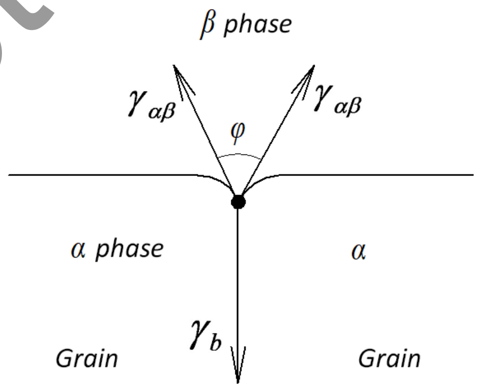

Figure 4. Schematic of the intergranular region in contact with the second phase

For an equilibrium boundary, there must be a relationship between the values of surface energy at the crystal-vapor and crystal-crystal boundary:

$$\gamma_b = 2\gamma_{\alpha\beta} \cos\frac{\phi}{2}.$$

The angle φ is called the dihedral angle. Its value does not depend on gas pressure, but only on the ratio between $\gamma_{\alpha\beta}$ and γ_b. If the β phase is gaseous, the relationship $\gamma_{\alpha\beta} \rangle \gamma_\beta$ is true and the dihedral angle takes on a value greater than 120°. The surface energy γ_b changes when the crystallographic orientation of the grains relative to each other changes. In real structures, this is the reason for the presence of different values of the dihedral angle that can be detected in ceramics at the initial moment when the porosity is high enough. The variation of angles in real samples is also observed because of the system's non-equilibrium. One of the options for bringing the system to an equilibrium state is to expose the system to a temperature at which liquid-phase sintering will take place under the action of the flow of one of the phases.

Thus, to describe the sintering process it is necessary to understand to what state a polycrystalline material consisting of grains and pores will tend to. As a result of the disappearance of pores during the sintering process, a polycrystal is formed in which the surface energy of the grain boundaries takes on a minimum value for a given number of grains and the grains form a dense, non-porous packing. Eventually, in the equilibrium state, all grains will have the same shape and size.

Ceramic samples of BeO + 5 wt% TiO_2^{nano} composition representing a two-phase system were subjected to a sintering temperature of 1800 °C (above transition to liquid-phase sintering — 1670 °C (Figure 1)) to achieve a liquid-phase sintering mechanism. We will consider BeO beryllium oxide as the first phase, and TiO_2 nanoparticles, which should tend to occupy the grain contact area near the tops of the BeO crystal, as the second phase with lower temperature. In a structure close to equilibrium, the values of contact angles tend to be values given by the ratio of surface energies at the interfaces. In such a case, the shape of the ternary intersection in the two-dimensional microstructure will be different, as well as the values of the dihedral angles (Figure 5).

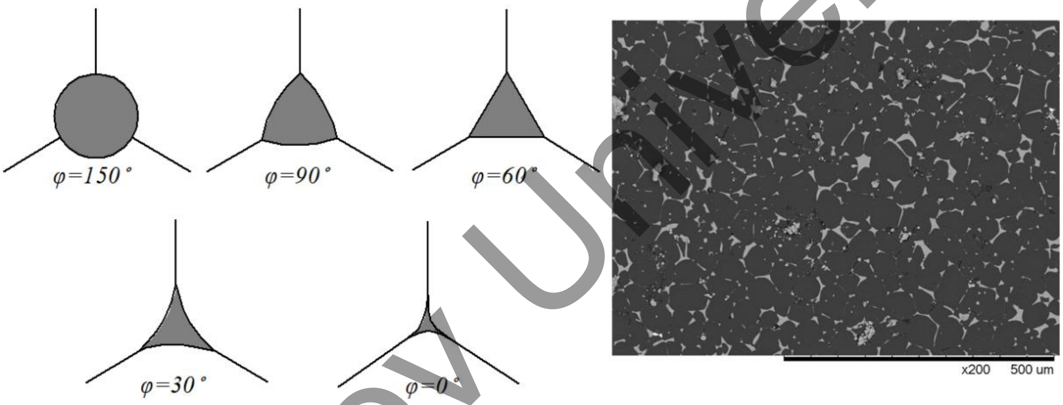

Figure 5. The shape of the triple crossing in the two-dimensional microstructure. In the inset on the right microstructure of ceramics of BeO + 5.0 wt. % sintered by the mechanism of liquid-phase sintering at T = 1800 °C

