

# Comprehensive study of changes in the optical, structural and strength properties of ZrO<sub>2</sub> ceramics as a result of phase transformations caused by irradiation with heavy ions.

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## Abstract

This work is devoted to the study of the effect of irradiation with Kr<sup>15+</sup> and Xe<sup>23+</sup> heavy ions with energies of 147 and 220 MeV, respectively, on the change in the optical, structural and strength properties of ceramics ZrO<sub>2</sub>. Polycrystalline ZrO<sub>2</sub> ceramics with a tetragonal type of crystal structure, which are highly resistant to external influences, mechanical strength to cracking, and hardness were chosen as the object of research. The choice of heavy ions Kr<sup>15+</sup> and Xe<sup>23+</sup> is due to the possibility of simulating the effect of nuclear fission fragments in an atomic reactor, and the choice of irradiation doses of  $1 \times 10^{13}$  -  $1 \times 10^{14}$  ion/cm<sup>2</sup> is due to the possibility of simulating the effects of overlapping defect regions arising along the trajectory of ions in the material. Using the X-ray diffraction method, it was found that in the case of irradiation with heavy ions, an increase in the radiation dose leads to phase transformations of the tetragonal type of the crystal lattice into a cubic one. In this case, for the samples irradiated with Xe<sup>23+</sup> ions at an irradiation dose of  $1 \times 10^{14}$  ion/cm<sup>2</sup>, an almost complete phase transformation is observed. Dependences of changes in strength and optical characteristics on the type of irradiation and dose load have been established.

**Keywords:** zirconium dioxide, construction materials, optical properties, form factor, phase transformation, heavy ion irradiation

## Introduction

Today, among Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, BeO, MgO, ThO<sub>2</sub> oxide ceramics, ZrO<sub>2</sub> ceramics are of particular interest, which have higher mechanical and strength characteristics, excellent optical properties and resistance to various external influences, including radiation damage [1-5]. Due to these properties, ZrO<sub>2</sub> ceramics are one of the promising materials for inert nuclear fuel matrices, radioactive waste storage, and structural materials [6,7]. At the same time, in the case of using ZrO<sub>2</sub> ceramics as structural materials, special attention should be paid to phase polymorphic transformations in ceramics, since it is known that ZrO<sub>2</sub> has several phases that are capable of turning into one another as a result of external influences [8-10]. As a rule, the processes of phase transformation into ZrO<sub>2</sub> occur as a result of temperature heating or mechanical action, followed by the formation of solid solutions. At the same time, in some cases of practical application polymorphic transformations are used for so-called transformational hardening caused by stabilization of high-temperature phases [11,12]. The result of this process is a significant increase in the strength and fracture toughness of ceramics, which makes these materials promising in the field of mechanical engineering and reactor engineering.

Characteristics of resistance to radiation damage and stability of structural and mechanical properties during long exposure time play an important role in practical application of oxide ceramics as structural materials [13-15]. At the same time, all studies of radiation damage can be divided into three groups, according to the type of ionizing radiation: 1) studying the processes of helium and hydrogen swelling as a result of irradiation with large doses of helium or protons;

2) ion implantation and modification; 3) study of mechanisms of damages and deformations, as well as processes of cracking when irradiated with heavy ions. Among these areas, special attention is paid to the third group of studies, which not only allow obtaining new fundamental data on the nature of radiation damage, but also with high accuracy allow simulating the conditions of radiation exposure in an atomic reactor during the formation of uranium fission fragments [16-20].

Based on the foregoing, the main goal of this work is to study the processes of radiation damage arising from irradiation with  $\text{Kr}^{15+}$  and  $\text{Xe}^{23+}$  heavy ions with energies of 147 and 220 MeV, respectively, as well as to study the kinetics of polymorphic transformations in  $\text{ZrO}_2$  ceramics as a result of irradiation. The relevance of this study lies not only in obtaining new experimental data, but also in assessing the radiation resistance of  $\text{ZrO}_2$  ceramics to radiation comparable to fission fragments. At the same time, the choice of radiation doses  $1 \times 10^{13}$ - $1 \times 10^{14}$  ion/cm<sup>2</sup> is due to the possibility of simulating the effect of overlapping defective areas during irradiation, which significantly change the kinetics of radiation damage. Considerable attention is paid to the study of changes in optical properties, which characterize changes in the optical and electron density of ceramics under irradiation. The choice of  $\text{ZrO}_2$  ceramic type as an object of study is due to its great potential for use as a basis for structural materials operating at high temperatures, as well as a high radiation background. The use of  $\text{ZrO}_2$  ceramics as a basis for structural materials is due to their high thermal conductivity and melting point, as well as their good resistance to external influences. However, despite all the prospects for using these types of ceramics, there are still many questions regarding the radiation resistance of ceramics and the mechanisms of defect formation.

## Experimental part

The objects under study were  $\text{ZrO}_2$  polycrystalline ceramics manufactured by Dongguan Mingrui Ceramic Tech. Co. Ltd. (Dongguan city, Guangdong, China).

Irradiation with heavy ions  $\text{Kr}^{15+}$  and  $\text{Xe}^{23+}$  with energies of 147 and 220 MeV, respectively, was carried out at a DC-60 heavy ion accelerator (Nur-Sultan, Kazakhstan). The irradiation doses were  $1 \times 10^{13}$ ,  $5 \times 10^{13}$ ,  $1 \times 10^{14}$  ion/cm<sup>2</sup>. Irradiation was carried out in vacuum at room temperature. The samples were placed on water-cooled targets in order to prevent overheating of the samples and partial annealing of defects as a result of heating.

