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Application of EPR spectroscopy method for comparative analysis of structural damage accumulation kinetics in two-phase lithium-containing ceramics

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A R T I C L E I N F O

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A B S T R A C T

The aim of this study is to determine the differences in the damaged layer degradation kinetics in two-phase lithium-containing ceramics based on Li_2ZrO_3 and Li_4SiO_4 compounds in the case of irradiation with protons and helium ions, simulating the gas swelling and blistering processes, as well as the accumulation of radiolysis products in the damaged layer. During the conducted studies it was established that in the case of proton irradiation, the dominant role at fluences of 10^{15}–10^{17} cm^{-2} is played by oxygen vacancies, the change in the concentration of which upon reaching critical values causes a decrease in the thermophysical properties, and disordering of the damaged layer. In this case, the accumulation of radiolysis products in the form of HC_2 – and Zr^{3+} -defects in the structure of the damaged layer is observed at fluences of 5×10^{17} cm^{-2}, while when irradiated with He^{2+} ions, the formation of these types of HC_2 – and Zr^{3+} -defects is observed at a fluence of 10^{17} cm^{-2}. Comparison of the concentration dependences of defects in the damaged layer on the atomic displacement value under irradiation with protons and He^{2+} ions revealed that the formation of oxygen vacancies under irradiation with He^{2+} ions is more intense than in the case of irradiation with protons, which in turn results in more pronounced processes of accumulation of radiolysis products in the case of high-dose irradiation.

1. Introduction

The study of the degradation kinetics of the near-surface layers of ceramic materials used as various types of structural materials in nuclear and thermonuclear energy is one of the important issues in modern materials science that requires great efforts [1–3]. Interest in the topic of radiation damage and its evolution in near-surface layers, in particular, in dielectric ceramics, is not only due to the need to expand the fundamental aspects in understanding the defect formation mechanisms, as well as the role of various types of defects in alteration of the material properties, but also to establish critical doses of radiation, at which an irreversible change in the material, associated with its embrittlement, loss of strength characteristics and degradation resistance, alongside a change in thermophysical parameters, the deterioration of which causes the occurrence of overheating effects of structural materials, which results in accelerated degradation, occurs [4,5].

In the case of materials used in the active zone or subject to continuous exposure to ionizing radiation in the form of neutron irradiation or nuclear fuel fission fragments, it is necessary to consider not only the effects of the direct impact of radiation on the crystalline structure, but also the kinetics of degradation processes caused by the accumulation of radiation damage or nuclear reaction products in the damaged layer [6,7]. At the same time, the key role is played by processes associated with the degradation rate of the material, and the resistance of the material to radiation damage caused by irradiation, which are based on ionization and athermal processes arising as a result of the interaction of ions with the crystal structure [8–10]. In the case of direct exposure to ionizing radiation, as a rule, the interaction mechanisms are described by the processes of Coulomb explosion or thermal peaks, the occurrence of which during the interaction of incident

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particles causes an anisotropic measurement of the electron density in a small volume along the trajectory of the charged particle until it comes to a complete stop in the material [11,12]. At the same time, along the trajectory of motion, the mechanisms of interaction of the particle with the crystal structure are usually described by an alteration in the value of ionization losses, and the dominance of one type of ionization losses over others (in most of the cases considered, electron ionization losses play a dominant role) [13,14]. Moreover, during consideration of the combination of structural changes, as a rule, attention is paid to the final effect associated with the change in the structural, strength, thermal or dielectric properties of the damaged layer, without detailing the mechanisms or types of defects caused by these changes.

