



Article

Study of the Effect of Variation in the Phase Composition of ZrO₂/MgO Ceramics on the Resistance to Radiation Damage during Irradiation with Kr¹⁵⁺ Ions

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Abstract: Interest in the modification of zirconium-containing ceramics is rooted in their great prospects for application as materials for creating inert matrices of dispersed nuclear fuel, which can replace traditional fuel containing uranium dioxide, as well as increase the degree of its burnup. Moreover, among the variety of different types of ceramics offered, zirconium dioxide is the most promising, since it has higher thermal conductivity values compared to other types of ceramics, as well as low volumetric thermal expansion. Moreover, the key limitations in the application of these types of ceramics as materials for creating inert matrices are polymorphic transformations, which have a negative impact on changes in the properties of ceramics under external influences. The evaluation results of the impact of change in the ZrO₂ ceramics' phase composition on the radiation damage resistance when subjected to irradiation with heavy ions, comparable in energy to fission fragments, are presented. The objects of study were samples of ZrO₂ ceramics doped with MgO, the variation in the concentration of which leads to an acceleration of the processes of polymorphic transformations during thermal sintering, as well as the formation of a ZrO₂/MgO-type structure with inclusions in the form of MgO grains. The results of the irradiation effect on the stability of the crystal structure of ceramics to deformation swelling due to the accumulation of deformation inclusions showed that ceramics with a monoclinic structure type are the least stable, for which, in the case of high irradiation fluences, the accumulation of deformation distortions leads to polymorphic transformations of the m—ZrO₂ → t—ZrO₂ type. During the evaluation of the irradiation effect on the change in mechanical properties and the softening degree, it was found that phase transformations of the m—ZrO₂ → t—ZrO₂ and t—ZrO₂ → c—ZrO₂ types lead to an increase in crack resistance by 1.5–2.0 times. Meanwhile, the formation of a structure of the ZrO₂/MgO type with inclusions in the form of MgO grains in the interboundary space results in a softening resistance growth by over 7-fold. During tests for determining thermophysical parameters, as well as maintaining stability to crystal structure thermal expansion during prolonged thermal exposure, it was found that phase transformations associated with polymorphic transformations of the t—ZrO₂ → c—ZrO₂ type led to the preservation of the stability of thermophysical properties, even in the case of high irradiation fluences.



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1. Introduction

Interest in the study of radiation damage processes caused by the impact of heavy ions, similar in energy to nuclear fuel fission fragments, is due to the possibility of evaluating the mechanisms of structural disorder and strength softening, which, in turn, will expand

the choice of criteria in the selection of materials for the development of dispersed nuclear fuel [1,2]. Moreover, as a rule, the main processes associated with the formation of radiation damage and their subsequent accumulation occur in a fairly small near-surface layer, about 10–20 μm thick, as a result of which the concentration of accumulated damage in the case of high-dose irradiation in this damaged layer can be very high [3,4]. In this case, the accumulation of radiation damage can lead to irreversible processes of changes in structural properties, including bulk swelling (due to the development of gas-filled inclusions), deformation distortion of the crystal structure, and the partial or complete amorphization of the damaged layer (in the case of reaching high concentrations of structural distortions and deformations) [5,6]. These processes, as a rule, in the case of irradiation with heavy ions, have a pronounced dependence on the types of ions and their energy, since the heavier the ion and the higher its initial energy, the more negative consequences it can leave behind due to its interaction with the crystal structure. At the same time, in the case of high-energy heavy ions (with initial energy over 100 MeV), the dominant processes in the creation of defects will be caused by the ionization losses of incident ions during interaction with electron shells, which, in turn, can result in the occurrence of ionization processes in the damaged layer, alongside changes in the electron density distribution along the ion trajectory in the material [7–9]. Also, when assessing the degree of radiation damage to ceramics, one should take into account their dielectric nature, according to which any changes in the electron density distribution are practically irreversible, which in turn can lead to the appearance of destabilized inclusions in the damaged layer as a result of ionization processes [10,11]. With the accumulation of such inclusions in the structure of ceramics, the effects of distortion and deformation of the crystal lattice can occur, a large concentration of which can lead to swelling or partial amorphization. At the same time, the destabilization of the crystal structure can adversely affect both the strength characteristics and the thermophysical parameters of the crystal lattice. This is a change that will lead to a deterioration in strength properties and heat transfer mechanisms, the degradation of which will negatively affect the service life of ceramics [12–15].

To solve these problems, it is proposed to use ceramics based on zirconium dioxide as materials for inert matrices of dispersed nuclear fuel, which, because of their strength and thermophysical characteristics, as well as the absence of the effect of thermal expansion during operation at high temperatures, have a clear advantage over other types of oxide ceramics (BeO , Al_2O_3 , SiO_2 , CeO_2 , and MgO) [16–20]. However, one of the limiting factors of the use of ZrO_2 ceramics as inert matrix materials is the polymorphism of the phase composition, which arises under external influences (mechanical and deformation). In addition, as was shown in a number of works, radiation damage accumulation occurs upon exposure to heavy ion irradiation, comparable in energy to uranium fission fragments [21–23]. In this case, one of the ways to enhance the radiation damage resistance and the resistance to the initiation of polymorphic transformation processes—which, as a rule, are accompanied by a destructive change in volume and a subsequent sharp deterioration in the thermophysical or strength properties of ceramics—is the use of stabilizing dopants, such as Y_2O_3 , CaO , CeO_2 , and MgO . The addition of these dopants to the composition of ZrO_2 ceramics can lead not only to an increase in resistance to the destabilizing effect of polymorphic transformations, but also to an increase in thermal and strength properties, since most of these dopants have reinforcing properties, as well as higher thermal conductivity values, which in the case of ceramics can lead to an increase in the rate of phonon heat transfer mechanisms [24,25].

