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Effect of Ca dopant concentration on the change in properties of ZrO_2 ceramics

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The work is devoted to the study of effects associated with polymorphic transformations in ZrO_2 ceramics stabilized by 0.1 M $CaCO_3$, with variations in the temperature of thermal annealing. Interest in this topic of research is due to the possibilities of determining the kinetics of structural changes caused by the addition of a stabilizing dopant, alongside thermal action, the change of which causes the initialization of the polymorphic transformation processes characteristic of ZrO_2 ceramics. Annealing of the samples was carried out in the temperature range from 1000 to 1500 °C, the choice of which was determined by the possibilities of initializing the processes of polymorphic transformations in ceramics due to thermal processes and dopant. According to the conducted studies, it was determined that the addition of 0.1 M $CaCO_3$ at annealing temperatures of 1000 – 1100 °C results in initialization of polymorphic transformation processes of the type monoclinic – ZrO_2 → tetragonal – ZrO_2, however, complete transformation is not observed, which in turn makes it possible to obtain two-phase ceramics. The annealing temperature growth to 1200 °C and above results in formation of a cubic $Zr(Ca)O_2$ phase, with tetragonal – ZrO_2 impurity inclusions, the presence of which leads to the dislocation hardening effect formation due to the filling of the intergranular space with finely dispersed particles and the buffer zone formation. The results of the analysis of the structural parameters of the studied ceramics demonstrated that the annealing temperature elevation leads to the emergence of substitution effect, manifesting itself in the form of the $Zr(Ca)O_2$ phase formation, the crystal lattice parameters of which indicate that part of the zirconium ions are substituted by calcium ions in octo- and tetrahedral positions.

Key words: doping, structural changes, optical properties, zirconium ceramics, deformation distortions.
PACS number(s): 61.72.Ww; 61.82.Fk.

1. Introduction

Today, much attention in practical applications is paid to ceramic materials based on oxide compounds such as ZrO_2, Al_2O_3, MgO, BeO, CeO_2, etc. Interest in this type of ceramics is due to their strength and high melting point (for most ceramics, the melting point is higher than 1500 – 2000 °C), which creates possibilities of their use in extreme conditions, which includes operation at high temperatures [1-3]. The possibility of using ZrO_2 ceramics, which have fairly good compatibility with most different materials, as well as degradation resistance during interaction with acidic and alkaline environments, opens up great prospects for this type of ceramics in alternative energy. In particular, these ceramics are considered as candidate materials for the creation of inert matrices for dispersed nuclear fuel, possessing sufficiently high resistance to radiation damage [4-6]. Good indicators of resistance to radiation exposure while maintaining thermal physical parameters also allow these ceramics to be used as thermal insulation materials. The mixed conductivity type opens up great prospects for this type of ceramics when used as materials for the creation of solid oxide fuel cells used to produce hydrogen [7, 8]. Interest in ceramic materials based on zirconium dioxide when used as solid oxide fuel cells is primarily due to their high resistance to thermal expansion, typical for high-temperature operating conditions, as well as their mixed type of conductivity, which ensures good capacity and, as a consequence, performance [9-11].

However, despite the great prospects of this class of materials as solid oxide fuel cells, the problem of deformation-induced polymorphic transformations

of the m – ZrO_2 → t –ZrO_2, t – ZrO_2 → c – ZrO_2 type can have a dual effect on the change in the thermophysical and capacitive characteristics of this type of ceramics [12,13]. To restrain the polymorphic transformation processes, various additives in the form of magnesium, yttrium or calcium oxide dopants are usually used, allowing stabilization of the crystal structure of zirconium dioxide due to partial substitution of zirconium by a dopant. The latter results in formation of stable phases in the composition of ceramics that are not subject to polymorphism, the main reason for the occurrence of which, in addition to the deformation effect, is the presence of a large number of oxygen vacancies in the composition [14-16]. In this case, the use of stabilizing dopants is usually not only due to the possibility of initializing the polymorphic transformation processes in zirconium dioxide, but also to a decrease in the temperature at which these transformations are initiated, which in turn makes it possible to reduce the effect of thermal agglomeration of grains at high temperatures, which plays a very important role in determining the effects associated with size factors, and the size of the specific surface area [17, 18].

