

The influence of variation in the ratio of components in two-phase lithium-containing ceramics on defect formation processes

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ABSTRACT

The aim of this study is to determine the effect of changing the ratio of components in the composition of two-component $x\text{Li}_2\text{TiO}_3 - (1-x)\text{Li}_2\text{ZrO}_3$ ceramics on structural distortions and degradation of strength and thermal parameters under high-dose neutron irradiation. The assessment of structural changes was carried out using the electron paramagnetic resonance (EPR) method, which is one of the most accurate methods that allows for a quantitative and qualitative assessment of structural changes caused by irradiation, as well as determining the concentrations of various types of defects depending on the irradiation fluence. It was found that in the case of two-component lithium-containing ceramics, the resistance to accumulation of radiolysis products is due to the effects of the presence of interphase boundaries that inhibit the formation of radiolysis products. According to the qualitative assessment of the EPR spectra, it was established that in the case of two-component ceramics, the formation of HC_2 – centers occurs at higher irradiation fluences (above 5×10^{20} neutron/cm²), while for one-component ceramics, the formation of radiolysis products is observed at irradiation fluences above 10^{19} neutron/cm². In this case, a comparative analysis of the concentrations of defects formed in the damaged layer and their evolution indicates an increase in resistance to defect formation processes due to a change in the ratio of components in the composition of two-component ceramics. The improved stability of two-component ceramics against disordering and defect accumulation is attributed to grain boundaries, which act as barriers to oxygen vacancy migration and defect clustering.

1. Introduction

The interest in the study of the radiation resistance of lithium-containing ceramics [1,2], as well as the search for opportunities to increase the resistance of ceramics to radiation-stimulated degradation processes associated with embrittlement and disordering, is primarily due to the need to solve the problem of tritium production for fusion installations, which are one of the promising solutions in the energy sector associated with the expansion of the applicability of alternative energy sources and the reduction of dependence on hydrocarbon fossil raw materials [3,4].

One of the ways to enhance the stability of lithium-containing ceramics is to use a method of combining various components, varying the

ratio of which makes it possible to select the optimal composition of the ceramics, which allows you to increase resistance to external influences in the form of ionizing radiation, which can generate internal processes that can lead to destabilization of the crystal structure [5,6]. This method is based on the possibility of combining the properties of different types of ceramics, which allows for increased resistance to mechanical impacts due to increased strength during the formation of interphase boundaries, which act as barriers for dislocations and structural defects, preventing softening caused by external influences. However, the use of a method for increasing the stability of lithium-containing ceramics to softening processes by varying the ratio of components is currently being actively studied, which in turn opens up a fairly large scope for conducting such studies aimed at finding optimal

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conditions for obtaining ceramics with high resistance to external influences [7–9]. For example, several works [10,11] propose the use of size factors associated with a reduction in grain size to nanoscales, which allows for an increase in resistance to destruction processes under high-dose irradiation. These effects are based on the hypothesis that with small grain sizes (less than 100 nm), the number of boundaries created by them will allow for the creation of barriers for migrating defects and vacancies in the damaged layer, thereby reducing their diffusion rate, as well as the ability to agglomerate in pores, creating gas-filled cavities. Another way to enhance the resistance of lithium-containing ceramics to the processes of destruction that occur during operation is to use the method of combining two or three different types of lithium-containing ceramics by mixing them [12–16]. This method is based on the hypothesis that the use of different types of lithium-containing components when combined will allow combining the properties of each of the selected components, thereby creating the most stable ceramics that combines the positive qualities of each component. Also, an important role in the selection of components is played by the possibility of formation of the effect of interphase boundaries in the composition of ceramics due to the variation of the concentration of components, which leads to an increase in resistance to mechanical impacts, alongside an increase in radiation damage resistance [17,18]. However, this method requires a large amount of research aimed at selection of the optimal ratios of components in the composition of ceramics, since the presence of various phases can also play a negative role, consisting in the formation of many internal stresses and deformations, which, when irradiated, can accelerate the destruction process.

The main aim of this research work is to determine the influence of the component ratio in the composition of two-component $x\text{Li}_2\text{TiO}_3 - (1-x)\text{Li}_2\text{ZrO}_3$ lithium-containing ceramics on the resistance to neutron irradiation, which can provoke the formation of vacancy defects in the damaged layer, as well as radiolysis products in the form of HC_2 – centers, Ti^{3+} and Zr^{4+} defects. The main focus of the study is on determination of the role of changes in the ratio of components in the mechanisms of defect formation associated with both the accumulation of oxygen vacancies and the inhibition of the accumulation of radiolysis products due to the presence of interphase boundaries in the samples [19–21]. In this case, the formation of interphase boundaries makes it possible to create barriers in the path of defects formed as a result of irradiation, which leads to the inhibition of the processes of destruction of the near-surface layers. The review papers cited [19–21] present various methods for increasing the stability of lithium-containing ceramics as blanket materials, and also describe the prospects for their use for tritium breeding and solving the problem of its production for thermonuclear reactors. Much attention in the works is given to the description of the possibilities of using lithium-containing ceramics, as well as their resistance to external influences.

It should be noted that the interest in the use of two-component ceramics is primarily due to the possibility of enhancement of resistance to softening due to the presence of interphase boundaries and dispersion hardening effects (associated with dimensional factors), which make it possible to solve such problems as low resistance to degradation of lithium-containing ceramics during the accumulation of radiation damage, the need to slow down the processes of accumulation of radiolysis products that reduce the efficiency of tritium release, increasing compatibility with other materials and the possibility of operation at high temperatures due to the leveling of the effect of thermal expansion.

An important role in changing the properties of ceramics that determine their applicability as tritium breeding materials is played by the resistance of thermophysical parameters to radiation damage, as well as the change in thermal conductivity depending on the concentration of accumulated structural damage associated with the accumulation of oxygen vacancies, as well as radiolysis products. In this case, interest in such studies is primarily due to maintaining the stability of

effective heat removal under conditions of tritium production, which occurs directly during irradiation with a neutron flux, accompanied by destabilization and disordering of the crystalline structure. In turn, the use of two-component ceramics, by selecting the optimal ratio of components in the composition, will allow solving several issues related to the need to achieve maximum efficiency of tritium multiplication, while maintaining the stability of strength and thermal parameters [22–24]. For example, as shown in works [22–24], the use of two-phase ceramics allows not only to increase the efficiency of tritium release, but also to increase resistance to destruction processes caused by the accumulation of structural damage. In the case of high-dose irradiation, especially with neutrons, the processes of tritium production as a result of nuclear reactions are accompanied not only by the release of tritium, but also by the accumulation of helium and other products of nuclear reactions, capable of causing deformation distortion as a result of agglomeration in pores with a subsequent increase in pore size due to accumulation. In this case, the processes of destruction can be restrained due to the presence of interphase boundaries acting as barriers, thereby reducing the overall degree of distortion of the crystalline structure.

2. Materials and methods

The following samples were selected as objects for study of the resistance of lithium-containing ceramics to neutron irradiation: 0: 0.25 $\text{Li}_2\text{TiO}_3 - 0.75 \text{Li}_2\text{ZrO}_3$, 0.50 $\text{Li}_2\text{TiO}_3 - 0.50 \text{Li}_2\text{ZrO}_3$, 0.75 $\text{Li}_2\text{TiO}_3 - 0.25 \text{Li}_2\text{ZrO}_3$, and single-component Li_2TiO_3 and Li_2ZrO_3 ceramics. The choice of one-component ceramics was based on the ability to compare the effectiveness of two-component ceramics in terms of resistance to structural degradation and radiolysis products compared to one-component ceramics.

The following samples were selected as objects for study of the resistance of lithium-containing ceramics to neutron irradiation, as well as for assessment of the effect of variation of the ratio of components in two-phase ceramics on the resistance to the radiation damage accumulation: 0.25 $\text{Li}_2\text{TiO}_3 - 0.75 \text{Li}_2\text{ZrO}_3$, 0.50 $\text{Li}_2\text{TiO}_3 - 0.50 \text{Li}_2\text{ZrO}_3$, 0.75 $\text{Li}_2\text{TiO}_3 - 0.25 \text{Li}_2\text{ZrO}_3$, and single-component Li_2TiO_3 and Li_2ZrO_3 ceramics were also selected to compare the effectiveness of two-component ceramics on the resistance to structural degradation and radiolysis products caused by irradiation. The initial ceramic powders Li_2TiO_3 (PCode – 1003372420), Li_2ZrO_3 (PCode – 1003614190) were purchased from Sigma Aldrich (Sigma Aldrich, USA). The average grain size was about 2 – 3 μm , the chemical purity was 99.95 %. To control purity, the X-ray diffraction method, the application of which made it possible to evaluate the presence of impurities in the composition of the initial powders, as well as to determine the phase composition after synthesis, was used (see Table 1).

X-ray phase analysis of the studied samples was performed on a D8 Advance ECO X-ray diffractometer (Bruker, Germany). The diffraction patterns were recorded in the Bragg-Brentano geometry, in the angular range of $2\theta = 15-90^\circ$, the recording step was 0.05° , the acquisition time at a point was 1 sec. The analysis and decoding of diffraction patterns were carried out in the DifractEVA v.4.0 software code; phase refinement was carried out using the PDF-2 database.

The Archimedes hydrostatic weighing method was used for ceramic density. Distilled water with a temperature of $(22 \pm 1^\circ\text{C})$ was used as a working medium. Before weighing, the samples were subjected to ultrasonic cleaning and drying for contaminant removal from that of. The changes were carried out on series of samples, each of which consisted of at least 5 samples. Based on the data obtained, measurement errors and standard deviation values were determined.