Based on the above, the key goal of this study is to study the effect of the ZrO_2 doping of MgO ceramics with different concentrations on the resistance to radiation damage when irradiated with ions. Variation in the MgO concentration, according to the data of previous studies [26], results in the initiation of the polymorphic phase transformation processes of the $m\text{-ZrO}_2 \rightarrow t\text{-ZrO}_2$ and $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$ types, as well as a rise in the resistance of ceramics to external influences (mechanical strength growth). Moreover, the study of the radiation damage processes, as well as methods for increasing the resistance to

their accumulation, and subsequent structural disorder and reducing the strength and thermophysical parameters in oxide ceramics, constitutes a promising and topical research direction in the domain of radiation materials science and nuclear energy.

2. Materials and Methods of Research

The synthesis of ZrO_2 ceramics in order to change the phase composition by varying the concentration of the MgO dopant was conducted via the mechanochemical solid-phase grinding of the initial components in a given stoichiometric ratio in a PULVERISETTE 6 classic line planetary mill (Fritsch, Berlin, Germany). ZrO_2 and MgO oxides, chemical purity 99.95%, produced by Sigma Aldrich (Sigma, St. Louis, MO, USA) were used as initial components. Following the grinding process, the initial mixtures were subjected to annealing in a muffle furnace at a temperature of 1500 °C for a duration of 5 h, followed by the cooling of the ceramic samples together with the furnace for 24 h. The variation in the MgO dopant concentration from 0.03 to 0.20 M was chosen in order to form ceramics with different phase compositions.

The simulation of radiation damage processes in ceramics was carried out via the irradiation of ceramic samples with Kr^{15+} ions with an energy of 150 MeV and fluences of 10^{10} – 10^{14} ion/cm². The selection of ion types for irradiation, along with their fluences, is based on the ability to simulate radiation damage effects that are akin to the impacts of fission fragments from nuclear fuel on the surface layer when in contact with fissile nuclear materials. An assessment of the ionization losses of incident ions during their interaction with ceramics, depending on its phase composition (i.e., changes in density during phase polymorphic transformations), was conducted using modeling methods in the SRIM Pro 2013 program code. The modeling results are presented in Figure 1.

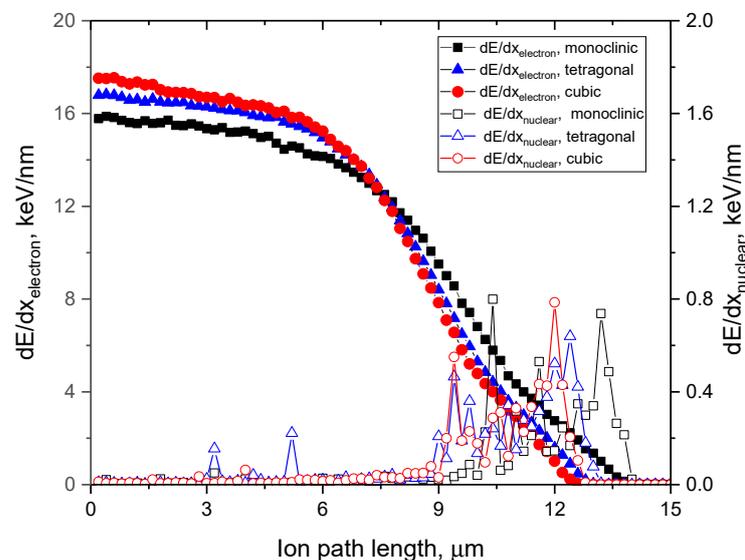


Figure 1. Results of modeling ionization losses of incident Kr^{15+} ions.

As is evident from the presented modeling data, the maximum ion path length in all three types of ceramics (i.e., in various phase modifications) is about 12–13 μm , and the magnitudes of ionization losses during the interaction of ions with electron shells (dE/dx_{electron}) are of the order of 14–17 keV/nm (almost over most of the ion path length), with nuclei (dE/dx_{nuclear}) of the order of 0.5–0.8 keV/nm (at maximum). In this case, the transition from the monoclinic to the tetragonal and cubic phases leads to a slight decrease in the maximum ion path length (about 0.3–0.5 μm), which in turn leads to an increase in ionization losses of incident ions in the material.

The characterization of the phase composition, the study of the processes of polymorphic transformations occurring with a change in the dopant concentration in ceramics, as

well as the assessment of changes in structural parameters due to exposure to irradiation, and, as a result, the accumulation of radiation damage, were conducted via X-ray phase analysis. To calculate the structural parameters, the DiffracEVA v4.2 software code was used. The phase composition and the dynamics of its change were determined using the PDF-2(2016) database. X-ray diffraction patterns were taken with a D8 Advanced ECO powder diffractometer (Bruker, Berlin, Germany).

The study of the mechanical properties of ceramics—and, in particular, the determination of hardness—was carried out using the indentation method, implemented by utilizing a LECO LM700 microhardness tester (LECO, Tokyo, Japan). A Vickers diamond pyramid was applied as an indenter.