The aim of this study is to determine the prospects of using $CaCO_3$ as a stabilizing dopant for the initialization of polymorphic transformation processes in ZrO_2 ceramics, and to establish the effect of annealing temperature on the phase formation processes associated with polymorphic transformations of the m – ZrO_2 → t –ZrO_2, t – ZrO_2 → c – ZrO_2 type, alongside the possibility of controlling them by varying the synthesis conditions. An important role in the research is played by the study of the influence of synthesis conditions not only on the processes of phase formation, but also on changes in strength characteristics, which play an important role in determining the potential for using this type of ceramics as structural materials. Interest in this research topic is due to the possibilities of controlling the polymorphic transformation processes in zirconium dioxide by adding stabilizing dopants, the use of which allows not only to initiate the polymorphic transformation processes, but also to reduce the temperature of these transformations, the reduction of which allows reduction of the production cost of ceramics, possessing strong potential for application both in structural materials and as fuel cells used to produce hydrogen, viewed as one of the auspicious alternative fuel types.

2. Materials and methods

The synthesis of ceramics was carried out using the method of mechanical activation combined with thermal annealing, the change in temperature of which allows initiating processes of change of both morphological properties and structural ones, associated with the variation of structural parameters and processes of polymorphic transformations, the occurrence of which in ZrO_2 ceramics can be initiated both by changing the sintering temperature and in the case of variation of the concentration of the stabilizing dopant. Calcium carbonate ($CaCO_3$) was used as a stabilizing dopant in a molar ratio of 0.1 M of the total mass of powders used for the synthesis of ceramics using the mechanical activation method. The mechanical activation process itself was carried out using a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany), the use of which allows obtaining ceramics that are homogeneous in size and uniform in composition by mechanically grinding the initial components in a given volume in a special tungsten carbide grinding cup, in which 10 mm tungsten carbide balls are used as grinding media. The volume of balls in relation to the ground powders is 3 to 1, the total volume of the glass is 80 ml. Grinding is carried out at a grinding speed of 300 rpm for 30 minutes, after which the ground powders are removed from the glass and subjected to thermal annealing at various temperatures. Annealing of samples is carried out in a PM-1700 muffle furnace (Rusuniverstal, Chelyabinsk, Russia) using an annealing program that includes heating the samples to a given temperature at a rate of 20 °C/min, holding the samples at a given temperature for 5 hours and then cooling for 12 hours until the samples reach room temperature, which remain in the chamber the entire time until complete cooling. The range of variable annealing temperatures was from 1000 to 1500 °C, the choice of this range is based on the possibilities of initializing the polymorphic transformation processes in ZrO_2, the control of which using stabilizing dopants is one of the important methods of monitoring the phase transformation processes in zirconium dioxide.

To determine the grain sizes, the laser optical diffraction method was used, which was implemented on the ANALYSETTE 22 NeXT Nano particle analyzer (Fritsch, Berlin, Germany). The

measurements were carried out in several parallels, which made it possible to establish not only the dynamics of grain size changes depending on the annealing temperature, but also to determine the convergence of the results obtained in various experiments aimed at identification of the synthesis method repeatability.

The morphological features of the synthesized ceramics depending on the annealing temperature were obtained using the scanning electron microscopy method implemented on a Phenom™ ProX microscope (Thermo Fisher Scientific, Eindhoven, The Netherlands). Before analyzing the morphological features, the samples were dispersed on holders using a Nebula disperser (Thermo Fisher Scientific, Eindhoven, The Netherlands).