Figure 5 points out that the contact area between grains decreases with decreasing dihedral angle value, while the contact area of grains with the second phase increases. For the investigated sample, the dihedral angle is 0–30°. Based on the analysis of the macrostructure, grains during sintering of ceramics tend to take the shape characterized by a minimum of free energy. To achieve the minimum interfacial surface energy of the two-phase system, the minimum value of the dihedral angle is necessary, which tends to decrease at a temperature of 1800 °C.

Thus, the possibility of increasing the sintering temperature of ceramics by adding nanoparticles TiO_2 will reduce the interfacial surface energy, hence increasing the density, hardness, mechanical strength and possibly other physical and chemical properties, provided that the growth of the crystal size of BeO is contained.

The observed discrepancies in the theoretical calculations of the grain growth rate and the experimental data are due to the influence of impurities. In turn, if the impurity forms the second phase, its very presence slows down the movement of the grain boundary, as shown in Figure 6.

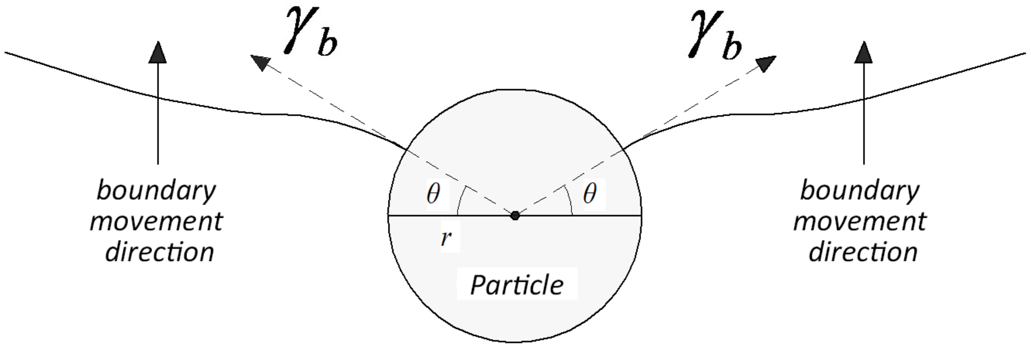

Figure 6. Illustration of the slowing down of the grain boundary movement by the second phase impurity

In ceramics of BeO + $TiO_2^{\mu m}$ + TiO_2^{nano}, the impurity TiO_2^{nano} is soluble in the phase $TiO_2^{\mu m}$, whose concentration in the volume and at the grain boundary differ from each other. If the energy of impurity atoms at the grain boundary is lower than in its volume, the segregation of impurity at the grain boundary is observed. To assess the influence of impurity atoms on the segregation processes we consider the distribution P atoms of impurity on N available positions in the crystal lattice of the main substance and p atoms of impurity distributed on n available positions in the area of the grain boundary. When an atom of the main component is replaced by an atom of the impurity in the volume of the grain, the internal energy E increases, which is accompanied by the change in energy e at the replacement of the atom at the grain boundary. Due to the dissolution of impurity atoms, the change in free energy G can be expressed in the form that is typical for solutions:

$$G = pe + PE - kT[ln!\,N\,! - ln(n-p)!\,p!\,(N-P)!\,P!]$$

Under the conditions of equilibrium $\frac{dG}{dp} = 0$ and $\frac{dG}{dP} = 0$. Given the large value of N, in the presence of nanoscale impurities, the Stirling approximation is valid:

$$ln\,N\,! \approx N\,ln\,N - N\;.$$

Considering these circumstances, the equilibrium distribution of atoms at different locations is described by the equation:

$$\frac{n}{n-p} = \frac{P}{N-P}exp\left(-\frac{e-E}{kT}\right).$$

This equation takes a simpler form if instead of the number of atoms and distribution sites we use their mole fractions. Thus, we obtain that the impurity atoms B, replace the atoms of the main substance A. Accordingly, the molar fractions of the atoms in the volume of the grain and at the boundary: X_A, X_B, X_A^b, X_B^b. In this case, the equation takes the form:

$$\frac{X_B^b}{X_A^b} = \frac{X_B}{X_A}exp\left(-\frac{\Delta E}{kT}\right),$$

where $\Delta E = e - E$ is the change in energy due to the segregation of impurities at the grain boundary.