To determine the thermophysical parameters of the studied ceramics depending on the phase composition, as well as the conditions of external influences, and, in particular, irradiation with ions, the method of longitudinal heat flow was used. The KIT-800 device (Moscow, Russia) was used for the experiments. The measurement of the thermal conductivity coefficient was carried out according to the standard procedure for determining the temperature difference on both sides of the sample during its heating. All measurements were carried out using standard samples, the size of which was 10 mm in diameter. The measurements were carried out serially in order to refine the methodology and obtain stable results, as well as to exclude any artifacts or inaccuracies. The determination of the thermal conductivity coefficient was carried out using Formula (1):

$$\lambda = \frac{q\delta}{t_{c1} - t_{c2}} \quad (1)$$

where q is the heat flux density, W/m^2 ; t_{c1} and t_{c2} are sample temperatures on both sides, K; and δ is the sample thickness.

Tests for maintaining stability to thermal expansion (volumetric and linear) were carried out by heating the samples for 100 h at a temperature of 1000 K in a muffle furnace with an oxygen atmosphere. The purpose of these experiments was to determine the effect of prolonged thermal exposure on irradiated samples, which can lead to destabilization due to broadening. After testing, X-ray diffraction patterns were taken for all the samples under study, a comparative analysis of which made it possible to determine the parameters of volumetric and linear broadening by comparison with the data of the crystal structure before high-temperature tests. These experiments make it possible to simulate conditions as close as possible to reactor tests in the case of high-temperature operation, as well as to determine the effect of the degree of radiation damage on the change in the volumes of ceramics.

Formulas (2) and (3) were used to calculate the volumetric thermal expansion coefficient ($\beta_V(T)$) and isotropic linear expansion ($\alpha_{ac\ isotr}$):

$$\beta_V(T) = \frac{1}{V_{initial}} \frac{\Delta V}{\Delta T} \quad (2)$$

where $V_{initial}$ is the volume of the crystal lattice in the initial state; ΔV is the difference between the volumes of the crystal lattice before and after thermal expansion tests; and ΔT is the temperature difference.

$$\alpha_{ac\ isotr} \cong \beta_V(T) / 3 \quad (3)$$

3. Results and Discussion

Four types of ceramics with different phase compositions were selected as objects of research in order to determine the radiation resistance to irradiation with Kr^{15+} ions: monoclinic structure, tetragonal, cubic, and two-phase ceramics consisting of a $c\text{-ZrO}_2/\text{MgO}$ interstitial solid solution. The samples were obtained using mechanochemical solid-phase synthesis by varying the MgO dopant from 0.03 to 0.20 M. Figure 2 illustrates X-ray diffrac-

tion patterns of the initial samples, reflecting the change in the phase composition of ceramics with varying MgO dopant concentrations.

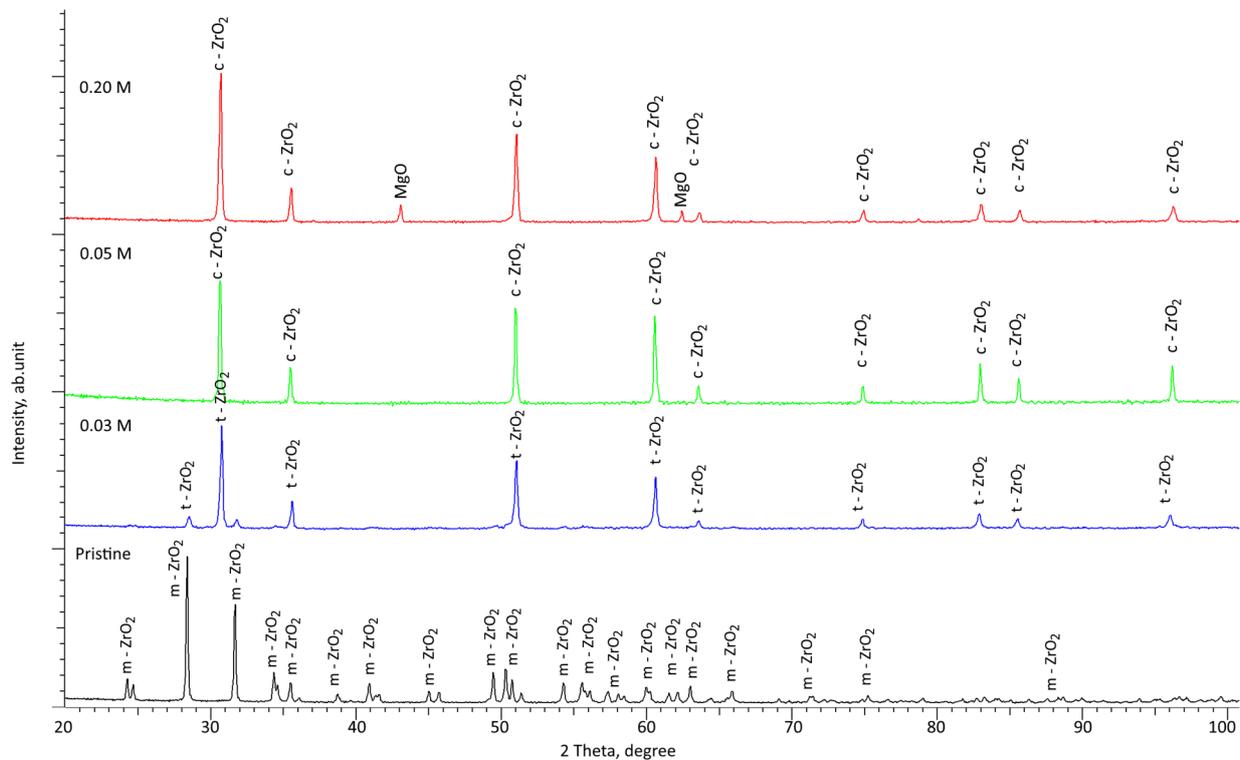


Figure 2. Results of X-ray phase analysis of the studied ceramic samples selected as objects for research to determine radiation resistance.