The ceramics' phase composition was established through the X-ray diffraction method, which consists in establishment of the main and impurity phases in the composition of the powders under study, and the change in structural parameters subject to the synthesis conditions. X-ray diffraction patterns were obtained on a D8 ADVANCE ECO powder diffractometer (Bruker, Karlsruhe, Germany). The diffraction patterns were recorded in the Bragg-Brentano geometry, in the angular range of 2θ=20 – 70°, the measurement step was 0.03°, the spectrum acquisition time at a point was 1 sec. The DiffracEVA v.4.2 software was used to determine the structural parameters and their change depending on the phase transformations associated with a change in the annealing conditions. The structural parameters were refined by comparing the reference values with the experimental data, as a result of which the main parameters of the crystal lattice, as well as the degree of structural ordering, were established. The synthesized ceramics were also studied using the Raman spectroscopy method, the use of which made it possible to establish the kinetics of polymorphic transformations, since, unlike X-ray diffraction, the Raman spectroscopy method is more sensitive to structural changes and deformations that occur as a result of external influences or variations in synthesis conditions. The spectra were obtained on an Enspectr M532 Raman microscope (Spectr-M LLC, Chernogolovka, Russia).

To gauge the hardness of ZrO_2 ceramics contingent upon the annealing temperature, the microindentation method, implemented using a Duroline M1 microhardness tester (Metkon, Bursa, Turkey), was applied. The measurements were conducted using a Vickers pyramid, with a constant load on the indenter of 100 N. The choice of load range is determined by the standard hardness measurement procedure.

3. Results and discussion

Figure 1 illustrates the grain distribution assessment results in ZrO_2 ceramics stabilized by $CaCO_3$, contingent upon the annealing temperature, and reflects the annealing temperature effect on the grain agglomeration processes associated with both polymorphic transformations and thermal sintering of samples, resulting in formation of large agglomerates of large sized grains. The general form of the presented dependencies of the grain distribution diagrams is for trends that clearly depend on the annealing temperature, associated with the coarsening of grains and the formation of fairly large agglomerates that are not amenable to dispersion in ultrasound. At annealing temperatures of 1000 – 1200 °C, the particle distribution has weakly expressed maxima in the region of 1-5 μm, which indicates fairly small grains, as well as a fairly large dispersion of particle size distribution associated with thermal exposure and phase transformation processes. In the case of the annealing temperature growth above 1200 °C, a sharp shift in the size distribution to the region above 10 μm is observed. This indicates agglomeration processes, which can be caused by both the effects of sintering at high temperatures and processes caused by phase transformations, the initialization of which occurs at high temperatures and, as a rule, is accompanied by coarsening of grains, resulting in compaction of ceramics. Moreover, the observed effects of asymmetry in the distribution of grains at temperatures of 1400 – 1500 °C may be associated with the formation of a finely dispersed fraction in the structure, the presence of which is due to the processes of phase formation and their enlargement.

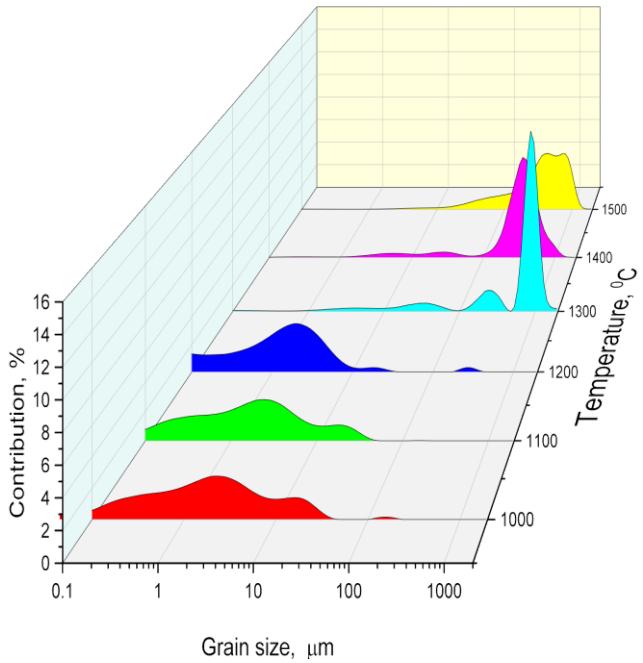


Figure 1 – Results of the evaluation of grain distribution in the composition of ceramics using the optical laser diffraction method for the studied samples depending on the variation of the annealing temperature