According to the calculated ionization loss data obtained using the SRIM Pro 2013 program code [21], the maximum ion path length in  $\text{ZrO}_2$  ceramics with a density of 6.15-6.17 g/cm<sup>3</sup> is  $11.8 \pm 0.5$   $\mu\text{m}$  and  $12.3 \pm 0.5$   $\mu\text{m}$  for  $\text{Kr}^{15+}$  and  $\text{Xe}^{23+}$  ions with energies of 147 and 220 MeV respectively. The energy losses for  $\text{Kr}^{15+}$  ions upon collisions with electron shells are 17200 keV/ $\mu\text{m}$ , with nuclei 43.9 keV/ $\mu\text{m}$ , 96.5 % of the energy is spent on ionization processes, the number of vacancies formed by one ion when passing through the material is  $29800 \pm 200$  vacancies/ion. The energy losses for  $\text{Xe}^{23+}$  ions upon collisions with electron shells are 27100 keV/ $\mu\text{m}$ , with nuclei 98.3 keV/ $\mu\text{m}$ , 97.3% of the energy is spent on ionization processes, the number of vacancies formed by one ion when passing through the material is  $54600 \pm 200$  vacancies/ion. As can be seen from the data presented, an increase in the ion energy and mass leads to a slight increase in the ion range in the material; however, the energy transfer to the nuclear and electronic subsystem during the interaction of  $\text{Xe}^{23+}$  ions with the crystal structure is almost 1.5-2 times higher than the analogous values for  $\text{Kr}^{15+}$  ions.

Nondestructive control of changes in structural characteristics, as well as assessment of phase transformations were carried out using the X-ray diffraction method. This method of analysis was carried out using a D8 Advance Eco powder diffractometer (Bruker, Germany). The X-ray diffraction patterns were recorded in the Bragg-Brentano geometry, in the angular range  $2\theta = 20$ - $90^\circ$ , with a step of  $0.03^\circ$  and a spectrum acquisition time at a point of 1 sec. Decoding of diffractograms, as well as determination of the phase composition and structural parameters was

carried out using the DiffracEVA v.4.2 program code, which is based on a full-profile analysis of diffractograms. The lattice parameters were calculated based on the diffraction maxima position and their displacement from the reference values using the Nelson-Taylor method. Refinement was carried out for the most intense peaks. The determination and subsequent refinement of the phase composition was carried out according to the standard method of phase selection based on the values of interplanar distances, intensities, and positions of diffraction maxima for reference values from the PDF-2 database. The crystallinity degree of the studied samples of ceramic was estimated by analyzing the profiles of diffraction peaks and comparing them with background radiation.

The optical properties of the ceramics before and after irradiation were evaluated by analyzing the UV-Vis spectra obtained using a Specord-250 UV spectrophotometer (Jena Analytic, Germany). The spectra were recorded in the wavelength range from 350 to 800 nm with a step of 0.1 nm and a spectrum acquisition rate of 1 nm/s.

The study of the morphological features of changes in the surface of the samples as a result of changes in the concentration of defects was carried out using the method of atomic force microscopy, implemented using an atomic force microscope AIST-NT SPM microscope (Chernogolovka, Russia).

Determination of the microhardness of the ceramic surface and its changes as a result of dose loads was carried out using the standard method for determining the hardness by the Vickers method using a microhardness tester. The ceramic hardness value was determined according to the standard procedure for analyzing the indentation of the indenter on the sample, by measuring its geometric parameters with subsequent recalculation according to the standard Vickers method.

## Results and discussion

Figure 1 shows the data on changes in the X-ray diffraction patterns of the studied ceramics, obtained using the method of X-ray phase analysis. The general view of the X-ray diffraction patterns of the initial samples indicates a polycrystalline structure of ceramics, with a distinguished direction of grain orientation (011)/(111), which is characteristic of the tetragonal or cubic type of crystal structures. Using the Rietveld method based on the approximation of diffraction lines and estimates of the contributions of different phases, it was found that the structure of the initial ceramics is a mixture of two phases characteristic of the tetragonal and cubic  $ZrO_2$  phases. The comparison of the obtained phase data with the reference values was carried out by selecting the most suitable card values for the position of the diffraction lines, as well as evaluating the shape of the diffraction reflections. As a result of this analysis, it was found that the dominant phase in the structure is the tetragonal phase of  $ZrO_2$ , corresponding to the card data PDF-00-050-1089 (the probability of coincidence is more than 90%). The contribution of this phase was more than 80%. The second phase, which was determined by changing the shape of diffraction reflections and their distortion, was the cubic phase of  $ZrO_2$ , corresponding to the card values PDF-01-071-4810 (the probability of coincidence is more than 70%). This phase composition may be due to synthesis processes that are associated with thermal sintering and subsequent processes of the formation of substitutional or interstitial solid solutions.

Also, the analysis of the shape of the diffraction lines and their comparison with the background radiation made it possible to establish that in the initial state the degree of perfection of the crystal structure is more than 95%, which indicates a high degree of ordering and a low content of the defective fraction, the presence of which may be due to the processes of obtaining ceramics.