The ceramics were synthesized using the method of mechanochemical grinding of the initial components in order to obtain a homogeneous and equally probable distribution of the two ceramic compositions in the resulting samples. Grinding was carried out in a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany) at a mixing speed of 200 rpm for 20 min. The choice of these conditions is due to the need to eliminate

Table 1

provides data on grain sizes, as well as density and porosity values determined using the Archimedes method.

Parameter	Li ₂ TiO ₃	0.75 Li ₂ TiO ₃ – 0.25 Li ₂ ZrO ₃	0.50 Li ₂ TiO ₃ – 0.50 Li ₂ ZrO ₃	0.25 Li ₂ TiO ₃ – 0.75 Li ₂ ZrO ₃	Li ₂ ZrO ₃
Density, g/cm ³	3.24 ± 0.08	3.37 ± 0.06	3.66 ± 0.11	3.89 ± 0.12	4.06 ± 0.11
Porosity, %	13.5 ± 0.4	12.4 ± 0.2	11.2 ± 0.5	10.5 ± 0.4	11.4 ± 0.5
Grain size after mechanochemical grinding.	500 – 600 nm	500 – 600 nm with inclusions of finely dispersed fraction with sizes of about 250 – 300 nm	400 – 450 nm with inclusions of finely dispersed fraction of about 100 – 150 nm	400 – 450 nm with inclusions of finely dispersed fraction of about 150 – 200 nm	400 – 450 nm

the effects of cold welding of ceramic samples during prolonged mechanical action on the walls of grinding cups, as well as to eliminate the effect of strong deformation of the crystalline structure of the original powders that occurs during intensive mechanical action by grinding bodies over a long period of time during high-speed grinding. After milling, the obtained powders were pressed into tablets of 10 mm diameter and about 1 mm thickness to enable studies related to irradiation and subsequent determination of thermal and strength characteristics. The samples were pressed by placing the powders in a special press mold, pressing was carried out at a pressure of 250 MPa with holding for 1 h and subsequent extraction of the pressed tablets from the press mold. Pressing was carried out at room temperature. The removal of deformation distortions arising during grinding and pressing of samples was carried out by thermal annealing at a temperature of 600 °C for 10 h. In this case, the choice of thermal annealing conditions was based on the need to initiate the relaxation processes of deformation distortions caused by mechanochemical crushing during grinding and subsequent pressing. At the same time, at these temperatures, phase transformations do not occur, which allows preservation of the phase composition of the initial powders for obtaining two-component ceramics.

Simulation of the processes of structural damage in two-phase lithium-containing ceramics caused by neutron irradiation and associated with the formation of structural distortions in the near-surface layers of ceramics, as well as radiolysis products, the accumulation of which results in destructive embrittlement of the near-surface layers of ceramics, was carried out by irradiating the studied samples with a fluence of thermal neutrons with doses from 10^{18} to 10^{21} neutron/cm². Neutron irradiation of lithium-containing ceramic samples was carried out at the WWR-K reactor. The flux density was about 2×10^{13} n/(cm² × s), the reactor power was 6 MW, the temperature of the samples during irradiation did not exceed 320 – 330 K. The irradiation of the samples was carried out in an argon environment.

Irradiation was carried out in special capsules that eliminated heating of the samples, which made it possible to eliminate thermal effects on the processes of accumulation of structural damage in the surface layer of ceramics, as well as to determine the direct influence of radiation on changes in the structure of ceramics, as well as to establish the influence of variations in the ratio of components in two-phase ceramics on resistance to radiation-induced softening.

The results of destructive impact associated with the processes of accumulation of radiation damage caused by the impact of neutron irradiation in the surface layer of ceramics, as well as the influence of the phase composition, the variation of which was carried out by changing the ratio of components in the composition, were assessed using the EPR method. The measurements were performed on a Bruker BioSpin X-band spectrometer, the range was from 298 mT to 350 mT, at a modulation frequency of 100 kHz, operating at the X-band frequency (around 9.4 GHz). the measurement temperature was 25 ± 2 °C, an inert atmosphere was used for the measurements. The analysis and processing of spectra was carried out using the Bruker WinEPR software code, and the EasySpin software was used to fit the spectra and determine the defect concentrations and g-factors. The defect concentration was assessed using the internal standard method, which used samples in the initial non-irradiated state, which allowed for a comparative analysis of a

series of samples exposed to irradiation under the same conditions and irradiation doses.

The concentration values of defective formations depending on their type, as well as the irradiation fluence, were determined by integrating the peaks and normalizing them by mass. The application of this method to assess changes in structural parameters as a result of accumulation of radiation damage in lithium-containing ceramics was shown in [25–27]. The EPR method used was used to determine not only the quantitative assessment of structural damage, but also the qualitative one, including the determination of the types of defects formed depending on the irradiation fluence.

The use of the EPR spectroscopy method was chosen to determine the types of defects formed during irradiation, as well as changes in their concentration depending on the irradiation dose, which is one of the advantages of this method. However, unlike the methods of X-ray diffraction and Raman spectroscopy, it is impossible to establish deformation distortions and amorphous inclusions formed during irradiation using the EPR spectroscopy method, since in the case of using EPR spectroscopy only paramagnetic defects and radiolysis products are detected, while using the method of X-ray diffraction and Raman spectroscopy it is possible to determine volumetric structural changes caused by irradiation.

The determination of changes in the strength characteristics of the studied lithium-containing ceramics depending on the ratio of components and irradiation fluence was carried out using two methods: the indentation method (to determine hardness) and the single compression method (to determine resistance to cracking). Studies of the degradation of the hardness of the damaged layer in ceramics, as well as the determination of the effect of variation in the ratio of components in two-phase ceramics on increasing resistance to radiation-stimulated softening processes were carried out using a Durolin M1 microhardness tester (Metkon, Bursa, Türkiye). Testing of samples for resistance to mechanical impacts was performed on a series of at least 5 samples, which made it possible to determine the measurement error, as well as the repeatability of the observed changes caused by irradiation. Indentation of samples to determine microhardness was carried out by taking a series of measurements of at least 10 measurements on one sample. The distance between the indenter prints was about 50 – 100 μm, in order to eliminate the effect of superposition of deformation distortions caused by indentation on each subsequent measurement.

The crack resistance was determined using the single-compression method of the samples in a special cell on a single-column electromechanical testing machine LFM-L 10kH (Walter + Bai AG, Lönigen, Switzerland). Cracking was monitored using an extensometer, according to the readings of which the onset of crack initiation in the samples was determined.

The effect of neutron irradiation, as well as the associated accumulation of radiation damage in ceramics on changes in thermal characteristics, was assessed by measuring the longitudinal heat flow in ceramics before and after irradiation. The KIT-800 (Teplofon, Moscow, Russia) device was used for measurements; the measurements were carried out in the mode of assessing the thermal conductivity coefficient in the range of measured temperatures from 25 to 800 °C. The measurements were carried out in air atmosphere. To determine the repeatability of the observed effects, the measurements were performed

on a series of at least 5 samples for each radiation dose.

Test experiments to determine the effect of prolonged thermal exposure on changes in the strength properties of ceramics were carried out by thermal annealing of ceramic samples in the initial state and irradiated at maximum irradiation fluence, in a muffle furnace at a temperature of 550 °C for 500 h. At the end of the thermal exposure time, the strength characteristics were measured: hardness and the value of the maximum pressure under single compression, which made it possible to evaluate the resistance of ceramics to prolonged thermal exposure, as well as to establish the role of the influence of variations in the ratio of components in the composition of ceramics on resistance to high-temperature degradation. The choice of annealing temperatures is due to the working temperatures of tritium desorption using lithium-containing ceramics.

3. Results and discussions

Fig. 1 shows SEM images of the studied ceramics depending on the variation of the ratio of components in the composition. According to the data obtained, it is evident that in the case of mixing Li_2TiO_3 and Li_2ZrO_3 , the morphology of the resulting ceramics is represented by large diamond-shaped grains characteristic of Li_2TiO_3 and a finer fraction that corresponds to Li_2ZrO_3 . The presence of grains of different sizes in this case causes the formation of the effect of dispersion hardening associated with the presence of grain boundaries, which act as restraining barriers for defects [25,28], and also create obstacles to the propagation of microcracks and chips under mechanical influences. It should also be noted that a decrease in grain size, as shown in work [29], makes it possible not only to increase crack resistance and resistance to external influences, but also to reduce the gas swelling effect that occurs as a result of high-dose irradiation due to more open porosity, which allows the resulting tritium, helium and oxygen reach the surface without causing significant deformation distortions to the crystalline structure.

According to the data presented, alteration of the ratio of components in the composition of ceramics due to a growth in the proportion of Li_2ZrO_3 leads to an increase in density, which is due to differences in density values, the reference values of which for Li_2ZrO_3 are 4.21 g/cm³, and for Li_2TiO_3 – 3.43 g/cm³. Moreover, the difference in the experimental values of density for single-component ceramics in the initial state is due to structural changes caused by mechanical grinding and crushing of grains. It should also be noted that a change in the ratio of

components in the composition of ceramics results in compaction of ceramics, as evidenced by a decrease in porosity. Fig. 2 shows the results of X-ray diffraction of the samples under study. According to the data obtained, mechanochemical grinding and subsequent thermal sintering does not lead to the initialization of new phases in the composition of ceramics, which indicates a sufficiently high stability of ceramics and the possibility of forming two-component pure ceramics with different ratios of phases in the composition. Also, during assessment of the weight contributions of each phase in the composition of two-component ceramics, it can be concluded that the method used allows obtaining two-component samples with a ratio of the weight contributions of the phases close to the selected ratio of the components during mixing. As shown in the work [30], the use of the emulsion synthesis method makes it possible to obtain $\text{Li}_{2+x}\text{TiO}_{3+y} - \text{Li}_2\text{ZrO}_3$ solid solutions with sufficiently large prospects for their use as materials for tritium breeding by changing the ratio of components in the composition. The detailed analysis of the obtained diffraction patterns of the ceramic samples subjected to mechanochemical mixing revealed the formation of low-intensity reflexes in the Li_2ZrO_3 ceramic samples, as well as in the two-component $\text{Li}_2\text{TiO}_3 - \text{Li}_2\text{ZrO}_3$ ceramics, the most pronounced of which are in the region of $2\theta = 24 - 25^\circ$. The position of these reflexes is close to the position of the reflexes of the ZrO_2 phase with a monoclinic type of crystal lattice (PDF-00-037-1484). In this case, the shape of the diffraction maxima, as well as their intensity relative to the intensity of the main reflexes characteristic of the Li_2ZrO_3 phase, indicates a strong disordering of these inclusions, and their weight contribution is less than 1 wt%. The formation of these inclusions can be due to the processes of mechanical deformation action during grinding, which leads to the release of a small amount of a fraction in the form of ZrO_2 . In the case of mechanical action during grinding and subsequent pressing, micro-deformations occur in the structure, the presence of which leads to the formation of highly disordered inclusions characteristic of the monoclinic phase. At the same time, the selected annealing temperature does not lead to complete relaxation of this phase, as a result of which weak broadened and asymmetric reflexes characteristic of this phase are observed in the diffraction patterns. It should also be noted that changes in the ratio of components in the composition of ceramics lead to a decrease in the intensities of these reflexes.