Figure 2 shows the results of the morphological features of the synthesized ceramics obtained using the scanning electron microscopy method. The overall view of the presented changes in the morphology of the ceramics indicates the annealing temperature effect on the agglomeration processes, which can also be caused by the phase transformation effects associated with polymorphic transformations. Moreover, the overall appearance of the provided morphological features of ceramics contingent upon the annealing temperature has an analogous trend established during the particle size analysis through the optical laser diffraction method, the results of which are demonstrated in Figure 1. In the case of annealing temperatures of 1000 – 1200 °C, the morphology of the ceramics is represented by a finely dispersed fraction of spherical particles, characteristic of the monoclinic phase of ZrO_2 used for synthesis. From this, it can be concluded that during thermal annealing of ZrO_2 at temperatures below 1200 °C, morphological changes associated with the coarsening of grains due to their fusion or agglomeration are not observed. At an annealing temperature of 1200 °C, the initialization of the processes of agglomeration of grains into dendrite-like formations, alongside their compaction, is observed. The latter indicates that with an elevation in the annealing temperature, the particles become larger, which can also be caused by the processes of polymorphism, which was established using the X-ray diffraction method. In the case of annealing temperatures of 1400 – 1500 °C, the formation of large agglomerates of grains, in which a finely dispersed fraction is present, especially manifested at a temperature of 1500 °C, is observed. Moreover, the finely dispersed fraction is located at the boundary of large grains, thereby filling the intergranular space, forming a buffer zone, the presence of which can have a positive effect on strength properties. The nature of these grains, as well as changes in their concentration, may be due to the effects of polymorphic transformations that occur during the heat treatment of ceramics stabilized with $CaCO_3$, the addition of which can lead to a shift in the temperature of polymorphic transformations in zirconium dioxide.