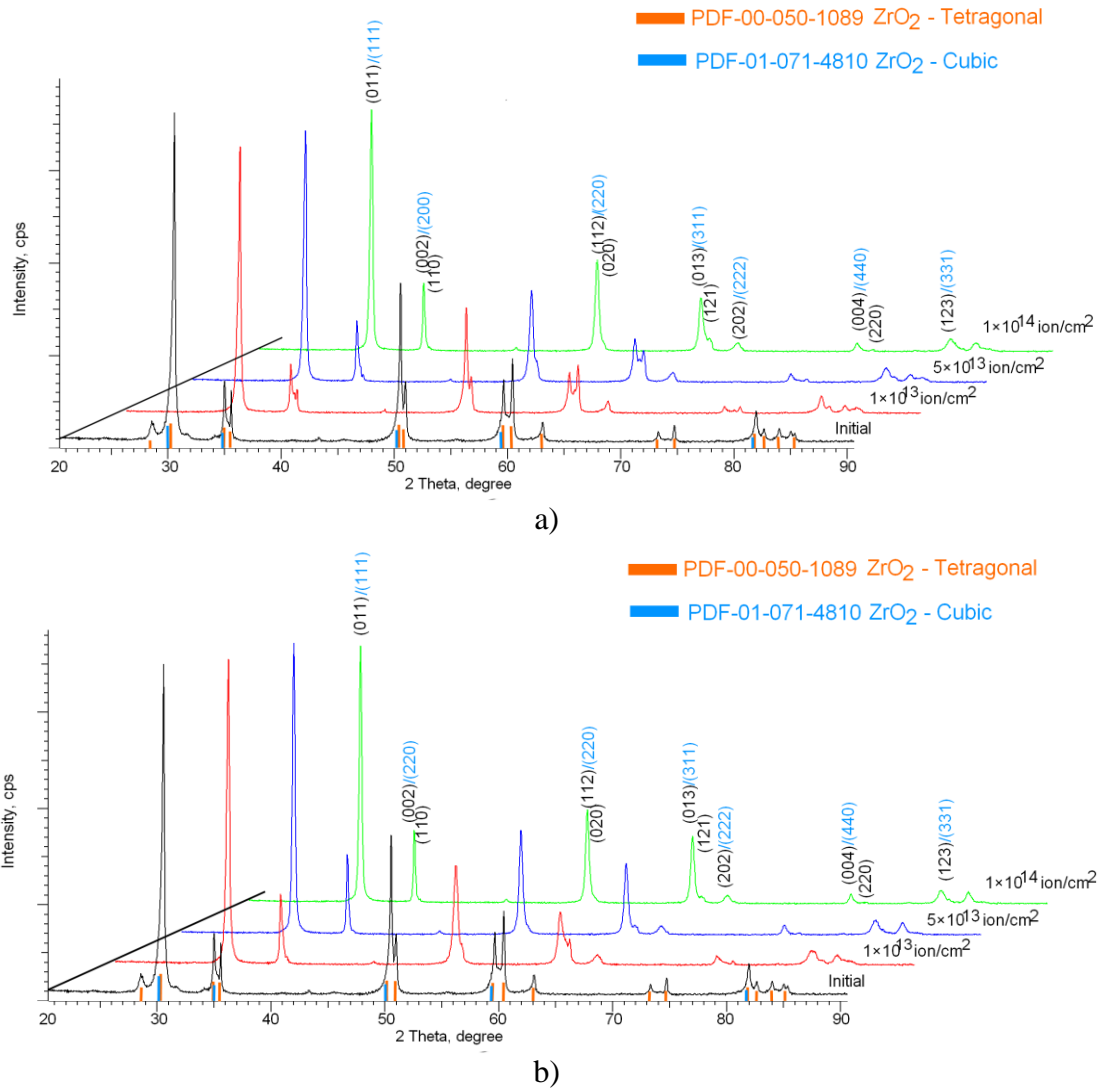


Figure 1. X-ray diffraction patterns of the studied  $\text{ZrO}_2$  ceramics before and after irradiation: a)  $\text{Kr}^{15+}$  ion irradiated; b)  $\text{Xe}^{22+}$  ion irradiated

For irradiated samples, changes in diffraction patterns are primarily associated with a slight decrease in the intensity of reflections, which indicates a change in the degree of perfection and in the sizes of coherent scattering regions (crystallite sizes). In this case, some of the diffraction lines disappear, and the main lines are shifted to positions characteristic of the positions of the peaks characteristic of the cubic phase. Figure 2 shows the most pronounced changes in the shape of diffraction reflections, indicating a phase transformation and displacement of the tetragonal phase. As can be seen from the presented data, in the case of irradiation with  $\text{Kr}^{15+}$  ions at an irradiation dose of  $1 \times 10^{13}$   $\text{ion/cm}^2$ , a sharp decrease in the intensity of the (110) reflection is observed, and a further increase in the irradiation dose leads to its complete dissolution in the background radiation. At the same time, the intensity of the (002)/(220) reflection, which is characteristic of both tetragonal (002) and cubic (220) phases, practically does not change with an increase in dose, and the position shifts to the region of angles characteristic of the positions of the cubic phase reflections. A similar picture, but with more pronounced changes and rearrangements of the structure, is also observed for samples irradiated with  $\text{Xe}^{22+}$  ions, for which the disappearance of the (110) reflection, characteristic only of the tetragonal phase, is observed already after an irradiation dose of  $1 \times 10^{13}$   $\text{ion/cm}^2$ .

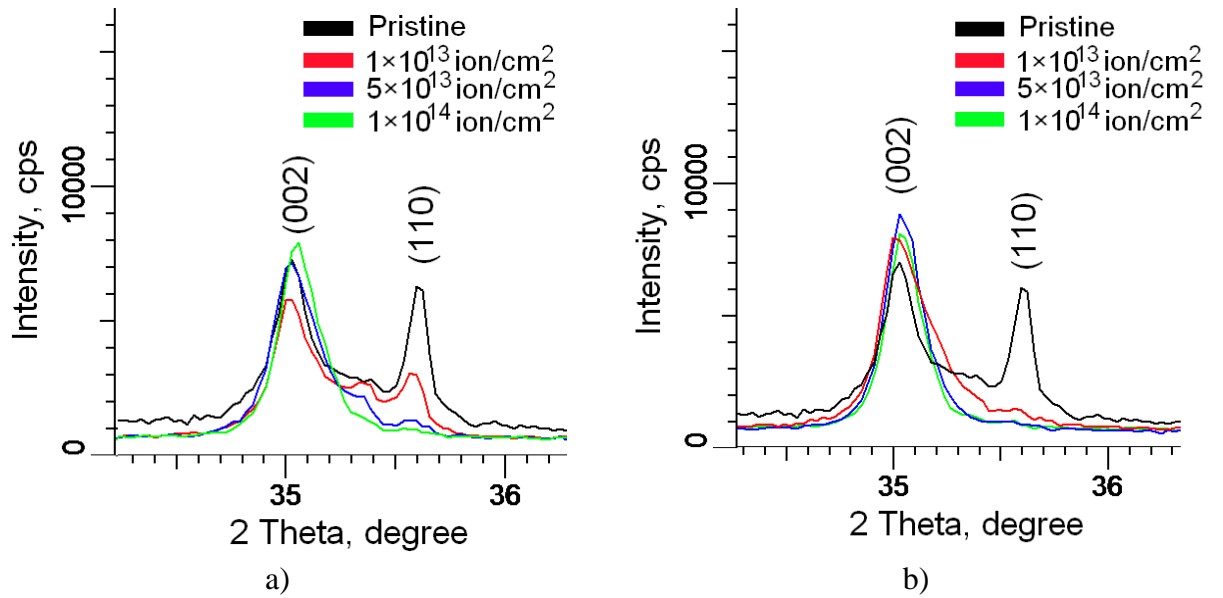


Figure 2. Change in shape and intensity of peaks (002) and (110) for the studied samples of ZrO<sub>2</sub> ceramics depending on the type of exposure: a) Kr<sup>15+</sup> ion irradiated; b) Xe<sup>22+</sup> ion irradiated

Based on the change in the shape and intensity of the diffraction peaks (002) and (110) using formula (1) [22], the shape factor (*M*) was determined, which allows determining the type of texture, as well as the shape of the grains and the change in their orientation depending on the type of external effects.

$$M = \frac{I_{002}}{(I_{002} + 2I_{110})}, \quad (1)$$

where *I*<sub>002</sub>, *I*<sub>110</sub> are the intensities of diffraction reflections. In the case when *M*=0, the block texture prevails in the structure; when *M*=1, the texture is lamellar. Figure 3 shows the results of calculating the form factor depending on the type of external effects.