In the case of initial samples of ZrO_2 ceramics, the phase composition is characterized by a monoclinic phase ($m\text{-ZrO}_2$) with crystal lattice parameters $a = 5.2889 \text{ \AA}$, $b = 5.1747 \text{ \AA}$, $c = 5.1279 \text{ \AA}$, and $\beta = 99.043^\circ$. As is evident from the data presented, the thermal annealing of ZrO_2 ceramic samples at a temperature of 1500°C does not lead to polymorphic transformations of the $m\text{-ZrO}_2 \rightarrow t\text{-ZrO}_2$ type, which allows us to conclude that in undoped ZrO_2 ceramics, the factor of thermal influence on polymorphic transformations as a result of exposure can be excluded.

When a MgO dopant with a concentration of 0.03 M is added to the composition of ZrO_2 ceramics during thermal annealing of the samples, a phase polymorphic transformation of the $m\text{-ZrO}_2 \rightarrow t\text{-ZrO}_2$ type is observed, with dominance in the composition of the tetragonal phase $t\text{-ZrO}_2$ with parameters $a = 3.5594 \text{ \AA}$ and $c = 5.0429 \text{ \AA}$. At a MgO dopant concentration of 0.05 M, thermal annealing leads to the initialization of the second type of polymorphic transformations $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$, with the dominance of the cubic body-centered phase with parameters $a = 5.0399 \text{ \AA}$.

Thus, it can be concluded that the main factor affecting polymorphic transformations in MgO-doped ZrO_2 ceramics obtained by mechanochemical solid-phase synthesis and annealed at a temperature of 1500°C —on the type of polymorphic transformations—is the MgO dopant concentration. The use of this dopant leads to the initialization of the processes of polymorphic transformations with subsequent stabilization of the resulting phases. It should be noted that an increase in the dopant concentration above 0.05 M leads to the formation of ceramics with a dominant cubic body-centered phase and an interstitial cubic MgO phase located near the grain boundaries of the main ZrO_2 phase (see the SEM image data illustrated in Figure 3). The content of the cubic MgO phase at a dopant concentration of 0.20 M is no more than 10 wt.%.