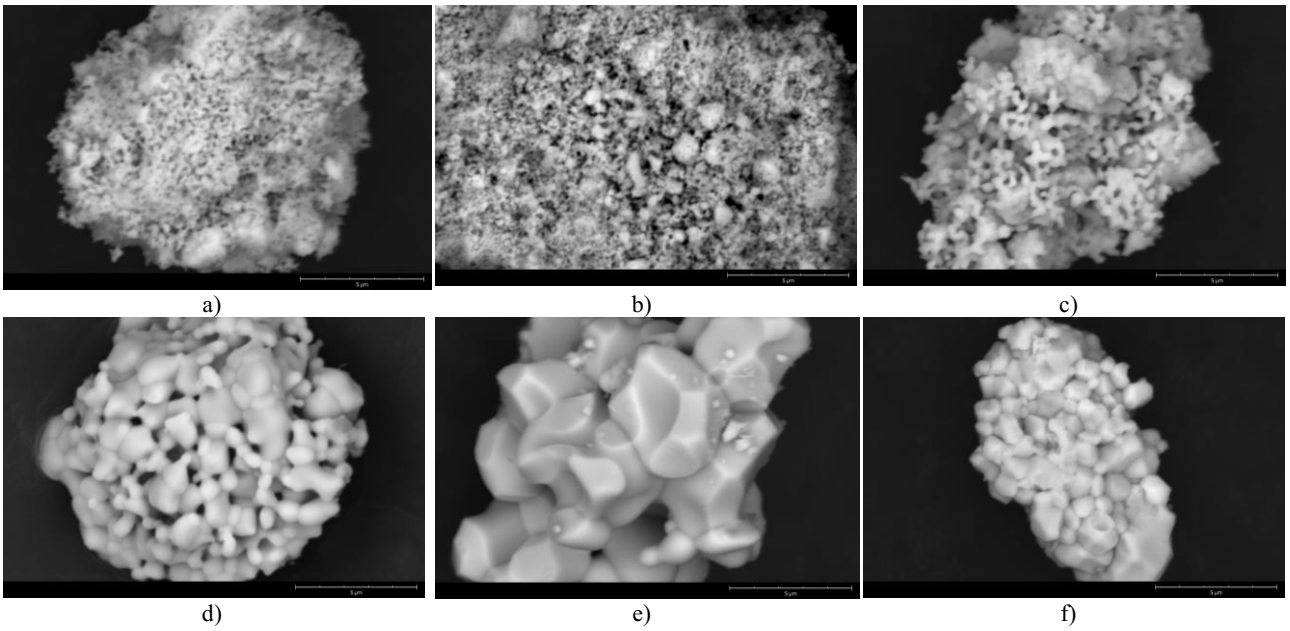
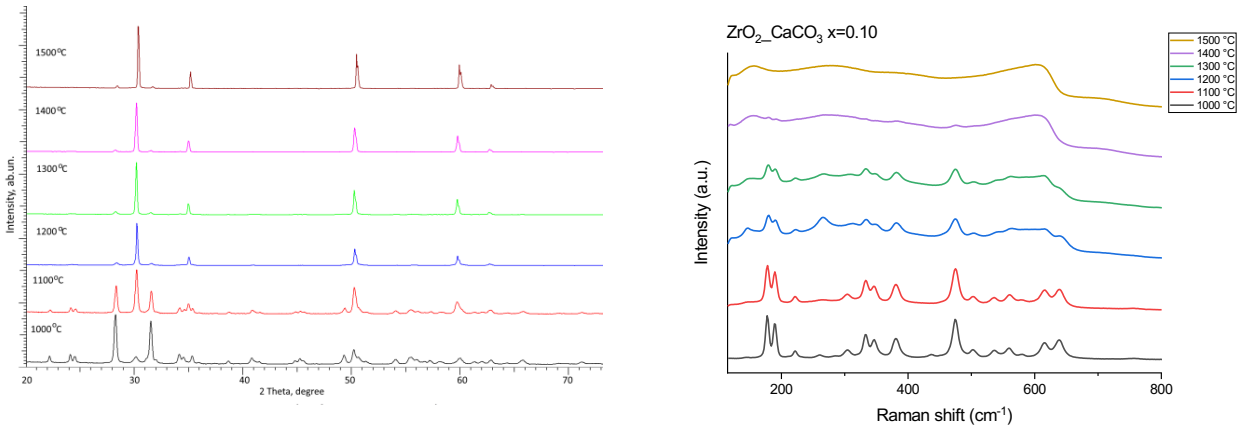


Figure 2 – Results of morphological features of synthesized ZrO_2 ceramics stabilized with 0.1 M $CaCO_3$ at variation of annealing temperature: a) 1000 °C; b) 1100 °C; c) 1200 °C; d) 1300 °C; e) 1400 °C; f) 1500 °C

Figure 3a illustrates the results of X-ray diffraction of the studied ceramic samples depending on the change in the annealing temperature of the ceramic samples, the variation of which allows for the initiation of phase transformation processes associated with polymorphic transformations. The dynamics of changes in the phase composition of ceramics with variations in the annealing temperature were determined by comparative analysis of the obtained X-ray diffraction patterns with the data of the PDF-2 database, which allows determination of the main and impurity phases in the composition of ceramics by comparison of card and experimental values, alongside determination of the type of polymorphic transformations that arise when the synthesis conditions change.