To calculate the ΔE values, the model of a regular solution of paired atom interactions is applied, ignoring the interactions between impurity atoms. If we assume that the impurity atom is a solid nondeformable sphere, the lattice distortion energy W is equal:

$$W = \frac{4\pi Y r_0^3}{1+v}\left(\frac{r_1 - r_0}{r_0}\right)^2,$$

where Y — Young's modulus, v — Poisson's ratio, r_0, r_1 — radius of atom of the main substance and impurity, respectively. Because of the difference in the Young's modulus in the volume of a grain and at its boundary with another grain, the elastic strain energy at the introduction of an impurity atom into the lattice may be different — ΔE $\neq 0$.

In the case of nanoscale particles as an impurity phase, impurity segregation and internal energy changes can occur by completely different mechanisms. Beryllium oxide belongs to the group of "insulating oxides" derived from metals of the left and right parts of the D.I. Mendeleev table. Titanium dioxide refers to semiconductors or metallic oxides located in the middle of the table. Sintered mechanical mixture (ceramics) of such oxides with the addition of nanoparticles can show anomalous physical and chemical properties. In the size range from 2 to 10 nm classical laws and laws of quantum chemistry are not acceptable. In nanoparticles of spherical shape sized 3 nm, half of the atoms or ions are located on the surface. This position allows the volumetric properties to change due to surface effects in the region of reaction chemistry near the stoichiometric composition. The presence of a strong chemical bond can lead to changes in chemical and physical properties. When particles become smaller in size, different morphologies are formed, which affect changes in surface chemistry and adsorption properties due to an increase in their specific surface area.

During the study of the interaction of BeO and TiO_2 in a wide range of temperatures, it was found that titanium practically does not form solid replacement solutions with BeO. However, weak chemical interaction between them, along the interface surfaces, is not excluded in the process of sintering ceramics containing TiO_2^{nano} where other impurities can be concentrated. In turn, titanium (Ti) with oxygen (O) forms a large number of oxides: TiO_2, Ti_2O_3, Ti_3O_5, homologous series of oxides Ti_nO_{2n-1} and possibly others. Increasing the sintering temperature, due to the presence of TiO_2 nanoparticles contributes to more effective recovery of TiO. When sintering ($BeO+TiO_2$)-ceramics in furnaces with carbon heaters in a reducing environment (in a carbon monoxide atmosphere) carbon penetrates the inner region of ceramic samples, which leads to a uniform chemical interaction and distribution of phases both inside and on the surface of the sample.

After analyzing the main chemical elements and compounds involved in the manufacturing process of conducting ceramics of the composition of $BeO + TiO_2$, Table 1 was compiled.

Table 1

Conductivity of chemical elements and compounds involved in the technological process of making ($BeO + TiO_2$)-ceramics

Conductor	Dielectric
Be	
C	
Ti	*BeO*
BeH	Be_2C
BeC_2	TiO_2
TiO	$Be(OH)_2$
Ti_2O_3	*TiC*
Ti_3O_5	
TiH	

The conductivity of each element depends on the sintering temperature, for example, when TiO_2 is heated at 750–1000 °C in hydrogen environment, the compound Ti_2O_3 is formed. At hydrogen pressure of 13–15 MPa and temperature 2000 °C — TiO_2 is reducing to TiO, the only compound that gives a maximum of three free electrons (Ti^{+3}) is TiH. During sintering of such ceramics in weakly reducing environment of carbon monoxide the following chemical reactions can take place:

$$BeO + 2CO_2 \rightarrow BeC_2 + 5O.$$

$$2BeO + 4C \rightarrow 2BeC_2 + O_2.$$

$$TiO_2 + CO \rightarrow CO_2 + TiO.$$

$$2TiO_2 + C \rightarrow CO_2 + 2TiO.$$

$$TiO_2 + C \rightarrow TiO + CO$$

$$2TiO_2 + C \rightarrow Ti_2O_3 + CO.$$

$$2TiO_2 + CO \rightarrow Ti_2O_3 + CO_2.$$

$$6TiO_2 + C \rightarrow 2Ti_3O_5 + CO_2;$$

$$6TiO_2 + 2CO \rightarrow 2Ti_3O_5 + CO_2.$$

$$BeO + CH \rightarrow BeH + CO.$$

$$TiO_2 + CH \rightarrow CO_2 + TiH.$$

$$3TiO_2 + H_2 = Ti_3O_5 + H_2O$$

To determine the possibility of interaction between BeO and TiO_2 at an increased sintering temperature, due to the presence of TiO_2 nanoparticles, we use the entropic method of calculating the equilibrium constants, — $\Delta G_T^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ}$, where T = 1550 °C [9]. The data of this calculation allow us to identify four main chemical reactions that can occur at this temperature (Table 2).

Table 2

Calculation of the change of Gibbs energy, which determines the possibility of spontaneous reaction at T = 1550 °C

№	Chemical reactions	ΔG, kJ/mol
1	$TiO_2 + C \rightarrow \mathbf{TiO} + CO$	$\Delta G_T^{\circ} < 0$
2	$2TiO_2 + C \rightarrow \mathbf{Ti_2O_3} + CO$	
3	$3TiO_2 + H_2 \rightarrow \mathbf{Ti_3O_5} + H_2O$	
4	$TiO_2 + CH \rightarrow CO_2 + \mathbf{TiH}$	

According to the results of calculation of possible electrically conductive phases responsible for the conductivity of ceramic composition (BeO+$TiO_2^{\mu m}$+TiO_2^{nano}), sintered at T = 1550 °C, the main electrically conductive phases are TiO, Ti_2O_3, Ti_3O_5 and TiH.

To describe the electrical conductivity of composite materials, we commonly refer to a conductive cluster of particles of any phase. After the percolation threshold, a conductive cluster can be called percolation, considering its limited size and the possibility of binding conductive phase clusters by dielectric layers that have local resistances comparable to those of particles in micro-and nano-clusters.

Figure 7 represents the results of the study of the frequency dependence of the real and imaginary components of the specific conductivity of serial ceramics of BeO+30 wt% TiO_2.

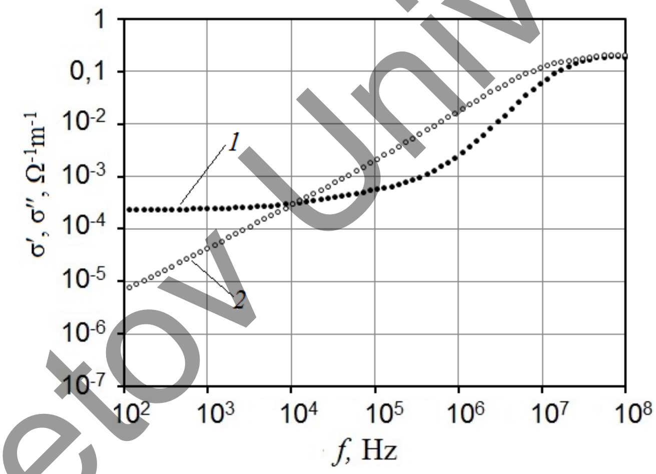

Figure 7. Frequency dependence of real σ' (1) and imaginary σ' (2) components of specific conductivity of serial ceramics of BeO+ $TiO_2^{\mu m}$ at T=1530 °C

Figure 7 shows that the real component of conductivity at low frequencies up to 104 Hz remains at the level of $2.4\cdot10^{-4}$ $\Omega^{-1}m^{-1}$. With further frequency increase conductivity stepwise increases up to the value of 0.15 $\Omega^{-1}m^{-1}$. The imaginary component of specific conductivity increases linearly over the whole range of frequencies understudy, coinciding with the real component at frequencies higher than $3\cdot10^{7}$ Hz.