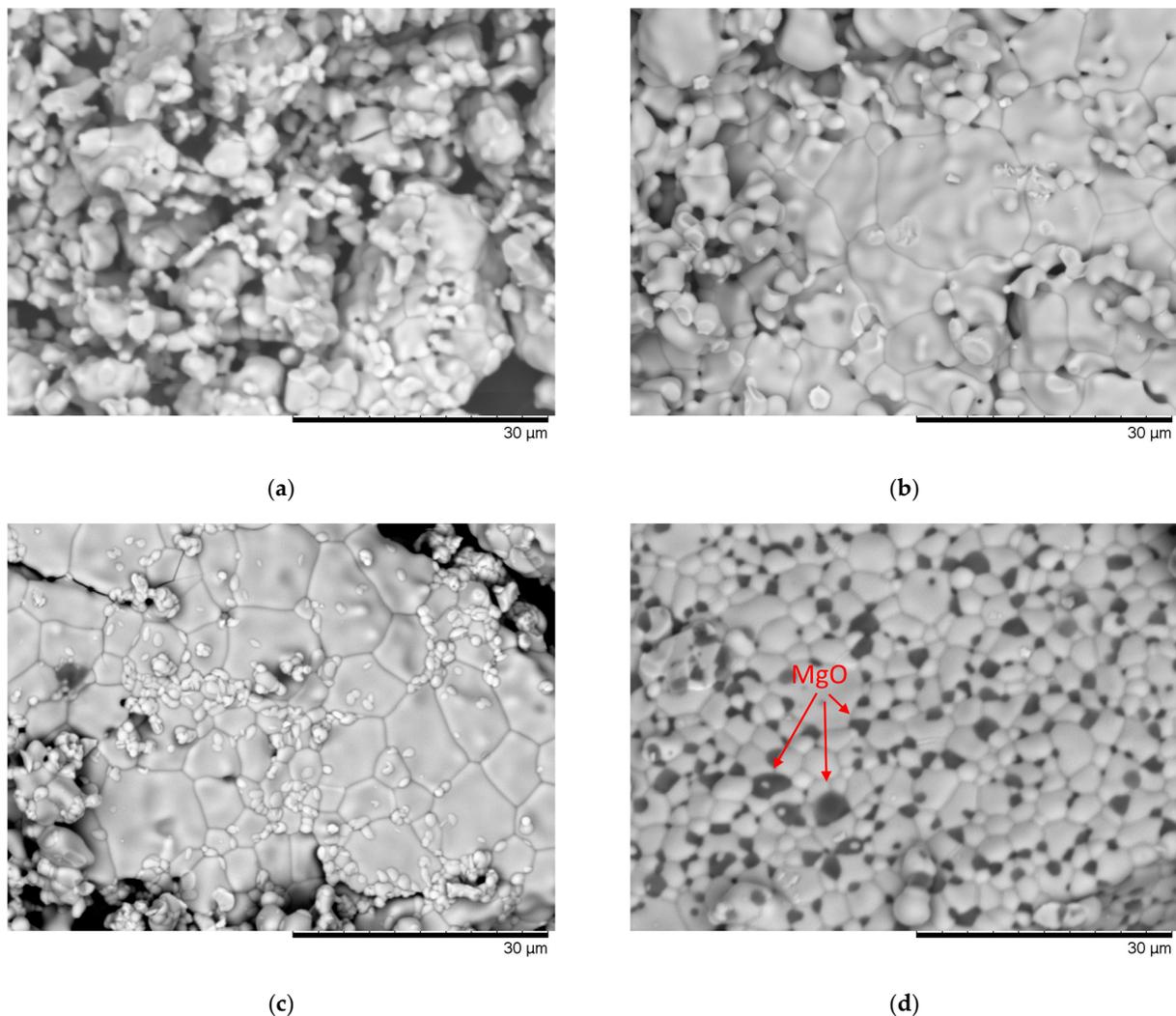


Figure 3. The results of the study of morphological features of ZrO_2/MgO ceramics: (a) pristine; (b) 0.03 M; (c) 0.05 M; and (d) 0.20 M.

Analyzing the SEM images of ceramic samples with varying MgO dopant concentrations, it is evident that polymorphic transformation processes coincide with alterations in grain morphology, including a reduction in grain size and the development of denser packing. The dispersion of grain sizes was carried out through a comparative analysis of photographs taken using the scanning electron microscopy method with optical laser diffraction data. As a result, good agreement was established between the data obtained using the two methods.

One of the most accurate ways to evaluate the effects of irradiation on the changes in the properties of ceramics, alongside determining their resistance to radiation damage, is the method of determining the deformation distortions of the crystal structure. This method is based on calculations of alterations in the crystal lattice parameters and volume in comparison with the initial values measured for samples before external influences. In this case, the nature of the dynamics of changes makes it possible to assess the type and direction of deformation distortions resulting from external influences. At the same time, the comparison of data depending on the conditions of external influences (i.e., with variation in the irradiation fluence) enables the assessment of radiation damage accumulation kinetics and their impact on the crystal structure. Figure 4 demonstrates the assessment results of the crystal lattice volume alteration in comparison with the initial value of the samples under study before irradiation. The data are given as a percentage of ΔV , which signifies the extent of the degree of structural swelling due to deformation distortions.

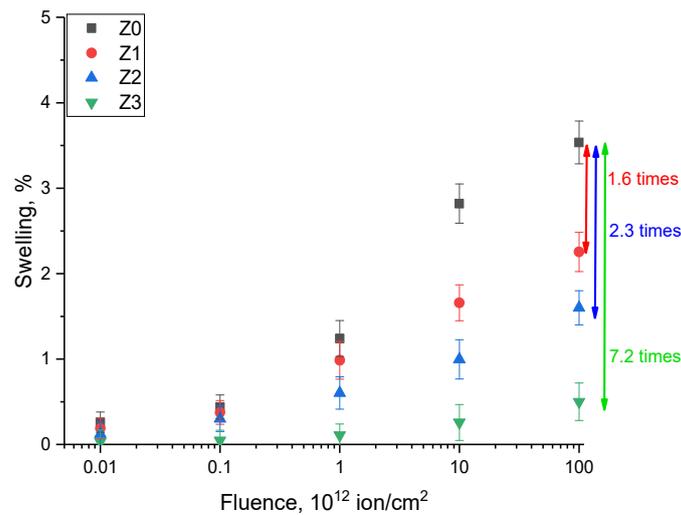


Figure 4. The results of the assessment of the crystal lattice swelling of the studied samples depending on the fluence of irradiation with Kr^{15+} ions.

For the convenience of characterizing changes in ceramic samples caused by irradiation, code names were introduced for samples: Z0 is the initial ceramic without a dopant; Z1 is a sample with a dopant concentration of 0.03 M; Z2 is a sample with a dopant concentration of 0.05 M; and Z3 is a sample with a dopant concentration of 0.20 M.

The general view of the dependences presented is characterized by a different trend of increasing the degree of swelling, and the very nature of the alteration in the value of ΔV as it varies with irradiation fluence suggests the accumulation of tensile deformation distortions of the crystal lattice resulting from the accumulation of radiation damage. Differences in the trend of ΔV values for doped ceramic samples in comparison with undoped samples depending on the irradiation fluence indicate a positive effect of the dopant and related polymorphic transformations on the stability of the structural degradation of ceramic samples with increasing irradiation fluence. However, it is important to highlight that in the case of the initial undoped samples with irradiation fluences of 10^{13} – 10^{14} ion/cm², a sharp change in the volume of the crystal lattice (values ΔV) is due to the effect of radiation-induced polymorphic transformation of the type $m\text{-ZrO}_2 \rightarrow t\text{-ZrO}_2$. This behavior of ceramics aligns well with the findings from experimental studies [21–23], in which it was shown that irradiation with ions with fluences above 10^{12} ion/cm² leads to polymorphic transformations in the damaged layer. Moreover, these polymorphic transformations are due to the accumulation of radiation-induced damage and structural distortions in the damaged layer, the accumulation of which leads to the destabilization of the monoclinic structure and its subsequent transformation into a tetragonal or cubic one, followed by an increase in volume due to deformation distortions. It should be noted that these polymorphic transformations have a pronounced dependence on the irradiation fluence, since they were not observed at fluences below 10^{13} ion/cm². This fact can be explained in terms of the cumulative effect of structurally deformed inclusions in the damaged layer, the accumulation of which occurs with a rise in the irradiation fluence. At low irradiation fluences (10^{10} – 10^{11} ion/cm²), the concentration of structurally deformed inclusions in the damaged layer is quite low. Moreover, these inclusions are isolated from each other and are located at a sufficiently large distance from each other due to their small size (diameter no more than 5–10 nm) and the stochastic interaction of ions with the crystal structure of ceramics. At fluences higher than 10^{12} ion/cm², the concentration of these structurally deformed inclusions increases, while due to the increase in irradiation density, the effect of overlapping of these areas or their association occurs, which leads to the appearance of structurally deformed areas of a larger size. In this case, an important role is also played by ionization effects associated with a change in the electron density distribution in the damaged layer, which, in turn, leads to the appearance of metastable states, the deformation of which can lead to the initialization of