The general view of the provided X-ray diffraction patterns when considering changes contingent upon the annealing temperature indicates a change in the phase composition of the ceramics, which clearly confirms the effect of adding the stabilizing dopant $CaCO_3$ on the processes of phase transformations of the m – ZrO_2 → t-ZrO_2 type and the t – ZrO_2 → c-ZrO_2 type, which are characteristic of zirconium dioxide.



a) b)

Figure 3 – a) X-ray diffraction results of ZrO_2 ceramic samples obtained at temperatures from 1000° C to 1500 °C; b) Raman spectra of ZrO2 ceramic samples obtained at temperatures from 1000 ° C to 1500 °C

Figure 3b shows the Raman spectra of ZrO_2 samples with a concentration of 0.1 M $CaCO_3$ at different annealing temperatures. The spectra of the samples obtained at temperatures of 1000 and 1100 °C contain only modes associated with the monoclinic ZrO_2 phase. At annealing temperatures of 1200 and 1300 °C, a background appears in the spectra, the peaks of the monoclinic phase become less pronounced, which is associated with a rise in the content of the cubic ZrO_2 phase in the samples. At a temperature of 1500 °C, the modes related to the monoclinic ZrO_2 phase disappear, while three very broad peaks are visible in the spectra at 154, 280 and 604 cm^{-1}, indicating the presence of the cubic phase of ZrO_2 [19].

Figure 4 demonstrates a diagram of the change in the phase ratio in the composition of ceramics depending on the annealing temperature. The phase composition of the ceramics, as well as the weight of each specific phase depending on the component ratio, was determined using expression (1):

$$V_{\text{admixture}} = \frac{RI_{\text{phase}}}{I_{\text{admixture}} + RI_{phase}}, \qquad (1)$$

where I_{phase} is the intensity of the main phase, $I_{admixture}$ is the intensity of the impurity phase, the presence of which is associated with phase transformations, R=1.45.

As is evident from the presented phase analysis data, at temperatures higher than 1200 °C, the c-ZrO_2 phase dominates in the ceramics, while the t-ZrO_2 phase content varies from 5 to 3 wt. % subject to the annealing temperature. Analyzing the observed reduction in the contribution of the t-ZrO_2 phase with an increase in the annealing temperature, it can be concluded that a further increase in temperature can result in complete transformation of t-ZrO_2 → c-ZrO_2, however, the decrease rate less than 1 % with the annealing temperature growth by 100 °C (with a change in temperature from 1400 °C to 1500 °C) indicates a low efficiency of the proposed increase in the annealing temperature for completing the processes of polymorphic transformations. In turn, the analysis of the shape of the diffraction reflections, alongside the data of the morphological features presented in Figures 1 and 2, indicate an increase in particle size with an increase in the annealing temperature, which in turn indicates that with a further growth in temperature to complete the processes of polymorphic transformations, the effect of uncontrolled sintering of particles into larger agglomerates can be observed. In turn, the observed alterations in the morphological characteristics of ceramics at temperatures of 1400 – 1500 °C indicate that larger particles represent the c-ZrO_2 phase, while smaller particles may represent the t-ZrO_2 phase, the proportion of which corresponds to the amount of finely dispersed fraction filling the intergranular space. Such filling, in turn, can lead to the effect of dispersion hardening associated with the filling of the intergranular space with small particles, which in turn inhibit the spread of microcracks under external mechanical influences.

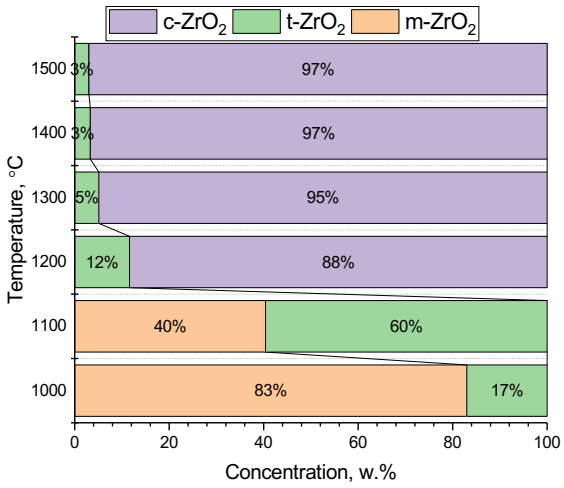


Figure 4 – Phase analysis results of the studied ceramics under variation in synthesis conditions associated with annealing temperature alterations