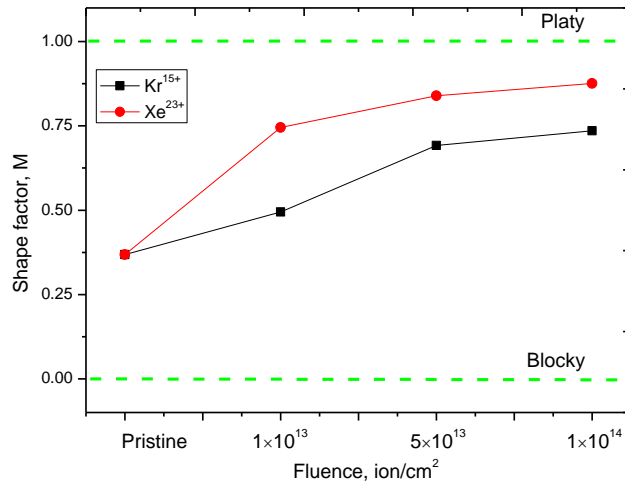


Figure 3. Graph of the form factor change depending on the radiation dose and the type of ions (the dashed lines indicate the values typical for the blocks and plates types)

In the initial state, the shape of the grains is of a mixed type (blocks and plates). Irradiation, which initiates the processes of phase transformations as a result of the interaction of ions with the crystal structure, leads to a change in the shape of grains and the predominance of a plate-like shape in the structure of ceramics. At the same time, under irradiation with xenon ions, the change in shape is more pronounced than in the case of irradiation with krypton ions.

Figure 4 shows the results of changes in the phase composition of the studied ceramics as a result of irradiation with various types of ions, which demonstrate the processes of phase transformations depending on the radiation dose. In the initial state, as mentioned earlier, the ceramics under study are a mixture of two phases: the dominant tetragonal ( $t\text{-ZrO}_2$ ) and cubic ( $c\text{-ZrO}_2$ ). This mixture is characteristic of the types of ceramics obtained by sintering at high temperatures. However, according to the literature, it is known that  $\text{ZrO}_2$  ceramics have the most pronounced polymorphism properties of all types of oxide ceramics, which directly depend on the parameters of external effects, such as heating, compression or irradiation. At the same time full polymorphic transformation of  $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$  happens only at very high temperatures (2000-2300°C) or in the presence of dopants, such as oxide of yttrium or aluminum. As can be seen from the data presented, irradiation leads to the initialization of polymorphic transformation processes, and depending on the type of particles and radiation doses, the rate of these processes varies. As is known, the processes of polymorphic transformation  $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$  occur either as a result of external mechanical influences or at high temperatures. In the case of irradiation when an ion passes through a material, the energy loss of the ions is primarily due to the processes of elastic and inelastic collisions with electron shells and nuclei. The result of such interactions is the transfer of a large amount of energy to the crystalline subsystem, which is converted from kinetic energy to thermal energy. At the same time, unlike metals, the presence of energy barriers in ceramics between rows of ordered atoms leads to the fact that all changes occur in a small volume limited by these barriers. As a result, local regions of overheating arise, which, according to the theory of radiation damage based on the model of thermal bursts [21-24], have dimensions of the order of several tens of nanometers, the temperature in which can be several thousand degrees. In the case of irradiation with large doses, there is an effect of overlapping defective regions called "latent tracks" of ions, the dimensions of which vary from several nanometers to 20-30 nm depending on the type and energy of the incident ions. At the same time, the structural changes caused by irradiation no longer become isolated, as in the case of low doses, but have a volumetric character, which leads to an increase in the rate of polymorphism processes. Thus, from graphs in Figure 4, it can be seen that in the case of irradiation with  $\text{Kr}^{15+}$  ions, the process of polymorphic transformation  $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$  with an increase in the irradiation dose leads to insignificant changes, and the formation of a mixture of two phases with approximately equal content of both at an irradiation dose of  $1 \times 10^{14}$  ion/cm<sup>2</sup>. At the same time, for samples irradiated with  $\text{Xe}^{22+}$  ions, irradiation at doses of  $5 \times 10^{13}$ - $1 \times 10^{14}$  ion/cm<sup>2</sup> leads to almost complete polymorphic transformation  $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$ . Thus, it can be concluded that irradiation with  $\text{Xe}^{22+}$  ions, which have a much larger size, and, therefore, large energy losses, as well as the size of defect regions when overlapping, at irradiation doses of  $1 \times 10^{14}$  ion/cm<sup>2</sup> leads to a complete polymorphic transformation  $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$ .