However, the proposed method of mechanochemical mixing of Li_2ZrO_3 and Li_2TiO_3 powders with subsequent pressing into tablets and thermal annealing in the presented article makes it possible to obtain structures of a mixture of two phases with an equally probable

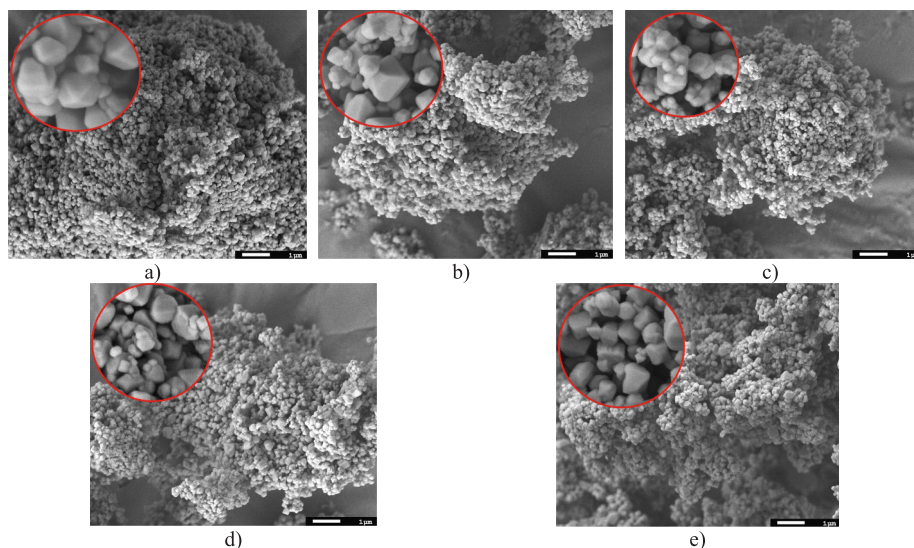


Fig. 1. SEM images of the studied ceramics depending on the variation of the ratio of components in the composition: a) Li_2TiO_3 ; b) 0.75 $\text{Li}_2\text{TiO}_3 - 0.25 \text{Li}_2\text{ZrO}_3$; c) 0.50 $\text{Li}_2\text{TiO}_3 - 0.50 \text{Li}_2\text{ZrO}_3$; d) 0.25 $\text{Li}_2\text{TiO}_3 - 0.75 \text{Li}_2\text{ZrO}_3$; e) Li_2ZrO_3 .

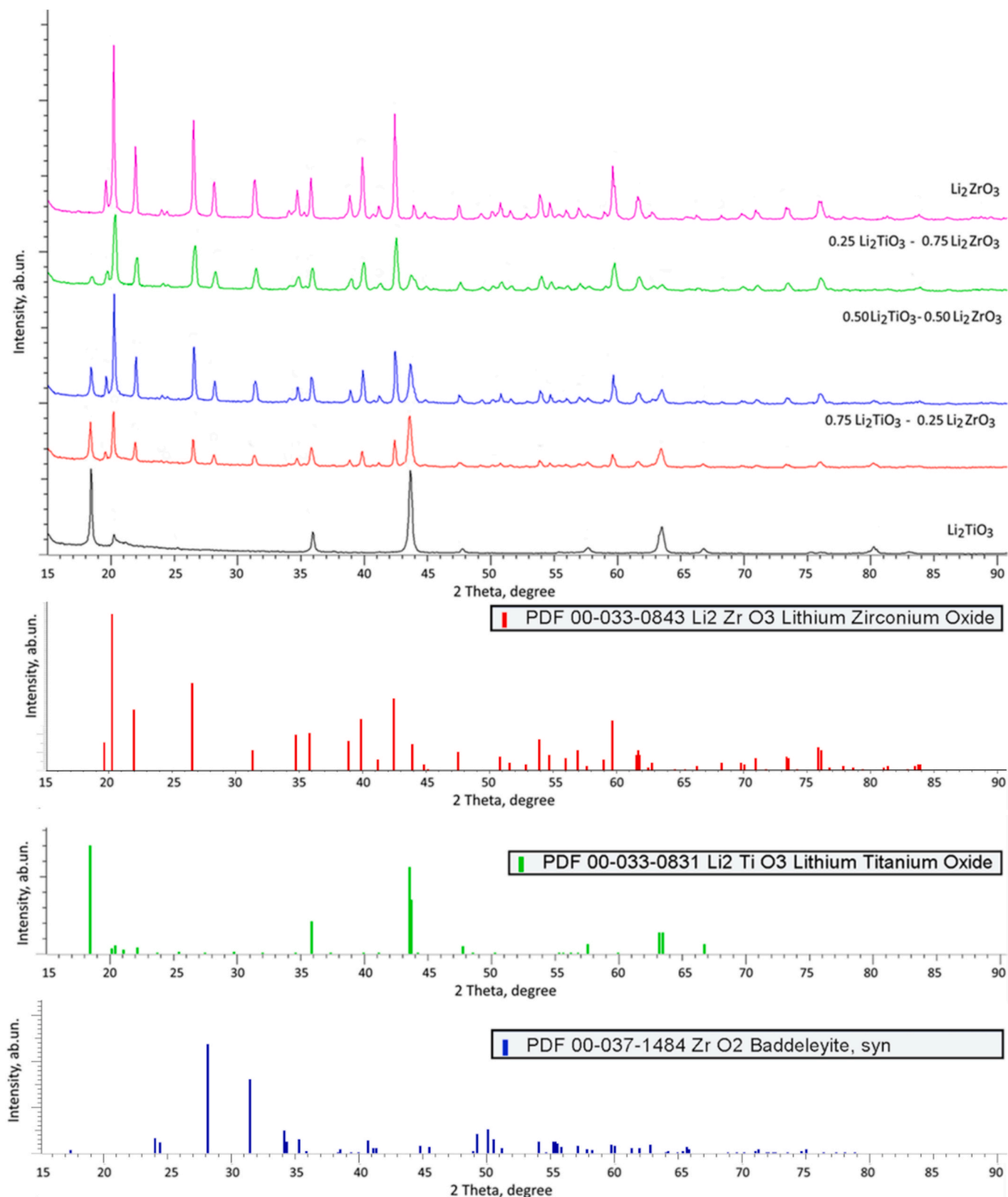


Fig. 2. Results of X-ray diffraction of the studied samples of lithium-containing ceramics (the figure shows the data of the cards from the PDF-2 database).

distribution of particles of each phase in the volume of ceramics. A distinctive feature of the proposed method from the method used in the work of Hoshino T. is the simplicity of the production of ceramic powders, from which tablets or pebbles of any shape and size can be made. It is important to highlight that in the case of the work of Hoshino T.,

where solid solutions of $\text{Li}_{2+x}\text{TiO}_{3+y} - \text{Li}_2\text{ZrO}_3$ were obtained, the samples studied in this research correspond to a mixture of two types of particles that have a fairly good structural ordering degree, according to X-ray structural analysis data.

Fig. 3 shows the results of the EPR spectra of the studied lithium-

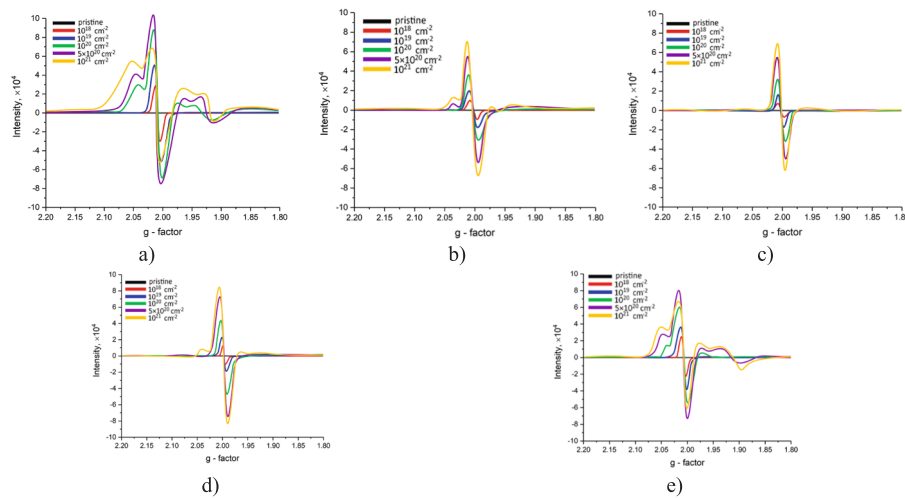


Fig. 3. The results of EPR spectroscopy of the studied ceramics depending on the irradiation fluence, reflecting changes in the concentration of accumulation of structural damage associated with vacancy defects, as well as radiolysis products: a) Li_2TiO_3 ; b) $0.75 \text{ Li}_2\text{TiO}_3 - 0.25 \text{ Li}_2\text{ZrO}_3$; c) $0.50 \text{ Li}_2\text{TiO}_3 - 0.50 \text{ Li}_2\text{ZrO}_3$; d) $0.25 \text{ Li}_2\text{TiO}_3 - 0.75 \text{ Li}_2\text{ZrO}_3$; e) Li_2ZrO_3 .

containing ceramics depending on the neutron irradiation fluence. The data are presented in the form of dependences of the change in the g-factor intensity, indicating the formation of defects in the structure of the ceramics, as well as their evolution depending on the irradiation fluence.