structure destabilization processes and their transformations. In the case of ions, structural changes primarily stem from the ionization energy losses of incident ions when they interact with electron shells. This, in turn, gives rise to effects related to the anisotropy of electron density distribution within ceramics. Such changes can subsequently lead to destabilization of the crystal structure, as well as the appearance of metastable states, which, as can be seen from the data of X-ray phase analysis, lead to polymorphic transformations.

In the case of doped ceramics with different concentrations of the MgO dopant, no polymorphic transformations were found, and the main alterations in the structural parameters were associated primarily with the distortion of the crystal lattice. It should be noted that a change in the phase composition of ceramics with an increase in the concentration of the MgO dopant leads to an increase in the stability and resistance to swelling of the crystal structure, which confirms the previously stated assumption about the higher stability to radiation softening of ZrO₂ ceramics in the tetragonal and cubic phases in comparison with the monoclinic one [21,22]. In the case of ceramics in which the presence of inclusions in the form of MgO grains was observed, the degree of swelling of the crystal lattice, depending on the irradiation fluence, was minimal in comparison with other types of ceramics, and the maximum swelling value was no more than 0.5% of the initial value.

Based on the obtained results of the assessment of swelling at the maximum irradiation fluence (10^{14} ion/cm²), it is possible to estimate the increase in the resistance of ceramics to radiation damage and swelling depending on the phase composition. Data are presented as insets in Figure 3. According to the calculations obtained, the increases in resistance to radiation-induced swelling for samples Z1, Z2, and Z3 in comparison with the swelling value for sample Z0 are 1.6, 2.3, and 7.2 times, respectively. At the same time, the difference of more than seven times for sample Z0 is due to the presence of interfacial boundaries, which prevent the deformation distortion of the ceramic structure during the accumulation of radiation damage.

The changes in strength characteristics depending on the phase composition and irradiation fluence are shown in Figure 5. These dependences reflect the effect of hardening with a variation in the phase composition due to a variation in the MgO dopant concentration in the case of initial ceramics, alongside the dynamics of radiation softening depending on the irradiation fluence. The presence of inhomogeneities associated with the formation of interphase boundaries at high concentrations plays a positive role, which consists of increasing stability to radiation damage, and also leads to a decrease in deformation distortions in the structure of ceramics at high irradiation fluences. In this case, for ZrO₂/MgO samples with a high concentration of the MgO dopant, the formation of interphase boundaries leads to the creation of additional barriers to the propagation of microcracks under external influences.

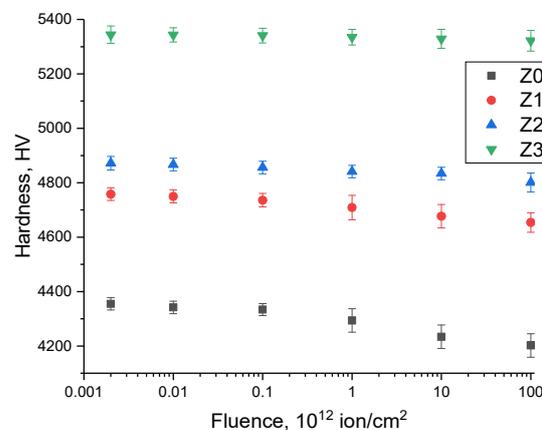


Figure 5. The results of changes in the hardness of ceramics depending on the irradiation fluence and the phase composition of ceramics.

The general view of the presented data on changes in the hardness of ceramics shows an increase in hardness with a change in the phase composition, which is more than 10–12% in the transition from monoclinic to a tetragonal and cubic structure, and more than 22% in the formation of ceramics of the ZrO_2/MgO type, with inclusions in the form of the MgO phase in the interboundary space. Moreover, the presence of these inclusions for ZrO_2/MgO ceramics of sample Z3 causes maximum hardening, as well as high resistance to embrittlement as a result of radiation damage accumulation when the irradiation fluence changes.

An evaluation of hardness variations relative to the irradiation fluence showed that ceramics with a monoclinic crystal structure are the least resistant to softening processes, for which, in addition to the accumulation of radiation damage and deformations, polymorphic transformation processes are observed at fluences above 10^{13} ion/cm². In this case, at the highest irradiation fluence, the maximum reduction in hardness exceeds 3.5% compared to the initial value for a non-irradiated sample.

For ceramics with tetragonal and cubic-crystal structure types, the decrease in hardness is much less pronounced in comparison with the monoclinic types of ceramics. This, in turn, indicates the effect of strengthening and increasing the resistance to cracking and embrittlement of ceramics with a change in their phase composition.