The data on the phase ratio alteration in the composition of ceramics with a variation in the annealing temperature, allows formulation of the basic formula reflecting the polymorphic phase transformation processes in ceramics stabilized by $CaCO_3$. This formula can be written as follows:

$$\text{monoclinic} - ZrO_2 \xrightarrow{1100\,℃} \text{tetraconal} - ZrO_2 \xrightarrow{1200-1500\,℃} \text{cubic} - Zr(Ca)O_2(\text{tetragonal} - ZrO_2)$$

Table 1 demonstrates the structural parameters of the studied ZrO_2 ceramics subject to the samples' annealing temperature.

According to the tabular data, the ionic radius of Zr^{4+} is about 79 pm, the ionic radius of Ca^{2+} is about 99 pm. In this case, the difference in ionic radii of about 20 pm causes the growth effect of the parameters of the crystalline cubic ZrO_2 phase, observed with the annealing temperature elevation from 1200 to 1500 °C. From which it follows that the formed c-ZrO_2 phase can be represented as c – $Zr(Ca)O_2$, characteristic of the effect of partial substitution of zirconium ions by calcium ions in octo- and tetrahedral positions.

Table 1 – Structural parameter data of ZrO_2 ceramics

Phase	**Temperature, °C**					
	1000	**1100**	**1200**	**1300**	**1400**	**1500**
m-ZrO_2	a=5.2781±0.0013 Å, b=5.1871±0.0015 Å, c=5.1315±0.0021 Å, β=99.425°	a=5.2802±0.0024 Å, b=5.1895±0.0014 Å, c=5.1317±0.0023 Å, β=99.424°	-	-	-	-
t-ZrO_2	a=3.5834±0.0026 Å, c=5.1701±0.0024 Å	a=3.5837±0.0023 Å, c=5.1705±0.0027 Å	a=3.5841±0.0026 Å, c=5.1714±0.0014 Å	a=3.5846±0.0013 Å, c=5.1725±0.0025 Å	a=3.5861±0.0023 Å, c=5.1731±0.0028 Å	a=3.5867±0.0021 Å, c=5.1734±0.0014 Å
c-ZrO_2	-	-	a=5.0831±0.0015 Å	a=5.0834±0.0012 Å	a=5.0835±0.0029 Å	a=5.0843±0.0023 Å
Crystallinity degree, %	91.1	91.6	92.5	94.5	95.4	95.7

Based on the data obtained, the structural ordering degree (crystallinity degree) of the studied ceramic samples depending on the annealing temperature, the data on the change of which are presented in Table 1, was evaluated. According to the assessment conducted, the annealing temperature increase leads to the structural ordering degree growth, which implies that the phase composition alteration results in perfection of the crystal structure, due to its ordering, alongside alterations in structural features. At the same time, the broadening of the crystal lattice parameters as the crystallinity degree increases is due to substitution effects, resulting in formation of the c –$Zr(Ca)O_2$ phase.

Figure 5 reveals the hardness assessment results of the studied ZrO_2 ceramics depending on the annealing temperature. Hardness measurements were carried out by indenting the surface in different areas in order to determine the hardness and isotropy of the strength parameters.