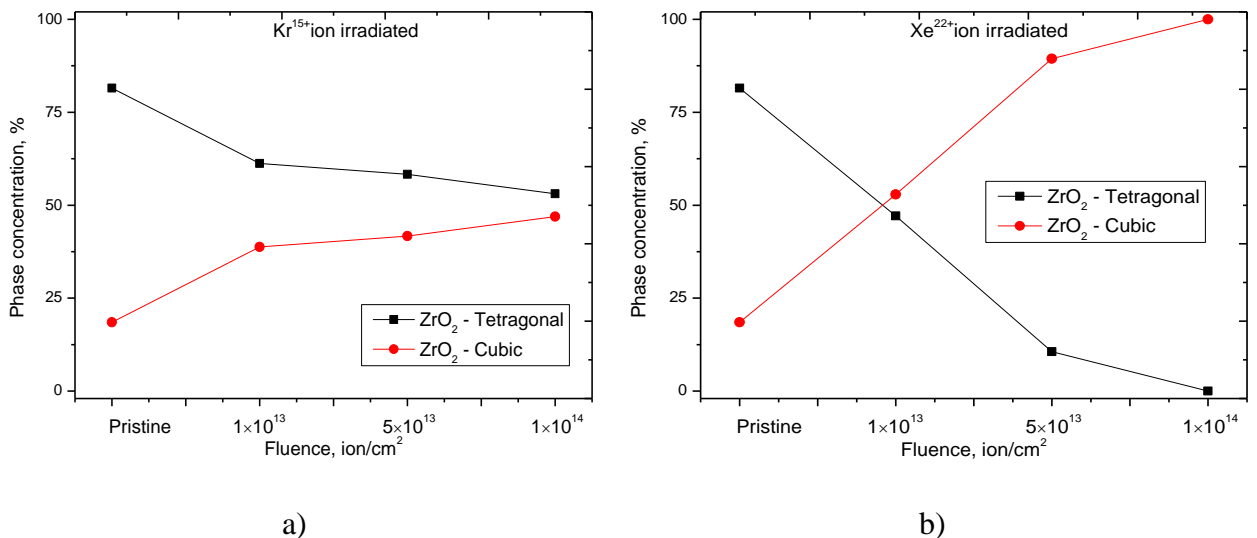


Figure 4. Diagrams of changes in the phase composition of ZrO<sub>2</sub> ceramics depending on type of radiation and radiation dose: a) Kr<sup>15+</sup> ion irradiated; b) Xe<sup>22+</sup> ion irradiated

Based on the obtained diffraction patterns, the structural parameters of the crystal lattice of the studied ceramics were evaluated, as well as the change in its volume as a result of irradiation and polymorphic transformation processes. The evaluation results obtained by determining the provisions of diffraction maxima and their relationship with the reference values of the database with further refinement using the full-profile analysis method are presented in Tables 1-2. As can be seen from the presented data, the main changes of crystal lattice parameters for both phases are related to its distortion and volume increase, which indicates deformation processes of swelling caused by radiation. Moreover, for ceramics irradiated with Xe<sup>22+</sup> ions, the deformation processes of the crystal lattice are more pronounced, which is associated with large energy losses of ions and more transferred energy to the sublattice, which can cause additional distortion of interplane distances.

Table 1. Data on changes in structural parameters of ZrO<sub>2</sub> ceramics irradiated with Kr<sup>15+</sup> ions

Impact type	Irradiation with Kr <sup>15+</sup> ions				
	Parameter	Pristine	1x10 <sup>13</sup> ion/cm <sup>2</sup>	5x10 <sup>13</sup> ion/cm <sup>2</sup>	1x10 <sup>14</sup> ion/cm <sup>2</sup>
Lattice parameter, Å	Cubic, Fm-3m (225)	a=5.0912±0.0013	a=5.0932±0.0011	a=5.0973±0.0016	a=5.0993±0.0015
	Tetragonal P42/nmc(137)	a=3.5624±0.0014, c=5.1045±0.0015	a=3.5681±0.0014, c=5.1168±0.0011	a=3.5709±0.0017, c=5.1193±0.0021	a=3.5799±0.0014, c=5.1153±0.0023
Lattice volume, Å <sup>3</sup>	Cubic, Fm-3m (225)	131.97	132.12	132.44	132.6
	Tetragonal P42/nmc(137)	64.78	65.14	65.23	65.56

Table 2. Data on changes in the structural parameters of ZrO<sub>2</sub> ceramics irradiated with Xe<sup>22+</sup> ions

Impact type	Irradiation with Xe <sup>22+</sup> ions				
	Parameter	Pristine	1x10 <sup>13</sup> ion/cm <sup>2</sup>	5x10 <sup>13</sup> ion/cm <sup>2</sup>	1x10 <sup>14</sup> ion/cm <sup>2</sup>
Lattice parameter, Å	Cubic, Fm-3m (225)	a=5.0912±0.0013	a=5.0950±0.0021	a=5.0992±0.0024	a=5.1009±0.0019
	Tetragonal P42/nmc(137)	a=3.5624±0.0014, c=5.1045±0.0015	a=3.5709±0.0021, c=5.1227±0.0014	a=3.5744±0.0011, c=5.1177±0.0016	-
Lattice volume, Å <sup>3</sup>	Cubic, Fm-3m (225)	131.97	132.26	132.58	132.73
	Tetragonal P42/nmc(137)	64.78	65.32	65.69	-

As is known, according to the theory of radiation-induced grain size change involving processes of growth or crushing as a result of irradiation, grain size change is directly related to energy losses of incident ions, as well as the amount of energy transferred to the crystal lattice. According to the model of thermal peaks, the transmitted energy of the incident particles is able to form cascade effects causing local heating of the irradiated area along the trajectory of ion movement, thereby inducing not only the processes of defect formation, their annihilation, but also having a significant effect on grain mobility, their fragmentation or recrystallization caused by distortion and deformation of the crystal structure [23-26]. At the same time, the mobility of grains directly depends not only on the size of grains, but also on the number of radiation defects

arising in the structure of ceramics. Figure 5a shows a graph of the grain mobility factor change ( $K$ ), which was estimated from the ratio:  $(D^3 - D_0^3) \approx K\Phi$ , where  $D$ ,  $D_0$  – grain sizes before and after radiation exposure,  $\Phi$  – radiation flux. As can be seen from the presented data, in the case of irradiation with a dose of  $1 \times 10^{13}$  ion/cm<sup>2</sup>, the mobility coefficient is quite large, with the greatest changes observed for samples irradiated with Xe<sup>22+</sup> ions, for which the energy losses are rather large compared to similar values for Kr<sup>15+</sup> ions. An increase in the irradiation dose and therefore an increase in the defect overlapping areas results in a sharp decrease in the grain mobility coefficient, which indicates an inhibition of grain crushing processes. Such a sharp drop in mobility can be due to both the processes of phase transformations resulting from irradiation and the change in grain shape. At the same time, an increase in the radiation dose leading to grain crushing leads to an increase in dislocation density ( $\delta$ ), since this value is inversely proportional to the square of the grain size value  $\delta \approx 1/D^2$  (see Data of Figure 5b). An increase in the dislocation density leads to a decrease in the mobility of grains in the structure, thereby reducing the likelihood of their fragmentation and deformation. Also, an important role in reducing the mobility of grains is played by the process of polymorphic transformation  $t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2$ .