Determining the thermophysical parameters of ceramics, as well as the dynamics of their change as a result of the accumulation of radiation damage, is one of the key criteria when choosing ceramics as inert matrices for dispersed nuclear fuel. The high values of thermal conductivity, as well as the preservation of its stability during the accumulation of radiation damage during operation, will increase the service life of nuclear fuel, as well as the degree of its burnup. Figure 6 shows the dependences of the change in the values of the thermal conductivity calculated using Formula (1), reflecting the effect of the phase composition of ceramics with a variation in the dopant concentration, alongside the accumulation of radiation damage with the irradiation fluence growth. The general trends in the alteration in the thermal conductivity coefficient for the initial samples are characterized by an increase in heat transfer due to the addition of magnesium oxide, which, unlike zirconium dioxide, has higher thermal conductivity. The maximum increase in thermal conductivity in this case is observed for sample Z3, for which the increase was more than 40% compared with the value of thermal conductivity of sample Z0.

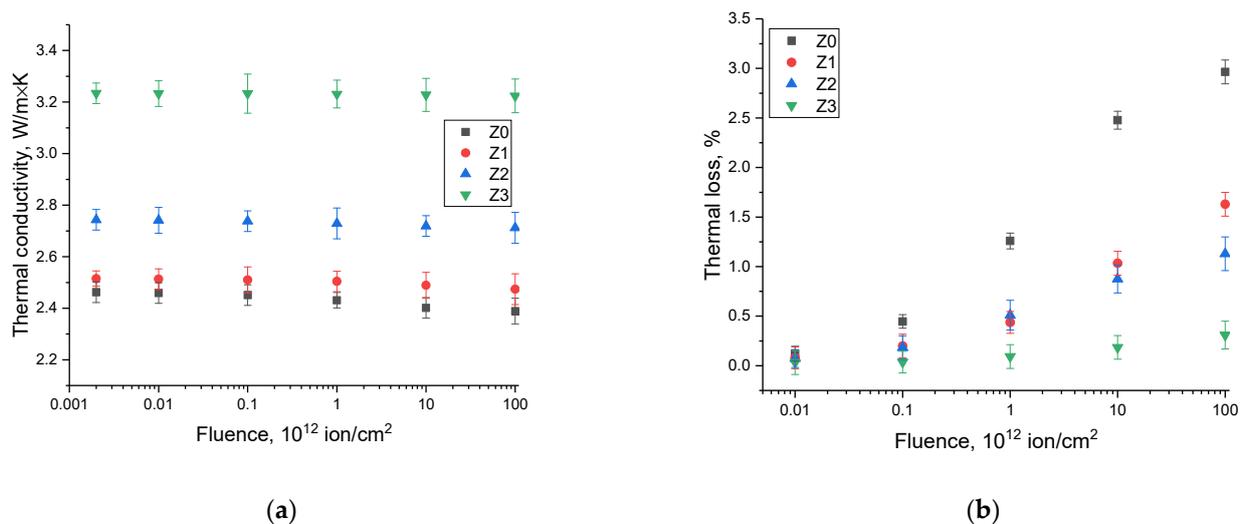


Figure 6. Results of changes in thermophysical parameters: (a) change in the thermal conductivity coefficient; and (b) change in heat loss.

In the case of a variation in the irradiation fluence for all the samples under study, a decrease in the thermal conductivity for sample Z0 was observed, which at the maximum irradiation fluence was more than 3%.

At the same time, the decrease in thermal conductivity (increase in heat losses) aligns well with the alterations in structural parameters (the amount of swelling of the crystal lattice due to its deformation), which indicates a direct relationship between the disordering of the crystal structure and the phonon heat-transfer mechanisms. The explanation for this may be the following. In the case of dielectric ceramics, the main mechanisms of heat transfer are phonon mechanisms, which consist of the scattering of phonons in the crystal lattice. In this case, the formation of defects or dislocations leads to a decrease in the transmission rate due to an increase in heat dissipation and an increase in heat loss. In this case, an elevation in the concentration of defects due to deformation distortion of the crystal structure leads to a decrease in thermal conductivity, which is clearly seen in the dependences presented in Figure 6. When forming ceramics with a crystal structure that is more resistant to deformation distortion (in the case of samples Z1 and Z2), a decrease in heat losses for irradiated samples is observed, which indicates an increase in stability and preservation of the stability of thermophysical parameters. For sample Z3, the decrease in the thermal conductivity in the case of large irradiation fluences is no more than 0.5%, which is within the permissible error range. Thus, it can be concluded that the formation of ceramics with a cubic structure, as well as when there are inclusions in the form of MgO in the ceramic structure, leads to an increase not only in the resistance to external influences, but also in maintaining the stability of thermophysical parameters.

The results of experiments to determine the resistance of ceramics to the thermal expansion of the crystal structure, as a result of long-term thermal annealing, are presented as dependences of changes in the volumetric and linear thermal expansion coefficients on the irradiation fluence (see Figure 7). Formulas (2) and (3) were used to estimate these values.