Figure 8 displays the dependence of the specific conductivity on the concentration of TiO_2 nanoparticles of composition BeO + (28.0 — 29.9 wt% $TiO_2^{\mu m}$, $\sum TiO_2^{\mu m} + TiO_2^{nano}$=30 wt%) at the sintering temperature of ceramics 1550 °C.

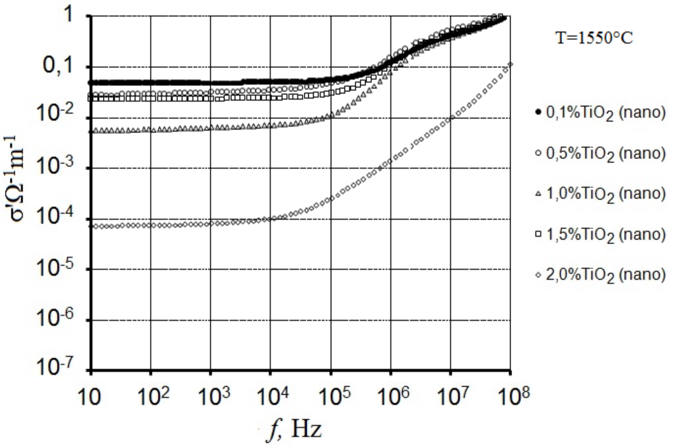

Figure 8. Frequency dependence of the real σ' component of specific conductivity on the content of TiO_2 nanoparticles, at T = 1550 °C

The conductivity curves, depending on the content of TiO_2 nanoparticles, are parallel to each other in the frequency range from 10 to 105 Hz. The minimum conductivity value in this range, is $\sigma'_{(1.0\ \%)} = 5.5\cdot10^{-3}$ $\Omega^{-1}m^{-1}$, the maximum $\sigma'_{(0.1\ \%)} = 4.8\cdot10^{-2}$ $\Omega^{-1}m^{-1}$. With the increasing frequency of electric field, specific conductivity on all samples increases sharply, at a maximum frequency of 10^8 Hz conductivity curves practically coincide, maximum value $\sigma'_{(0.5\ \%)} = 1.36$ $\Omega^{-1}m^{-1}$.

The conductivity mechanism can be explained by the fact that during sintering of ceramics TiO_2 nanoparticles are pushed to the surface of micron crystals (i.e., to the intercrystalline interlayers). Thus, conduction follows by a random grid of interlayers between the crystals. Some interlayers of adjacent crystals may not interact, therefore, there is a finite resistance and a hopping mechanism of conductivity from one layer to another (between the interlayers). As the concentration of titanium dioxide nanoparticles increases up to 2.0 wt%, they begin to stick together with each other or with titanium oxide microparticles inside the crystal and do not go into the intercrystalline interlayers, so the material becomes a dielectric.

Conclusions

The solid-phase sintering mechanism, the schemes of the mechanisms of enlargement and densification of the ceramic structure of BeO + $TiO_2^{\mu m}$ + TiO_2^{nano}, during sintering, confirmed by real photographs of the microstructure in the temperature range 1500–1550 °C, were described. According to the results of the study of the dihedral angle during liquid-phase sintering of ceramics containing BeO + 5 wt% TiO_2^{nano}, T = 1800 °C, the angle values are within 0–30 °, which characterizes the presence of a minimum interphase surface energy of the two-phase system.

The slowing mechanism of the grain boundary movement by the second phase impurity was described as the segregation of nano-impurities on the grain boundary, provided that the energy of the impurity atoms on the grain boundary is lower than in its volume.

Chemical elements and compounds related to the conducting phase in the ceramics of BeO + $TiO_2^{\mu m}$ + TiO_2^{nano} composition were determined by calculating the binding energy of possible chemical reactions. The reactions with the formation of the conducting compound TiO, Ti_2O_3, Ti_3O_5, and TiH were established.