The process of interaction of neutrons with the crystal structure of lithium-containing ceramics includes two types of interactions – nuclear collisions and ionization excitations of the electron subsystem. As a result of nuclear collisions, nuclear reactions of the type ${}^6\text{Li}(n,\alpha)\text{T}$ and ${}^7\text{Li}(n,\alpha)\text{T}$ are initiated, as a result of which Li- and O- vacancies are formed, as well as helium and tritium, the accumulation of which leads to filling of pores in ceramics, or, given their high mobility, their migration to the surface and subsequent exit occurs. In this case, migration processes are accompanied by deformation distortions of the crystal structure, which leads to destabilization of the damaged layer, especially in the case of high radiation doses [5,23]. Ionization excitations in this case lead to a change in the distribution of electron density, which in turn destabilizes the crystal structure and also leads to acceleration of the processes of formation of oxygen vacancies. In the case of high radiation doses, changes in electron density can have a significant adverse impact on the stability of the crystal structure, which is expressed in a decrease in resistance to external influences.

At irradiation fluences of $10^{18} - 10^{19} \text{ cm}^{-2}$ in the case of single-phase Li_2TiO_3 and Li_2ZrO_3 ceramics, the presence of symmetric lines with $g = 2.001 - 2.004$, the intensity of which increases with increasing irradiation fluence, is due to the formation of E' -centers, the presence of which is associated with the formation of oxygen vacancies in the structure, which are one of the key types of structural defects that arise in the structure of ceramics as a result of external influences, as well as nuclear reactions occurring as a result of the interaction of neutrons with lithium. The formation of E' -centers in lithium-containing ceramics is due to the fact that during the interaction of neutrons with crystalline sublattices, the transferred energy is sufficient to knock oxygen out of the nodes due to the low binding energy, which leads to the formation of oxygen vacancies, the density of which increases with increasing irradiation fluence. Some of the formed oxygen vacancies can recombine with interstitial atoms, which leads to the collapse of defects, but in the case of high-dose irradiation, the number of formed vacancies is large enough, which leads not only to the accumulation of vacancy defects in the structure of the damaged layer, but also to the possibility of forming complex defects in the form of clusters. At the same time, the growth of the intensity of these lines depending on the irradiation fluence directly indicates the cumulative effect of oxygen vacancies as a result of

irradiation. In the case of irradiation fluences above $10^{19} \text{ neutron/cm}^2$ for single-component ceramics (Li_2TiO_3 and Li_2ZrO_3), the formation of bands characteristic of HC_2 centers, as well as Ti^{3+} (for Li_2TiO_3) [31] and Zr^{3+} (for Li_2ZrO_3) defects [32] is observed in the EPR spectra. In this case, HC_2 centers are localized defects in the ceramic structure associated with both oxygen vacancies modified by the presence of lithium and centers that capture electrons near crystal lattice defects. In the case of lithium-containing ceramics, HC_2 centers are considered to be traps for tritium or other radiolysis products that arise as a result of nuclear reactions. This type of HC_2 centers usually serves as a marker for radiation-induced defects that arise during irradiation and are associated with the formation of traps for electrons or ions localized near oxygen vacancies or interstitial ions.

Table 2 reveals the data on the observed positions of spectral lines and the corresponding type of defects in the structure.

The appearance of these bands in the spectra indicates the stage of accumulation of radiolysis products in the damaged layer, the formation of which indicates the destruction of chemical bonds, as well as the formation of various chemical radicals in the structure that are capable of migrating deep into the structure, thereby increasing damage to the crystalline structure due to ballistic damage. It is important to highlight that in the case of single-component Li_2TiO_3 and Li_2ZrO_3 ceramics, a clear difference in the changes in the EPR spectra is observed, both in the case of radiation doses at which the formation of E' -centers is characteristic, and in the case when accumulation of radiolysis products occurs, which indicates differences in structural resistance to external influences associated with the accumulation of damage under the same irradiation conditions. Also, these changes in the case of single-component ceramics can be caused by effects associated with differences in binding energy, which leads to higher resistance of Li_2ZrO_3 ceramics compared to Li_2TiO_3 ceramics to destruction processes caused by irradiation.

For two-phase $x\text{Li}_2\text{TiO}_3 - (1-x) \text{Li}_2\text{ZrO}_3$ ceramics, the changes in the intensities of the lines characteristic of E' -centers have a clearly expressed dependence on the ratio of components, the change of which leads to the inhibition of defect formation mechanisms in the structure of the damaged layer, which also indicates an increase in stability and resistance to radiation-stimulated softening.

Analysis of the obtained EPR spectra revealed that in the case of single-phase Li_2TiO_3 and Li_2ZrO_3 ceramics, at irradiation fluences above $10^{19} \text{ neutron/cm}^2$, the formation of characteristic bands associated with the formation of radiolysis products in the ceramics is observed, the occurrence of which is associated with the initialization of nuclear

Table 2

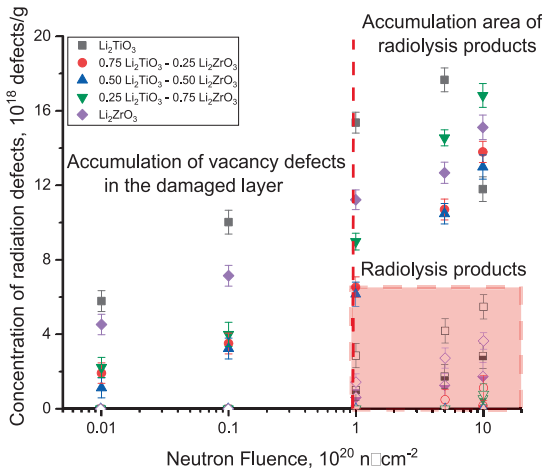
Data on the observed positions of spectral lines and the corresponding type of defects in the structure.

Type of defects	Position (g-factor)				
	Li ₂ TiO ₃	0.75 Li ₂ TiO ₃ – 0.25 Li ₂ ZrO ₃	0.50 Li ₂ TiO ₃ – 0.50 Li ₂ ZrO ₃	0.25 Li ₂ TiO ₃ – 0.75 Li ₂ ZrO ₃	Li ₂ ZrO ₃
E ⁺ -centers	g ≈ 2.001 – 2.004				
HC ₂ centers	g ≈ 2.005–2.002				g ≈ 2.002–2.006 (HC ₂ center associated with an oxygen vacancy or reduction of Zr ⁴⁺ to Zr ³⁺)
HC ₁ center (oxygen radical, O [•])	g ≈ 2.14–2.12 (has a weak intensity, appears only at maximum irradiation fluence in the case of single-component ceramics)	Not observed			
Ti ³⁺	g ≈ 1.98–1.96 Ti ³⁺ related defects in distorted octahedral coordination	The intensity of the spectral lines is minimal and decreases depending on the increase in the concentration of Li ₂ ZrO ₃ in the composition	–		
V _O – Ti type	g ≈ 1.88–1.85 appears only at high irradiation fluences	–	–	–	–
Zr ³⁺	–	–	–	g ≈ 1.98–1.96	
(Zr ³⁺ in distorted coordination (octahedron), possibly near Li ⁺ or O ²⁻ vacancies)					

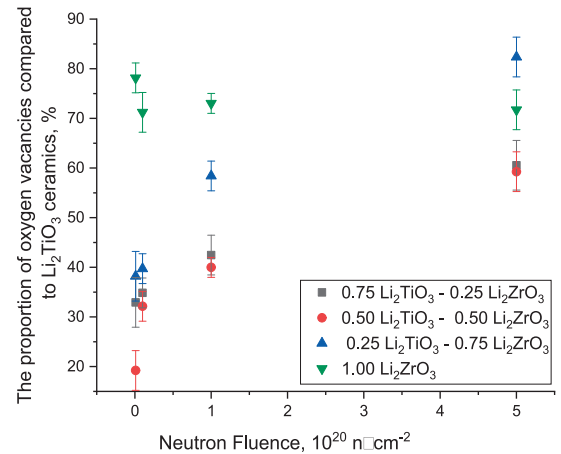
reactions of lithium with neutrons, as well as structural deformations caused by irradiation. In the case of two-phase ceramics, the main changes in the EPR spectra are associated with the formation of E⁺-centers, the presence of which indicates the occurrence of oxygen vacancies in the structure of the ceramics, and the spectral bands characteristic of radiolysis products are observed only at high irradiation fluences (above 5×10^{20} neutron/cm²).