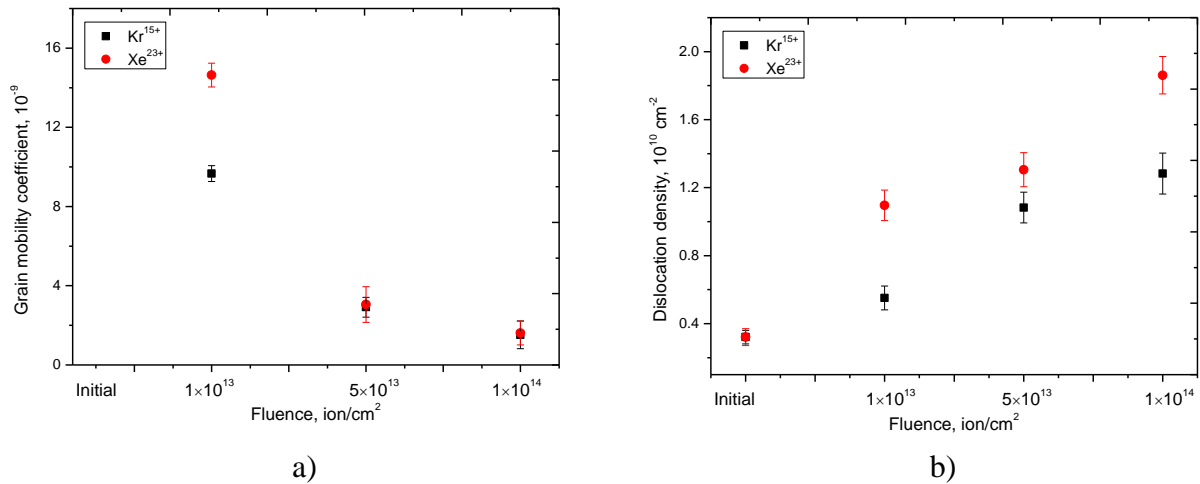


Figure 5. a) Graph of dependence of the grains mobility coefficient change under the action of irradiation; b) Graph of dislocations density change in ceramics structure, calculated on the basis of changes in grain sizes during irradiation.

Figure 6 shows the results of changes in the optical transmission spectra of ceramics before and after irradiation, obtained using the UV-Vis spectroscopy method. The general view of the spectra is characterized by a fundamental absorption edge in the 330-335 nm wavelength region and good transmission capacity in the region characteristic of visible light. For irradiated samples, the main changes in UV-Vis spectra are associated with a shift in the edge of fundamental absorption in the region of 340-360 nm depending on the radiation dose and type of radiation, as well as a sharp decrease in throughput, the drop of which is more than 75-82 % for samples irradiated with Kr<sup>15+</sup> ions and 65-75 % for samples irradiated with Xe<sup>22+</sup> ions. This dramatic change in transmittance is primarily due to a change in defect concentration and dislocation density, as well as phase changes resulting from irradiation.



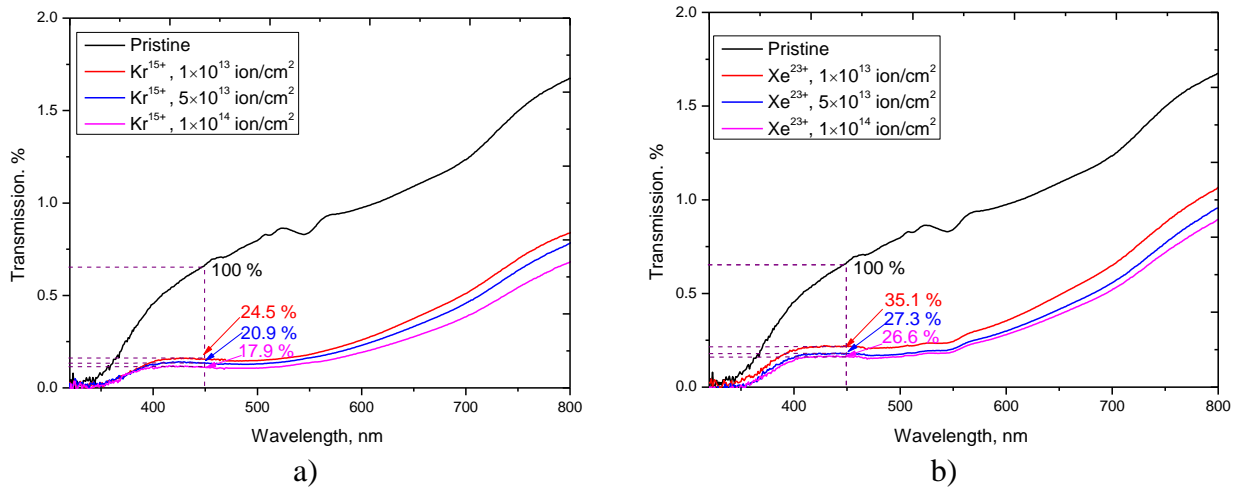


Figure 6. UV-Vis transmission spectra of the investigated ceramic  $ZrO_2$  depending on the type of irradiation and radiation dose: a)  $Kr^{15+}$  ion irradiated; b)  $Xe^{23+}$  ion irradiated (the dashed lines represent the transmission values at a wavelength of 450 nm)

The shift of the fundamental absorption edge, in turn, is associated with a change in the band gap, as well as the electron density in the ceramics. The change in the electron density is due to the fact that positively charged ions passing through the ceramic material pull electrons from their places along their trajectory, as a result of which depletion regions with low electron density appear. Unlike metals, in which the electron density recovery process is reversible, in dielectric ceramics, this electron density recovery process is difficult. Also, a change in the electron density and the formation of a large number of point defects as a result of irradiation leads to the appearance of additional electron traps in the structure, which affect the change in optical density. Figure 7 shows a graph of the dependence of optical density change (absorbance) on the type of exposure. The data obtained indicate that in the case of irradiation with  $Kr^{15+}$  ions, the change in optical density is greater than in the case of irradiation with  $Xe^{23+}$  ions. This difference may be due to the fact that for ceramics irradiated with  $Xe^{23+}$  ions, according to X-ray diffraction data, a complete polymorphic phase transformation  $t-ZrO_2 \rightarrow c-ZrO_2$  was observed, while for samples irradiated with  $Kr^{15+}$  ions this process was not completed in the selected dose range, and the structure of the ceramics was a mixture of two phases. The presence of two phases in the structure has led to the appearance of additional absorbing centers, which have a significant effect on the change in the optical and electron density.