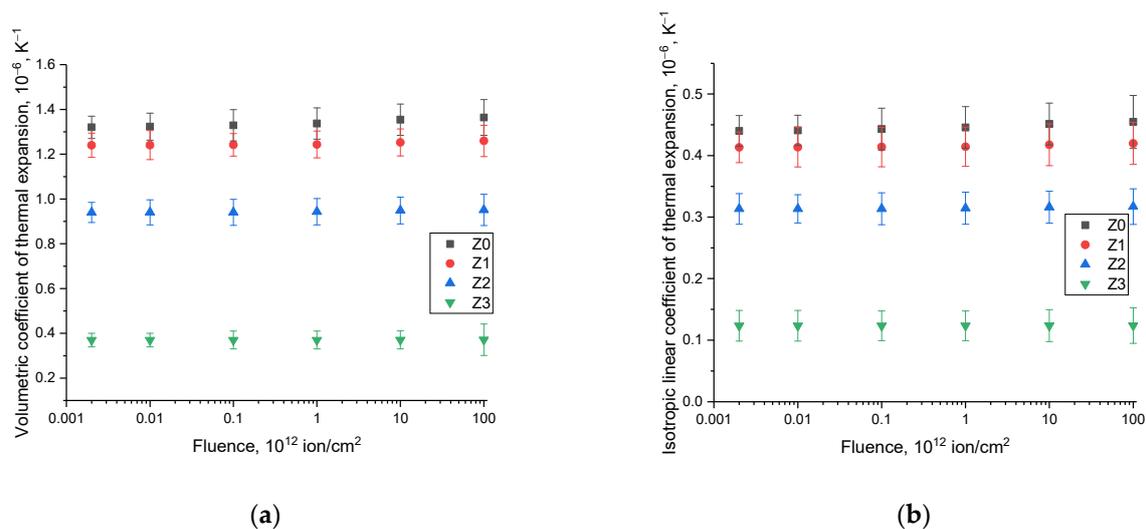


Figure 7. The results of experiments to determine the resistance to thermal expansion: (a) change in the coefficient of volumetric thermal expansion; and (b) change in the coefficient of linear thermal expansion.

As is evident from the provided data, the most significant alterations associated with an increase in thermal expansion coefficients in irradiated samples are observed for ceramics with a monoclinic structure, which, as a result of irradiation, undergo polymorphic transformations under high-dose irradiation. Such a change is due to the accumulation of a high concentration of structural distortions. The effect of high temperatures on these leads to an increase in their mobility, and, as a consequence, an increase in the expansion of the crystal structure. Moreover, this effect is more pronounced for high irradiation fluences, in the case where the concentration of defective inclusions is more than 3%. For ceramics with a body-centered crystal structure, there are practically no changes in the values of volumetric and linear thermal expansion, both in the case of initial samples and for irradiated samples. Such stability is primarily due to the high stability of the

crystal structure to swelling, as well as good thermal conductivity, which, under prolonged thermal exposure, prevents the occurrence of local overheating of the samples, as well as their destabilization, which is observed for sample Z0.

Summing up the general results of the obtained dependences of the influence of changes in the concentration of the MgO dopant on the resistance to radiation damage of ZrO₂ ceramics due to the formation of polymorphic transformations in them in the initial state, the following conclusions can be made. Firstly, the results of structural changes for ZrO₂ ceramics undoped with MgO, associated with the accumulation of radiation damage during irradiation with heavy ions, are in good agreement with the results of works [27,28]. According to these works, structural changes initiated by the interaction of ions with the crystal lattice during their accumulation lead to polymorphic transformations and the deterioration of ceramic properties. At the same time, in [27,28], it was suggested that when ZrO₂ ceramics transition to the tetragonal or cubic phase, the rate of accumulation of radiation damage decreases due to structural changes associated with polymorphic transformations [29–31]. The results of increased stability to radiation swelling and destructive changes in strength and thermophysical parameters due to increased dopant concentrations in the ceramic composition and the formation of interphase boundaries (at high concentrations) also have good agreement with the results of [32,33]. This strengthening is based on the following hypothesis: an increase in the contribution of interphase boundaries increases resistance to radiation damage by creating additional obstacles to the migration processes of point and vacancy defects, which reduces the likelihood of their agglomeration. In this case, at high concentrations of MgO, the effect of increasing resistance to radiation damage is influenced by a synergistic effect associated with the lower rate of destruction of ZrO₂ ceramics during their transition to the cubic phase, combined with their presence in the structures of interphase boundaries that arise during the formation of MgO grains.

4. Conclusions

The established dependences of changes in the structural, strength, and thermophysical parameters during studies on the effects of alterations in the phase composition of ZrO₂ ceramics, associated with a fluctuation in the MgO dopant concentration, have a good correlation with each other. The data obtained indicate that the main factor influencing the change in the strength and thermophysical parameters of ZrO₂ ceramics is the degree of structural disorder associated with swelling, and, as a consequence, the accumulation of a defective fraction in the damaged volume. At the same time, it was found that in ZrO₂/MgO ceramics, the highest radiation damage resistance occurred upon irradiation with Kr¹⁵⁺ ions, even in the case of high-dose irradiation. This occurred in the structure in which the presence of the MgO interstitial phase in the form of grains located in the intergranular space was observed. The presence of these inclusions in the composition of ceramics leads to an increase in radiation damage resistance by more than seven times in comparison with ZrO₂ ceramics with a monoclinic structure, in which, when irradiated with a fluence above 10¹² ion/cm², the formation of the m-ZrO₂ → t-ZrO₂ type polymorphic transformation occurs, which is accompanied by a destructive alteration in the volume and strength properties of ceramics.

In future, the proposed ceramic compositions, which have a higher resistance to radiation damage—and, as a consequence, associated structural changes and deformation distortions—can be used in the nuclear industry in the design of new types of nuclear installations. The use of new materials in the construction of nuclear power plants will increase their service life, which will reduce the dependence of the energy sector on hydrocarbon raw materials, as well as increase the reliability of nuclear physical installations for further use.

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