It was established that the specific conductivity of the synthesized ceramics of composition BeO + (28.0 — 29.9 wt% $TiO_2^{\mu m}$, $\sum TiO_2^{\mu m} + TiO_2^{nano}$ = 30 wt%) at sintering temperature of ceramics 1550 °C significantly increases in comparison with the serial sample.

Acknowledgments

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$\mathrm{TiO_2}$ нанобөлшектері қосылған ($\mathrm{BeO + TiO_2}$)- керамиканың құрылымын қалыптастырудың физика-химиялық процестері

Мақалада 1520–1550 °С температура аралығында $\mathrm{BeO} + \mathrm{TiO}_2^{\mu m} + \mathrm{TiO}_2^{nano}$ құрамындағы керамиканы қатты фазалық біріктіру механизмінің сипаттамасы берілген. Құрылымдық элементтер біріктіру кезінде керамиканың шөгу процесінде кеуектердің жоғалуы және түйіршіктердің өсуі нәтижесінде пайда болатындығы көрсетілген. $\mathrm{TiO_2}$ нанобөлшектерінің әсерінен мұндай керамиканың балқу температурасын 30 °С-қа көтеру мүмкіндігі бар екендігі анықталды, бұл $\mathrm{TiO_2}$ кристалды құрылымын орторомбалық құрылымы бар $\mathrm{Ti_3O_5}$ өткізгіш құрылымына айналдыруға ықпал етеді. Түйіршік шекарасындағы наноқоспалардың сегрегациясы ретінде екінші фазалық қоспамен түйіршік шекарасының қозғалысын баяулату механизмі сипатталған. Керамиканы біріктіру процесінде өздігінен жүретін химиялық реакциялардың байланыс энергиясы есептелді, 1550 °С температурада $\mathrm{BeO} + \mathrm{TiO}_2^{\mu m} + \mathrm{TiO}_2^{nano}$ құрамындағы керамикада өткізгіштік фазаға жататын химиялық элементтер мен қосылыстар анықталды. Синтезделген нанокомпозиттік материалдың меншікті өткізгіштігі микроұнтақтардан тұратын керамикамен салыстырғанда 1550 °С температурада 100 Гц–100 МГц жиілік диапазонында өсетіні көрсетілген.

Кілт сөздер: ($\mathrm{BeO+TiO_2}$)-керамика, нанобөлшектер, сұйық фазалық біріктіру, микроқұрылым, механикалық қоспа, меншікті өткізгіштік, фазалық диаграмма, байланыс энергиясы.

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Физико-химические процессы формирования структуры ($\mathrm{BeO+TiO_2}$)-керамики с добавкой наночастиц $\mathrm{TiO_2}$

В статье приведено подробное описание твердофазного механизма спекания керамики состава $\mathrm{BeO} + \mathrm{TiO}_2^{\mu m} + \mathrm{TiO}_2^{nano}$ в интервале температур 1520–1550 °С. Показано, что структурные элементы формируются за счет процессов исчезновения пор и роста зерен в процессе усадки керамики при спекании. Установлено, что под действием влияния наночастиц $\mathrm{TiO_2}$ представляется возможность повысить температуру спекания такой керамики на 30°С, что способствует трансформации кристаллической структуры $\mathrm{TiO_2}$ в более проводящую $\mathrm{Ti_3O_5}$ с орторомбической структурой. Описан механизм замедления движения границы зерна примесью второй фазы как сегрегация нанопримесей на границе зерен. Произведен расчет энергии связи самопроизвольно протекающих химических реакций в процессе спекания керамики, определены химические элементы и соединения, относящиеся к проводящей фазе в керамике состава $\mathrm{BeO} + \mathrm{TiO}_2^{\mu m} + \mathrm{TiO}_2^{nano}$при температуре спекания 1550 С. Показано, что удельная проводимость синтезированного нанокомпозитного материала возрастает в сравнении с керамикой, состоящей из микропорошков, в диапазоне частот 100 Гц–100 МГц, при температуре спекания 1550 °С.

Ключевые слова: ($\mathrm{BeO+TiO_2}$)-керамика, наночастицы, жидкофазное спекание, микроструктура, механическая смесь, удельная проводимость, фазовая диаграмма, энергия связи.

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