Mixing two components of lithium-containing ceramics leads to an increase in resistance to softening associated with the formation of radiation defects – oxygen vacancies (V_O), as evidenced by less pronounced changes in the EPR spectra presented in Fig. 3b – d. It should be noted that variation in the ratio of components leads to a change in the resistance of ceramics to radiation damage, from which it follows that disordering processes have a clearly expressed dependence on the

structural features of ceramics associated with size effects, which were indicated by the authors of works [25,33]. The obtained results of the experiments are in good agreement with data from previous studies reflecting the kinetics of destruction of the damaged layer depending on the type of external influence [33–36]. It is important to mention that in this case under consideration, neutron irradiation has a much greater penetrating ability than protons or α -particles, which leads to the formation of damage at a greater depth, and consequently, the results obtained are direct confirmation of the imitation of real irradiation conditions. It should also be noted that the observed effects of inhibition of the processes of formation of oxygen vacancies in the structure of two-component ceramics, as well as radiolysis products, can be explained by the fact that the migration energy of V_O in Li₂TiO₃ ceramics is higher than in Li₂ZrO₃ (0.9 eV for Li₂TiO₃ and 0.6 – 0.7 eV for Li₂ZrO₃).



a)



b)

Fig. 4. A) assessment results of the change in the concentration of defects in the damaged layer depending on the irradiation fluence, reflecting the accumulation of various types of defects in the structure (in the figure, the highlighted area reflects the change in the concentration of radiolysis products in the form of hc₂ centers, Ti³⁺ and Zr⁴⁺ defects, which are indicated by open and semi-closed symbols); b) Results of comparative analysis of oxygen vacancies (E⁺-centers) depending on the concentration of Li₂ZrO₃ components in lithium-containing ceramics.

Moreover, in Li_2TiO_3 the presence of oxygen vacancies promotes the capture of tritium, thereby creating complex defects of the $\text{V}_\text{O} - \text{Ti}$ type, and the presence of $\text{Zr} - \text{Li}$ type bonds in Li_2ZrO_3 acting as deep traps promotes increased resistance to the formation of complex defects.

Based on the obtained EPR spectra, a qualitative assessment of defects in the damaged layer composition was carried out depending on the neutron irradiation fluence. The assessment results are presented in Fig. 4a as dependencies of changes in various defect concentrations (E' -centers, HC_2 - centers, Ti^{3+} and Zr^{4+} defects) on the neutron irradiation fluence. As can be seen from the data presented, in the case of fluences below 10^{20} neutron/ cm^2 , the dominant role in the mechanisms of defect formation is played by mechanisms associated with the formation of oxygen vacancies, characterizing the change in the concentration of E' -centers in irradiated ceramics. Moreover, in the case of single-component ceramics at fluences above 10^{20} neutron/ cm^2 , as shown in the EPR spectra, the formation of lines characteristic of radiolysis products is observed, which indicates that at high irradiation doses the accumulation of oxygen vacancies leads to deformation distortion of the crystal structure. In the case of irradiation at a temperature of 320 – 330 K, the defects formed as a result of irradiation migrate quite actively in the damaged layer, which at a high concentration leads to the formation of complex defects. In the case of two-component ceramics, the presence of interphase boundaries leads to the inhibition of defect diffusion processes, which leads to a slowdown in deformation distortion and disordering of the crystalline structure. At the same time, diffusion processes have a clearly expressed dependence on the irradiation temperature, an increase in which can result in greater mobility of defects, which accelerates the process of deformation distortion, but in this case, the experiments were carried out at a temperature of 320 – 330 K, which makes it possible to exclude the temperature factor in the processes of defect formation.

In the case of two-component ceramics, an increase in the content of the Li_2ZrO_3 component in the composition leads to a decrease in the concentration of oxygen vacancies (E' -centers) at irradiation fluences of $10^{18} - 10^{20}$ neutron/ cm^2 in comparison with the results obtained for single-component ceramics. With an irradiation fluence growth above 10^{20} neutron/ cm^2 , the observed difference in the change in the concentration of oxygen vacancies in the structure of ceramics indicates that at high irradiation fluences in two-component ceramics, the process of formation of oxygen vacancies dominates over the processes of formation of radiolysis products, which are most pronounced at these irradiation fluences in one-component ceramics.

At the same time, the concentration of radiolysis products for two-component ceramics has a direct relationship with the ratio of components in ceramics. Higher resistance to destruction for two-component ceramics can be explained by two factors. A structural factor caused by the fact that zirconium-containing ceramics have a higher resistance to radiation damage than titanium-containing ceramics, due to the fact that titanium can promote the initialization of reduction reactions in the structure, leading to an increase in the probability of the formation of oxygen vacancies, and as a consequence, at high concentrations, the formation of stable complex defects of the $(\text{Li} - \text{V}_\text{O})$ type. The size effect, in this case caused by the presence of grain boundaries, which serve as restraining barriers to the propagation of defects and vacancies, which leads to a slowdown in the accumulation of oxygen vacancies (according to the data on the change in the intensities of spectral lines for E' -centers), as well as the formation of radiolysis products at higher doses of irradiation. The size effect also helps to restrain the disordering of the crystal structure, which in turn restrains the growth of oxygen vacancies formed as a result of deformation distortions and disordering of the crystal lattice during irradiation. According to the presented SEM images shown in Fig. 1, a change in the ratio of components in the composition of ceramics leads to a decrease in grain size, which in turn ensures increased stability to deformation distortions caused by defect migration, as well as resistance to destruction processes during the accumulation of defective inclusions in the damaged layer.

The comparative analysis results of changes in the concentration of E' -centers in the composition of two-component lithium-containing ceramics at addition of Li_2ZrO_3 to the composition are shown in Fig. 4b. Li_2TiO_3 ceramics was chosen for comparison, in which the concentration of E' -centers is maximum, which indicates the low stability of this type of ceramics to neutron irradiation. According to the data obtained, the addition of Li_2ZrO_3 to Li_2TiO_3 ceramics leads to a decrease in the concentration of E' -centers, which indicates the inhibition of disordering mechanisms associated with the formation of oxygen vacancies. In this case, the main mechanism for the formation of oxygen vacancies as a result of interaction with neutrons in Li_2TiO_3 ceramics is the ballistic collision of neutrons with lithium or oxygen atoms, which leads to their knocking out of the crystal lattice sites, resulting in the formation of an oxygen vacancy and an interstitial defect.

As is known, the formation of an oxygen vacancy in its pure form is possible mainly through the mechanism of Frenkel pair formation according to the type $\text{O}_\text{O}^\times \rightarrow \text{V}_\text{O}^\bullet + \text{O}_\text{i}^\bullet$, while the energy of pair formation of such a pair is about 7.35 eV, while the formation of a Zr-Frenkel pair requires about 19.56 eV, which significantly exceeds the formation of O-Frenkel pairs. [37]. At the same time, in the work [38], the authors provide close values for the formation of oxygen vacancies in the case of Li_2TiO_3 ceramics. In this case, the mechanism of oxygen vacancy formation is most predominant in the structure of ceramics, which at high irradiation doses leads to the accumulation of oxygen vacancies in the structure of ceramics. Also, as a mechanism for the formation of oxygen vacancies in this case, the reaction $\text{n} + {}^6\text{Li} \rightarrow {}^3\text{H} + {}^4\text{He}$ can be considered, as a result of which a destructive expansion of the crystal lattice occurs due to the accumulation of helium and tritium in the structure, which leads to an increase in not only structural defects, but also the migration of oxygen vacancies due to the destabilization of the crystal structure of irradiated ceramics. The growth in resistance to disordering, expressed in this case in a reduction in the concentration of E' -centers in irradiated samples due to the addition of Li_2ZrO_3 to the composition of ceramics, can be explained by structural features associated with the presence of interboundary effects that prevent the diffusion of structural defects, slowing down their agglomeration and restraining the formation of defect complexes of the $\text{V}_\text{O} + \text{Li}_\text{i}^+ \rightarrow (\text{Li} - \text{V}_\text{O})$ type.

The growth of oxygen vacancies for samples with a concentration of $0.75\text{Li}_2\text{ZrO}_3$ in the composition of ceramics is due to the structural features of these ceramics, which are associated with the fact that with an equal ratio of components in the composition, the created effects of interphase boundaries when mixing two components prevent defect formation processes, and also restrain the softening processes caused by irradiation. In this case, the dominance of one of the two components in the composition of ceramics leads to a decrease in the effect of interphase hardening, which is expressed in a decrease in the resistance of ceramics to destruction processes associated with the accumulation of defects during irradiation. A general analysis of the observed changes made it possible to conclude that the most optimal composition of two-component ceramics is $0.50\text{Li}_2\text{TiO}_3 - 0.50\text{Li}_2\text{ZrO}_3$ with an equal ratio of components in the composition.

Fig. 5 shows the assessment results of the change in the strength properties of the studied ceramics depending on the irradiation fluence. The data are presented as a dependence of the change in hardness and resistance to single compression for all studied types of ceramics, reflecting the degradation rate with a change in the concentration of accumulated structural distortions and radiolysis products. The general trends of the observed changes in the strength characteristics indicate the destructive nature of the accumulation of radiation damage caused by irradiation. At the same time, the nature of the observed changes in the values of hardness and crack resistance (the maximum pressure that ceramics can withstand under external load) indicate a positive effect of addition of Li_2ZrO_3 to Li_2TiO_3 ceramics, due to less pronounced trends in the reduction of strength parameters for two-component samples. The most significant changes are observed at fluences above 10^{20} neutron/ cm^2 , from which it can be concluded that the greatest contribution to the