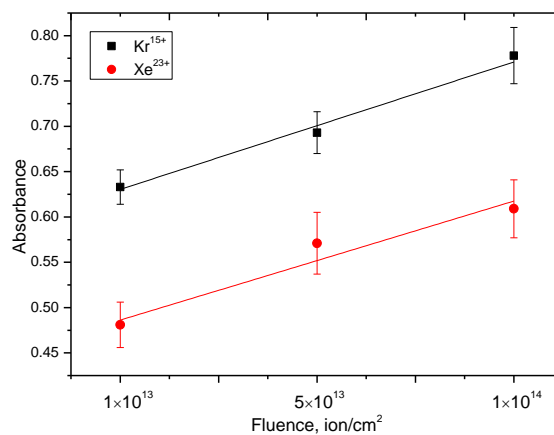


Figure 7. Graph of the dependence of the change in the absorption value of the studied  $ZrO_2$  ceramics at a wavelength of 470 nm, depending on the radiation dose

Figure 8 shows the results of changes in the surface morphology of ceramics depending on the radiation dose and the type of ions, obtained using the method of atomic force microscopy. The

surface of the original ceramic is a relatively smooth surface; the roughness value is no more than 30-50 nm. For irradiated samples, the formation of blisters and hillock-like inclusions on the surface is observed, the presence of which is associated with deformation processes under the action of irradiation. At the same time, an increase in the radiation dose in both cases leads to an increase not only in the concentration of these inclusions, but also in their geometric dimensions, which indicates the cumulative effect of radiation damage. This effect is due to the migration of defects and their agglomeration near the grain boundaries, which serve as sinks of defects. The accumulation of defects near defect sinks leads to an increase in deformation stresses in these areas and to a partial squeezing out of the volume onto the surface. The formation of extended defects is associated with the presence of texture in the structure of ceramics.

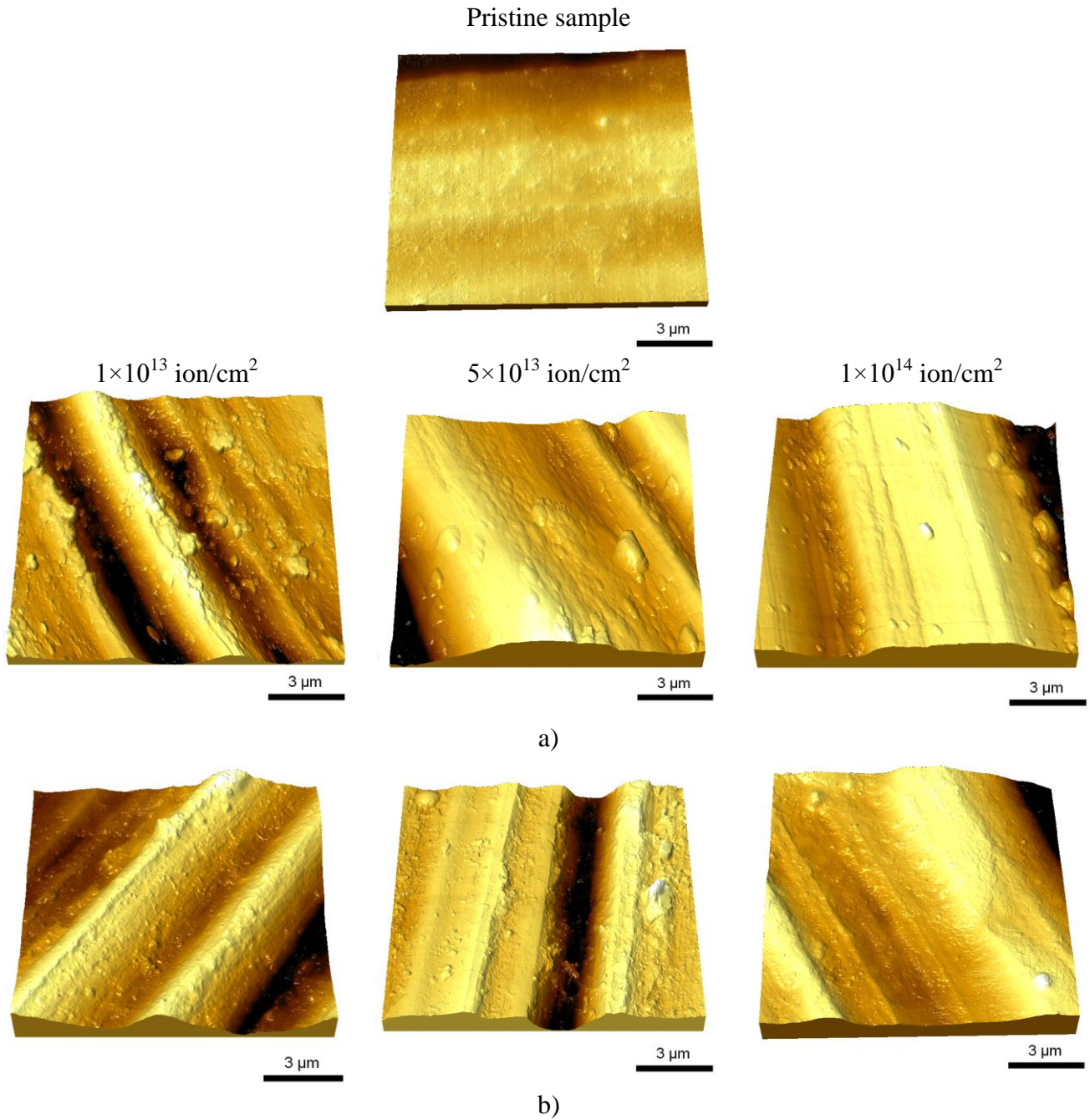


Figure 8. 3D images of changes in the surface morphology of the studied ceramics depending on the type of irradiation: a)  $\text{Kr}^{15+}$  ion irradiated; b)  $\text{Xe}^{22+}$  ion irradiated

Based on topographic changes in the surface of ceramics before and after irradiation, an analysis of the swelling degree of ceramics as a result of irradiation was carried out, the data of which are shown in Figure 9. The obtained dependences of the change in the degree of swelling clearly illustrate the change in surface morphology associated with its degradation as a result of irradiation.