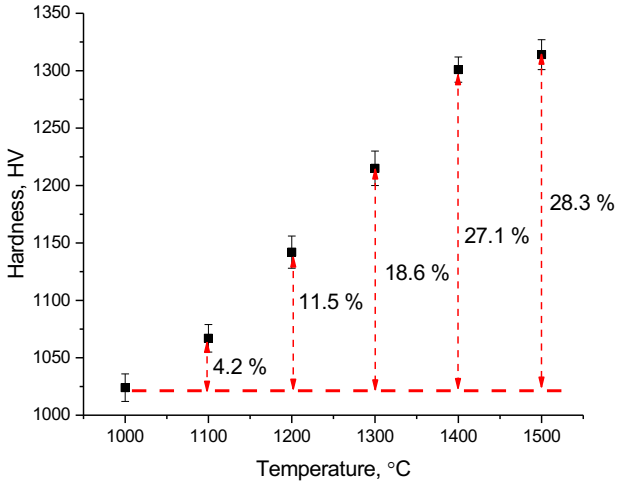


Figure 5 – Evaluation results of alterations in the hardness of ZrO_2 ceramics contingent upon the annealing temperature (the dotted lines indicate the hardening effect of ceramics obtained at temperatures of 1100 – 1500 °C in comparison with samples obtained at an annealing temperature of 1000 °C)

The overall trend of alterations in the hardness of ceramics with changes in the annealing temperature, which, as has been established, results in phase polymorphic transformations, implies a positive effect of polymorphic transformations on the ceramics' hardening. Moreover, the displacement of the monoclinic phase from the composition of ceramics due to the increase in the contribution of the tetragonal phase and subsequently the cubic phase causes a growth in hardness by more than 10-28 %. At the same time, in the case of dominance of the cubic phase, the hardening effect is caused by the dispersion effect associated with the filling of the intergranular space with a finely dispersed fraction of t-ZrO_2, which has a positive effect on enhancement of resistance to external mechanical influences (in particular, enhancement of resistance to external pressure created by an indenter during hardness measurements).

4. Conclusion

During the conducted studies of the influence of annealing temperature on the polymorphic transformation processes in ZrO_2 ceramics during their stabilization with 0.1 M $CaCO_3$, the following results were obtained:

1. An analysis of the morphological features of the obtained ceramics revealed that polymorphic transformations of the m – ZrO_2 → t-ZrO_2 type lead to the formation of a finely dispersed fraction with a porous structure, while at annealing temperatures above 1200 °C, the resulting polymorphic transformations of the m – ZrO_2 → c –$Zr(Ca)O_2$ type result in grain coarsening with the formation of large particle agglomerates.

2. According to the evaluation results of the phase composition of ceramics, it was established that the addition of 0.1 M $CaCO_3$ to the ZrO_2 ceramics' composition at temperatures higher than 1200 °C makes it possible to exclude polymorphic transformations associated with the tetragonal phase formation, while the main alterations are associated with the m – ZrO_2 → c –$Zr(Ca)O_2$ type polymorphic transformations, which are accompanied by the formation of a partial substitution phase of $Zr(Ca)O_2$, the formation of which leads to an elevation in structural ordering and, as a consequence, a reduction in the concentration of oxygen vacancies in the composition.

3. Analysis of structural parameter alterations confirmed the presence of the $Zr(Ca)O_2$ substitution phase, the formation of which occurs due to partial substitution of Zr^{4+} ions by Ca^{2+} ions, which leads to a rise in the crystal lattice parameters.

4. It has been determined that the formation of the t-ZrO_2 impurity phase in the composition of $Zr(Ca)O_2$ ceramics obtained at thermal annealing temperatures of 1400 – 1500 °C results in formation of an interphase hardening effect associated with the formation of a finely dispersed fraction in the interboundary space, leading to the

containment of microcracks under external mechanical influences.

Based on the conducted studies and analysis of structural changes, a general conclusion can be made that the addition of a stabilizing dopant $CaCO_3$ at a concentration of 0.1 M results in initialization of phase transformation processes of the m – ZrO_2 → t-ZrO_2 type at a temperature of 1000 – 1100 °C with the possibility of obtaining composite ceramics consisting of two phases, the ratio of which varies depending on the annealing temperature. At annealing temperatures above 1200 °C, the addition of $CaCO_3$ leads to the initialization of the m – ZrO_2 → c –$Zr(Ca)O_2$ processes, which makes it possible to obtain ceramics in which the dominant phase is c – $Zr(Ca)O_2$, and the finely dispersed fraction, the presence of which enhances the resistance of ceramics to external influences, is t-ZrO_2 grains.

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