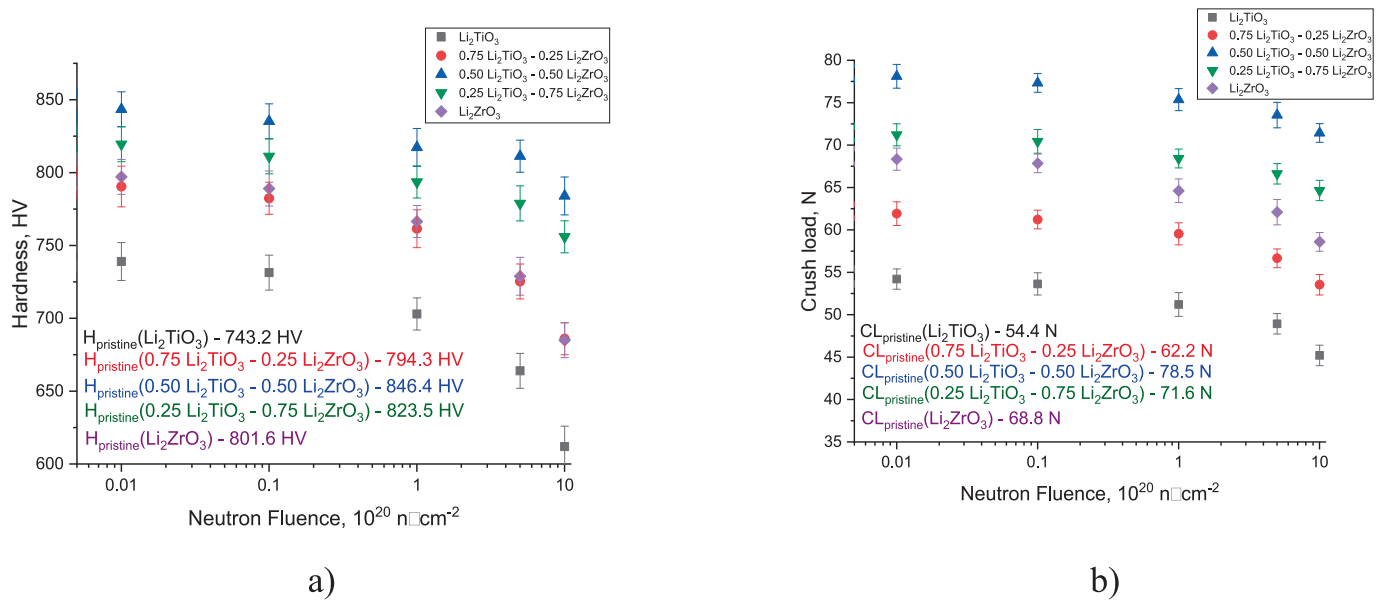


Fig. 5. Results of the assessment of changes in the mechanical properties of ceramics depending on their type and irradiation conditions: a) Results of the assessment of changes in hardness depending on the irradiation fluence (the graphs show the hardness values in the initial state in text); b) Results of the assessment of the change in the maximum pressure that ceramics can withstand during a single compression depending on the irradiation fluence (the graphs show the values of maximum pressure in the initial state in text).

destructive change in strength characteristics is made by the accumulation of radiolysis products in the structure of irradiated ceramics, the accumulation of which is associated with the destruction of crystalline and chemical bonds that reduce the stability of the crystalline structure to external influences.

Fig. 6 reveals the evaluation results of the degradation of the mechanical properties of ceramics depending on the irradiation fluence, also reflecting the influence of the variation in the ratio of components in the composition of ceramics on the resistance to radiation-induced degradation caused by the accumulation of vacancy defects and radiolysis products.

The general trend of changes in the strength parameters indicates that the presence of interphase boundaries not only inhibits the accumulation of vacancy defects in the structure of ceramics, but also

increases resistance to softening. At the same time, these effects are most pronounced for samples of $0.50 \text{ Li}_2\text{TiO}_3 - 0.50 \text{ Li}_2\text{ZrO}_3$ and $0.25 \text{ Li}_2\text{TiO}_3 - 0.75 \text{ Li}_2\text{ZrO}_3$, for which, in addition to the hardening factors associated with the presence of interphase boundaries, the effect of higher resistance of lithium metazirconate to degradation processes in comparison with lithium titanate also has an effect. In this case, the analysis of the obtained results of the destruction of strength parameters indicates that when radiolysis products are formed in the structure of single-component ceramics (at fluences above $10^{19} \text{ neutron/cm}^2$), the observed growth in the degree of reduction in hardness and resistance to cracking indicates an acceleration of the destabilization of the damaged layer, which is associated with an increase in the proportion of defects in the form of HC_2 centers, Ti^{3+} and Zr^{4+} defects. In this case, for two-component ceramics, the softening mechanisms are associated with a

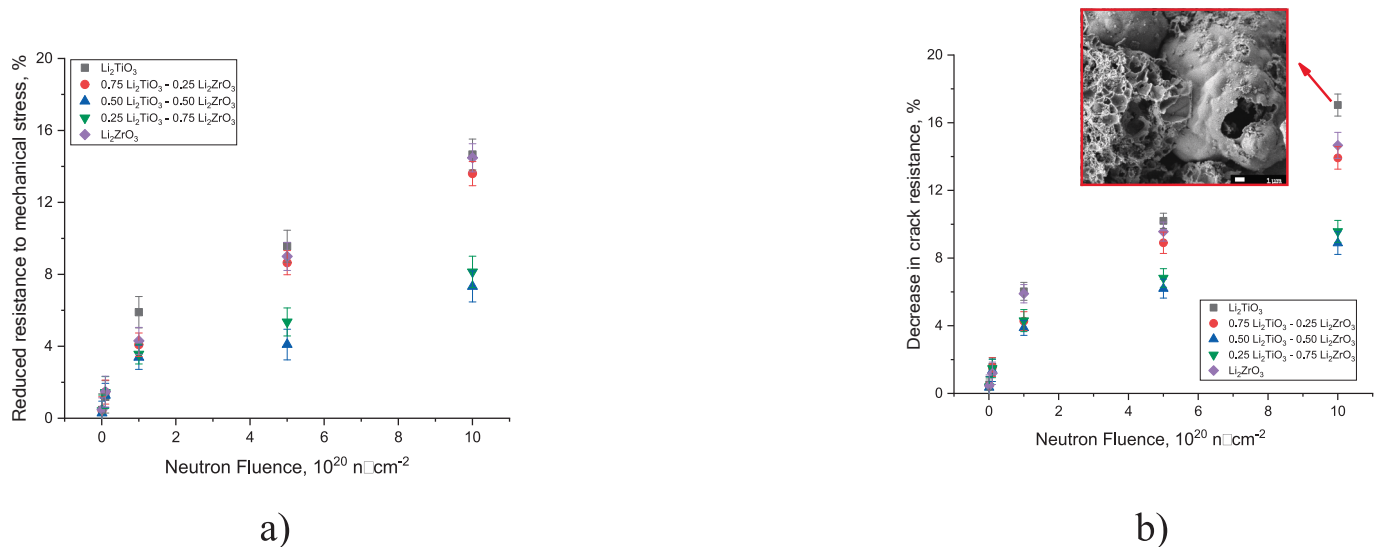


Fig. 6. Results of alterations in the factors of reduction of the mechanical properties of ceramics: a) Results of the assessment of the reduction in hardness, indicating the softening of ceramics; b) Results of reduction of resistance to cracking under single compression (the inset in Figure b shows an image of the surface of Li_2TiO_3 ceramics subjected to maximum irradiation fluence, reflecting the degradation of strength properties and surface cracking).

change in the concentration of E'-centers (oxygen vacancies), the proportion of which increases with increasing irradiation fluence. In turn, the observed growth in the stability of strength properties for 0.50 $\text{Li}_2\text{TiO}_3 - 0.50 \text{Li}_2\text{ZrO}_3$ and 0.25 $\text{Li}_2\text{TiO}_3 - 0.75 \text{Li}_2\text{ZrO}_3$ indicates a positive effect of the presence of interphase boundaries in the composition of ceramics, which restrain the softening of the damaged layer by reducing the diffusion of oxygen vacancies, as well as creating barriers for the formation of complex defects in the form of clusters. In this case, the increase in resistance allows two-component ceramics to withstand higher doses of radiation, which opens up opportunities for increasing their service life by slowing down the processes of destruction. The established dependences of the change in strength parameters on the radiation dose showed that for two-component ceramics, the values of the maximum decrease in strength and resistance to cracking are more than two times less than for one-component ceramics. It should be noted that with an elevation in the irradiation fluence, the differences in the values of destruction of strength parameters for one-component and two-component ceramics become more pronounced, which indicates that the main mechanism responsible for the acceleration of the processes of destabilization of strength characteristics is associated with the accumulation of radiolysis products in the structure in the form of HC_2 centers, Ti^{3+} and Zr^{4+} defects.

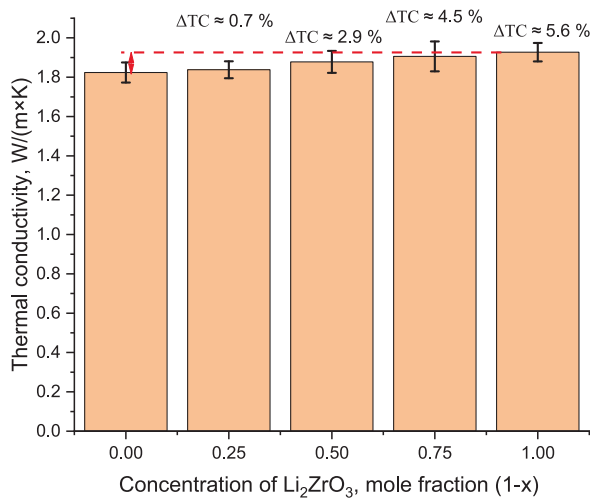
Fig. 7a illustrates the results of a comparative analysis of the change in the thermal conductivity coefficient of the studied lithium-containing ceramics in the initial state, reflecting the influence of variations in the ratio of components in the composition on the thermophysical properties. Regarding the TC data shown in Fig. 7a expressed in the diagram. These values reflect the differences in the ΔTC value alteration for two-component ceramics and Li_2ZrO_3 ceramics in comparison with the thermal conductivity coefficient for Li_2TiO_3 . These data reflect the effect of the ceramics' composition alteration on the thermal conductivity of ceramics, as well as the differences in values between one-component ceramics. According to the data presented, the addition of Li_2ZrO_3 to the ceramics leads to the thermal conductivity coefficient growth from 0.7 % to 4.5 % for two-component ceramics depending on the ratio of components, while for one-component Li_2ZrO_3 ceramics, the value of the thermal conductivity coefficient exceeds the similar value for Li_2TiO_3 ceramics by more than 5.6 %. The lower thermal conductivity coefficient values for two-component ceramics in comparison with the

thermal conductivity coefficient values for Li_2ZrO_3 ceramics are due to the influence of the Li_2TiO_3 component, the reduction of the proportion of which in the composition of ceramics leads to an increase in thermal physical properties.