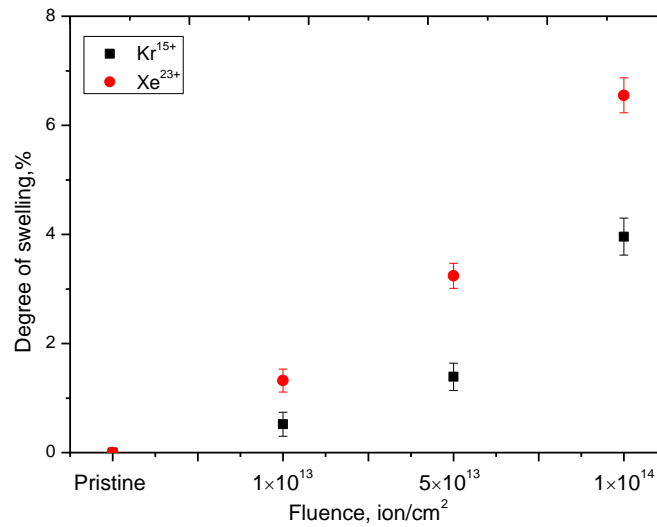


Figure 9. Graph of dependence of surface layer swelling of ceramics as a result of irradiation

Partial surface degradation due to swelling, as well as deformation processes resulting from polymorphic transformations and changes in the concentration of point defects, have a negative effect on the strength characteristics of ceramics. Figure 10 shows the results of the change in the hardness of the near-surface layer exposed to radiation and the change in indenter imprint dimensions that characterize crack resistance.

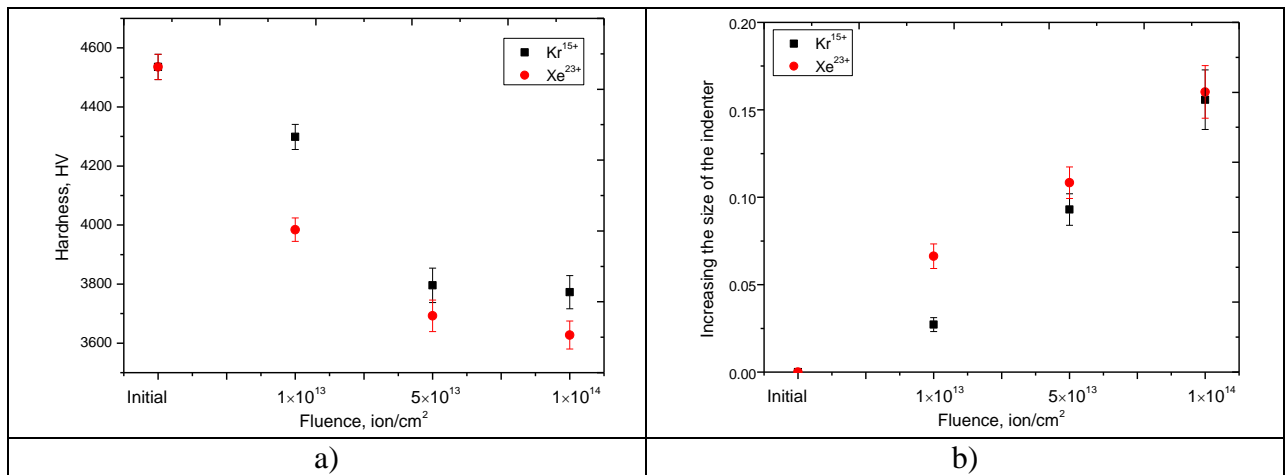


Figure 10. a) Dynamics of ceramics surface hardness change depending on the type of radiation; b) Graph of change in dimensions of indenter imprint characterizing change in value of resistance to crack formation

As can be seen from the data presented, the change in the value of hardness is of a two-stage nature. The first stage is characterized by a sharp decrease in hardness indices, which is associated with a change in the defect structure of the damaged layer, as well as the initiation of phase transformation processes. At the second stage, an increase in the radiation dose from  $5 \times 10^{13}$  to  $1 \times 10^{14}$  ion/cm<sup>2</sup> leads to insignificant changes in hardness indices, which is associated with an increase in the density of dislocations, which prevent the propagation of cracks. An increase in the irradiation dose above  $5 \times 10^{13}$  ion/cm<sup>2</sup> leads to an increase in the defects overlap regions, thereby their mutual contribution to the change in the concentration of dislocations and

point defects increases, which subsequently can lead to the formation of cluster defects. Also, a decrease in hardness for samples irradiated with doses above  $5 \times 10^{13}$  ion/cm<sup>2</sup> can be due to the formation of a cubic phase, the presence of which leads not only to an increase in dislocation density, but also creates additional obstacles to crack propagation during external actions, thereby increasing crack resistance. At the same time, the tendency for smaller changes in strength properties at high radiation doses is observed for both types of ions.

## Conclusion

In conclusion, studies of the resistance of ZrO<sub>2</sub> ceramics to exposure to heavy ions made it possible to evaluate the mechanisms of phase polymorphic transformations in ceramics under the influence of radiation. During the research it was established that radiation by Xe<sup>22+</sup> ions at radiation doses  $1 \times 10^{14}$  ion/cm<sup>2</sup> leads to full polymorphic transformation of t-ZrO<sub>2</sub> → c-ZrO<sub>2</sub> while radiation by Kr<sup>15+</sup> ions in the chosen dose leads to formation of the structure consisting of mix of two phases. It was found that irradiation with heavy ions leads to a change in the shape of grains and the predominance of a lamellar shape in the structure of ceramics.

According to UV-Vis spectroscopy data, it was found that for irradiated samples, changes in UV-Vis spectra are associated with a shift of the fundamental absorption edge to the region of 340-360 nm, depending on the radiation dose and the type of radiation. There was also a sharp decrease in throughput of 75-82 % for samples irradiated with Kr<sup>15+</sup> ions and 65-75 % for samples irradiated with Xe<sup>22+</sup> ions. Obtained data change of optical spectra indicates change of electronic and optical densities.

In the future, the results obtained can be used to supplement the database of oxide ceramics radiation resistance theory, as well as the resistance of ZrO<sub>2</sub> ceramics to heavy ion irradiation.

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## Compliance with Ethical Standards

**Conflict of Interest:** The authors declare that they have no conflict of interest.

**Ethical approval:** This chapter does not contain any studies with human participants or animals performed by any of the authors.

**Informed consent:** Informed consent was obtained from all individual participants included in the study.

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