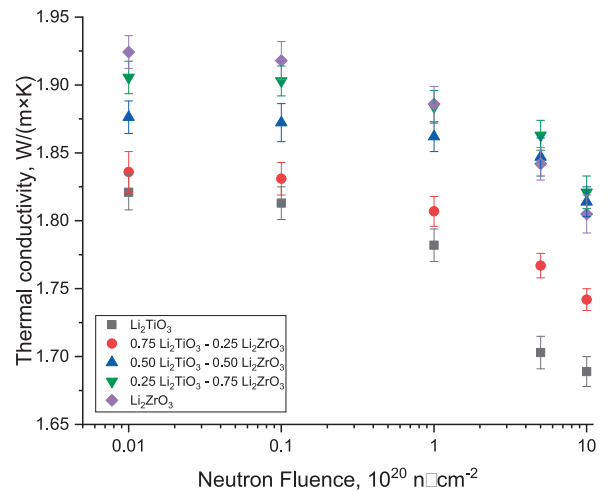
Fig. 7b reveals the assessment results of the change in the thermal conductivity coefficient of ceramics depending on the irradiation fluence, reflecting the influence of accumulated structural damage on the degradation of thermophysical parameters, consisting in the thermal conductivity coefficient reduction. The general changes in the thermal conductivity coefficient have similar reduction trends as the values of the strength parameters of ceramics, from which it can be concluded that the destruction of the structural features of ceramics, caused by the formation of oxygen vacancies at low doses of irradiation and the accumulation of radiolysis products at high doses of irradiation, has a negative effect on both strength and thermal properties. In this case, the main mechanism for reduction of thermal conductivity is the structural damage accumulation, leading to a slowdown in heat transfer (in the case of phonon heat transfer), due to the redispersion of thermal phonons on structural defects, an increase in the density of which leads to a greater decrease in thermophysical parameters.

Fig. 8 demonstrates the results of a comparative analysis of changes in thermal conductivity losses depending on the neutron irradiation dose, reflecting the degree of reduction in thermophysical properties as a result of the structural damage accumulation. In this case, the thermal conductivity degradation calculations shown in Fig. 8a were performed relative to the thermal conductivity values of the initial samples shown in Fig. 7a. The thermal conductivity degradation was assessed by calculation of the difference between the thermal conductivity values in the initial (non-irradiated) state for each ceramic composition and after irradiation with different fluences. The difference values are determined in percentage terms reflecting the effect of the irradiation fluence alteration on the reduction of thermal conductivity relative to the initial (non-irradiated) samples. In Fig. 8b, the data are presented as a comparison of two parameters of changes in the thermal conductivity coefficient, calculated using the above method, and the concentration of radiation defects determined from the analysis of the EPR spectra of irradiated samples with different fluences.

The general trends of changes presented in Fig. 8a-b reflect the relationship between the concentration of structural defects caused by



a)



b)

Fig. 7. A) results of changes in the value of the thermal conductivity coefficient depending on the ratio of components in the composition of lithium-containing ceramics (the data are given for the initial ceramic samples); b) results of changes in the thermal conductivity coefficient characterizing the effect of irradiation on the destabilization of the thermophysical parameters of ceramics depending on the irradiation dose.

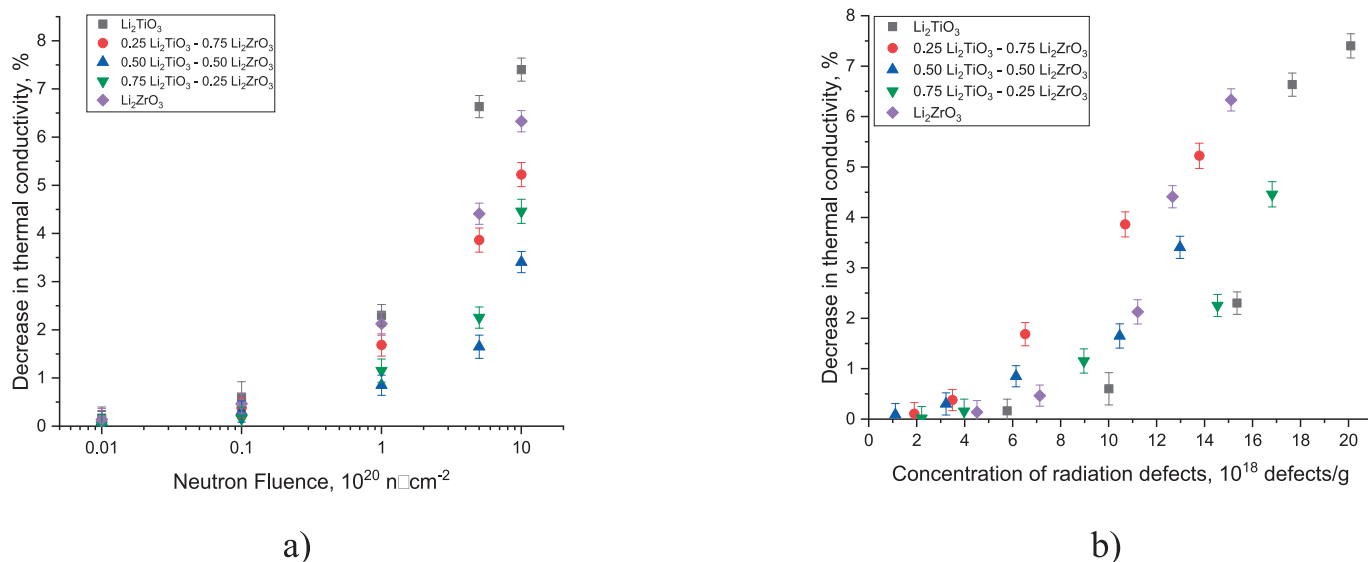


Fig. 8. Results of changes in thermal conductivity of ceramics: a) Results of comparative analysis of the decrease in thermal conductivity coefficient due to irradiation fluence; b) Connection between the change in the concentration of radiation defects in the structure and the decrease in the thermal conductivity coefficient of ceramics as a result of irradiation.

irradiation and the decrease in the thermal conductivity coefficient in the structure. It is important to note that in the case of the ceramics under study, the main contribution to the change in thermophysical parameters is made by oxygen vacancies, the growth in the density of which leads to the destabilization of heat transfer mechanisms. In this case, the increase in the density of structural defects due to the formation of oxygen vacancies as a result of irradiation leads to a rise in the number of thermal phonon scattering events, which, together with the change in the electronic structure, leads to a loss of thermal conductivity. The growth of micropores and deformation distortions in the structure due to deformation distortions also has a negative effect on the thermal conductivity reduction, which is confirmed by the results of the comparative analysis shown in Fig. 7b. The established slowdown in the reduction trends of thermal conductivity coefficient for single-component ceramics in the case of high irradiation doses is since the concentration of oxygen vacancies in the structure decreases due to the dominance of radiolysis products and the formation of large structural defects in the form of complexes.

The analysis of the obtained results of the change in mechanical properties (hardness, bending strength, resistance to single compression), as well as the thermophysical properties of the studied ceramics depending on the concentration of defects showed a direct correlation. An increase in the concentration of defects in the damaged layer, associated with the formation of oxygen vacancies at low doses of irradiation, leads to an insignificant decrease in both mechanical and thermophysical parameters. In this case, the observed small changes can be explained by the fact that the formed oxygen vacancies, despite their mobility, at low concentrations cannot have a significant effect on the deformation distortion of the crystalline structure of ceramics. At the same time, in the case of two-component ceramics, the presence of interphase boundaries leads to a slowdown in the diffusion of oxygen vacancies in the damaged layer, which leads to less pronounced changes in the mechanical and thermal properties of ceramics. This slowing down effect is due to the fact that migrating oxygen vacancies, as well as dislocations, are collected near grain boundaries, the density of which directly depends on the ratio of components in the ceramics. At higher irradiation doses, when the concentration of oxygen vacancies is about $10^{19} \text{ defects/g}$, the chemical bonds $\text{Ti} - \text{O}$, $\text{Zr} - \text{O}$ weaken, which, together with the increased mobility of dislocations, leads to more pronounced softening processes, i.e. a decrease in resistance to external mechanical effects. The formation of radiolysis products observed when

the concentration of oxygen vacancies reaches $10^{19} \text{ defects/g}$, in turn, indicates that irreversible chemical transformations and decomposition processes associated with the accumulation of radiolysis products are initiated in the damaged layer. In the case of single-component ceramics, these processes are more pronounced due to the high concentration of oxygen vacancies, as well as interstitial atoms in the form of lithium cations and oxygen anions, dislocations and point defects. At high defect concentrations, in the case of irradiation with high doses, the formation of areas with altered electron density, the depletion of which is caused by ionization processes of irradiation, is also observed. The combination of these factors leads to the formation of cluster defects, gas-filled pores, as well as the initialization of the so-called radiation-REDOX reactions associated with the reduction of Li^+ ions to Li^0 , as well as the formation of neutral oxygen, the accumulation of which, together with the products of nuclear reactions in the form of tritium and helium, leads to the destabilization of the near-surface layers due to the formation of gas-filled pores and their subsequent destruction (see data in the inset of Fig. 6b). Confirmation of the occurrence of radiation-REDOX reactions in the structure of ceramics under high-dose irradiation is the presence of a low-intensity peak with g-factor values of about 2.003 [6], observed during the decomposition of the EPR spectra, but their intensity is quite low.

In case of change of thermophysical parameters, increase of defect concentration in the structure leads to creation of additional scattering centers, which leads to slowing down of heat transfer processes, thereby reducing thermal conductivity. At the same time, formation of local structurally deformed areas can lead to uneven heating of samples, which in turn intensifies processes of destabilization of crystal structure, thereby increasing the degradation rate. In this case, changing the ratio of components in two-component lithium-containing ceramics allows for the suppression of softening mechanisms by slowing down the processes of diffusion of defects, and also increases the stability of the ceramic material to radiation-stimulated softening. Comparing the obtained results of the mechanisms of accumulation of radiation damage in $\text{Li}_2\text{TiO}_3 - \text{Li}_2\text{ZrO}_3$ ceramics caused by neutron exposure with the results of work [15], which studied the resistance of two-phase ceramics to H^+ and He^+ irradiation, and [25,26], which studied the resistance of two-component ceramics to proton irradiation, we can draw a general conclusion about the prospects of using a combination of two different components in lithium-containing ceramics to increase resistance to destruction processes caused by the accumulation of radiation damage.

At the same time, as in the case of proton and helium irradiation simulating gas swelling processes, and in the case of neutron irradiation, the key mechanism of defect formation is the formation of oxygen vacancies in the damaged layer with their subsequent accumulation and the formation of more complex defects, leading to the acceleration of the damaged layer destabilization processes. In this case, comparing the results with single-phase ceramics [25,26,34], it can be concluded that the use of the interphase boundary effect allows enhancement of resistance to destruction processes at high irradiation doses, which in turn allows extension of service life of ceramics, as well as enhancement of the efficiency of tritium release, which has an important role. Also, the obtained results of the experimental work carried out within the framework of this study are in good agreement with other experiments on neutron irradiation of two-phase ceramics [5,21,30]. The obtained results of experimental works related to testing of the resistance of Li_2TiO_3 – Li_2ZrO_3 ceramics to radiation damage indicate a sufficiently high resistance of ceramics to neutron irradiation, while further research in this direction will be aimed at testing of Li_2TiO_3 – Li_2ZrO_3 ceramic samples for tritium release to assess their applicability as materials for tritium reproduction. These studies will be aimed at determination of the potential of Li_2TiO_3 – Li_2ZrO_3 ceramics and their prospects in creation of competition with other two-phase ceramics such as Li_4SiO_4 – Li_2TiO_3 ceramics.

One of the key factors determining the prospects of using lithium-containing ceramics as blanket materials is their thermal stability under long-term exposure to high operating temperatures typical for tritium desorption operating modes. As a rule, these temperature modes are selected taking into account the stability of ceramics to thermal decomposition processes and destruction associated with the initialization of deformation embrittlement or sintering processes. Preliminary tests for thermal stability of the studied xLi_2TiO_3 – $(1-\text{x})\text{Li}_2\text{ZrO}_3$ ceramics were performed according to the experimental scheme given in Section 2. The assessment of the stability of the strength characteristics (hardness and resistance to cracking under single compression) for the original and irradiated with maximum fluence samples are shown in Fig. 9.

According to the obtained data, thermal action for 500 h on the initial samples of single-component ceramics (Li_2TiO_3 and Li_2ZrO_3), not exposed to irradiation, leads to a decrease in the strength characteristics

by 4.3—4.5 % from the initial values. These changes indicate destabilization processes as a result of thermal action, but the nature of the change values is quite low (does not exceed 5 %). In the case of two-component xLi_2TiO_3 – $(1-\text{x})\text{Li}_2\text{ZrO}_3$ ceramics, a change in the ratio of components in the ceramics leads to an increase in resistance to thermally induced softening, which is expressed in a decrease in the trends of decreasing strength parameters to 1.5—2.5 % depending on the ratio of components. In this case, an increase in resistance to thermally induced softening processes for two-component ceramics indicates a positive effect of the effect of the presence of two phases, leading to an increase in resistance to cracking and high-temperature destruction processes. For ceramic samples exposed to neutron irradiation with a fluence of 10^{21} neutron/cm², in the case of single-component ceramics, the decrease in strength parameters after thermal exposure is about 7—9 %, while for two-component ceramics, the decrease in strength parameters does not exceed 5 %. The results indicate that in the case of variation in the ratio of components in the composition of ceramics, the presence of interphase boundaries leads to an increase in not only resistance to radiation-induced processes of destabilization of strength properties, but also a slowdown in the destruction processes caused by thermal exposure over a long period of time. At the same time, the results obtained are a good help for further research in this direction, including the possibility of assessing the thermal stability of ceramics not only to long-term thermal exposure, but also to thermal shock effects.

4. Conclusion

Experiments on irradiation of xLi_2TiO_3 – $(1-\text{x})\text{Li}_2\text{ZrO}_3$ ceramic samples with different phase ratios in the composition with a thermal neutron flux with different irradiation fluences were conducted. Determination of the kinetics of ceramic degradation as a result of irradiation was carried out using the EPR spectroscopy method. Strength properties were determined using the indentation and single compression methods.

It has been established that in the case of two-component lithium-containing ceramics, resistance to the accumulation of radiolysis products is due to the effects of the presence of interphase boundaries that inhibit the formation of radiolysis products, as well as the migration of vacancy defects in the damaged layer.

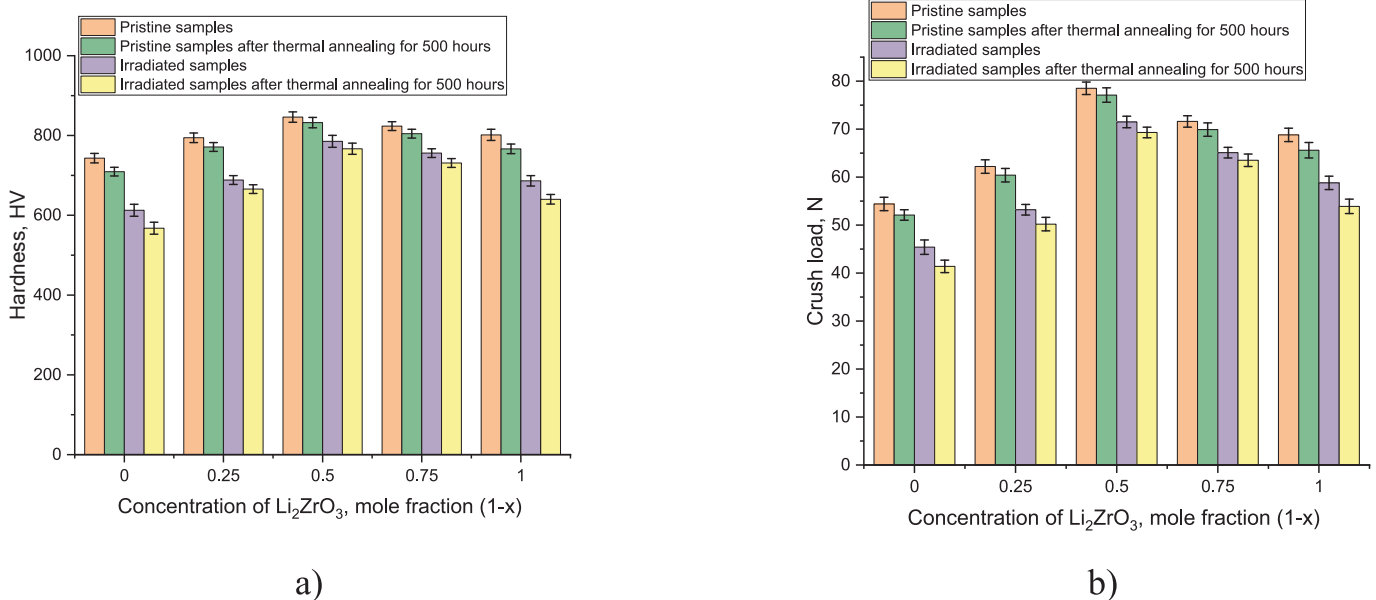


Fig. 9. Results of assessing the effect of long-term thermal exposure on xLi_2TiO_3 – $(1-\text{x})\text{Li}_2\text{ZrO}_3$ ceramic samples in the initial and irradiated with maximum fluence state: a) results of assessing the hardness before and after thermal exposure; b) results of assessing the change in the value of the maximum pressure withstood by the ceramics.

According to the assessment of changes in strength parameters, the presence of interphase boundaries in the composition of two-component lithium-containing ceramics leads to an increase in resistance to softening by more than 1.5 – 2 times for 0.50 Li₂TiO₃ – 0.50 Li₂ZrO₃ and 0.25 Li₂TiO₃ – 0.75 Li₂ZrO₃ ceramics in comparison with single-component ceramics.

The assessment results of changes in the thermal physical parameters showed that two-component ceramics have the greatest stability in maintaining thermal conductivity as a result of exposure to neutron irradiation. At the same time, it was established that oxygen vacancies play the main role in the destabilization of the thermal physical parameters, while the accumulation of radiolysis products leads to a slowdown in the processes of thermal conductivity degradation.

Based on the obtained experimental data, the durability and wear of lithium-containing ceramics were assessed when exposed to neutron radiation characteristic of the initialization of tritium multiplication processes, which made it possible to assess the prospects for using two-component ceramics as the most promising materials for tritium multiplication, possessing heightened resistance to destruction and disorder.

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CRedit authorship contribution statement

Dmitriy.I. Shlimas: Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Malik Kaliyekerov:** Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ainash Zhumazhanova:** Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Artem L. Kozlovskiy:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Bakytzhan Zh. Burkhanov:** Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gulnaz Zh. Moldabayeva:** Validation, Supervision, Software, Resources, Data curation, Conceptualization. **Maxim V. Zdorovets:** Resources, Project administration, Methodology, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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