In the case of lithium-containing ceramics considered as tritium breeding materials [15,16], the accumulation of radiation damage plays a very important role in determining the type of ceramics that are considered as the best candidates for blanket materials, since tritium breeding processes are inextricably linked to the accumulation of nuclear reaction products in the form of tritium, hydrogen isotopes, helium, alongside radiolysis products that occur at high levels of tritium production [17,18]. At the same time, great attention in the study of structural damage in lithium-containing ceramics is paid not only to the study of the mechanisms of accumulation of damage themselves, but also to methods for increasing resistance to them. In particular, one of the ways to enhance resistance to radiation damage associated with the accumulation of nuclear reaction products and radiolysis products is the use of two-component (two-phase) ceramics, in which one of the components is Li4SiO4, which is one of the types of ceramics with the highest tritium content [19,20], and Li_2ZrO_3, which, unlike a number of other types of lithium-containing ceramics, has some of the highest strength, corrosion resistance and resistance to aggressive environments [21,22]. The method of using two-component ceramics to enhance radiation damage resistance is based on the hypothesis about the influence of interphase boundaries, alongside differences in grain sizes, on hardening and growth of resistance to destruction under high-dose irradiation, which is confirmed by the results of several studies [23–25]. However, despite the fairly large number of experimental works in this area, interest in this topic does not wane due to the fairly large number of unresolved issues, a number of which are related to detailing the mechanisms of accumulation of structural damage associated with nuclear reaction products, alongside the kinetics of their accumulation in the damaged layer, as well as variations in the type of ceramics, the study of which is aimed at finding the most stable highly effective materials for tritium breeding.

This study is aimed at determination of the differences in the structural damage accumulation mechanisms in 0.5 Li_2ZrO_3 – 0.5 Li_4SiO_4 ceramics under proton and helium irradiation, the use of which is due to the possibilities of simulation of processes associated with hydrogenation and helium swelling, as well as the accumulation of products of physicochemical radiolysis processes in the near-surface layer of ceramics. The use of these types of irradiation is chosen in order to simulate the situation of accumulation of radiolysis products, comparable to the real operating conditions of this type of ceramics used for the breeding of tritium, the processes of obtaining of which are accompanied by the accumulation of nuclear reaction products in the form of helium and hydrogen.

2. Experimental part

The samples chosen for the study were 0.5 Li_2ZrO_3 – 0.5 Li_4SiO_4, which, according to a number of studies, have the highest resistance to mechanical impacts, including long-term loads, and the effect of heightened strength is due to the presence of interphase boundaries, as well as a finely dispersed fraction, which creates additional hardening due to a large number of dislocations [25,26]. To obtain ceramics, the method of mechanochemical solid-phase synthesis was used; the conditions and features of obtaining this type of ceramics using this method are presented in Ref. [26].

Simulation of structural damage in the case of high-dose irradiation was carried out by irradiation of the studied ceramic samples with protons with an energy of 500 keV and He^{2+} ions with an energy of about 40 keV. Irradiation fluences were selected from 10^{15} to 10^{18} cm^{-2}, at which the oxygen vacancy formation processes are simulated, as well as in the case of high-dose irradiation (above 10^{17} cm^{-2}) the effects of radiation-deformation volumetric swelling associated with the accumulation of radiolysis products, as well as the formation of gas-filled inclusions in the near-surface layer [27,28]. The atomic displacement values were estimated based on the calculated data of the simulation performed with the SRIM Pro 2013 software code, considering the formation of vacancy defects, alongside their number. The data were calculated for each type of ionizing radiation used for irradiation. Differences in the atomic displacement values are due to both energy losses during interaction and the ionizing radiation type used for simulation.

The study of radiation damage caused in the near-surface layer by irradiation with protons and He^{2+} ions was carried out using the electron paramagnetic resonance (EPR) method, which was implemented on a Bruker BioSpin X-band spectrometer. The measurements were carried out in the range from 298 mT to 349 mT, the modulation frequency was about 100 kHz, the measurements were carried out in an inert atmosphere at room temperature. The data are presented as a dependence I(g-factor), used for ease of interpretation of the obtained data and the possibility of their comparison with the results of other works. The concentration of defect inclusions was estimated by determination of the peak areas characteristic of each type of defect. For this purpose, a two-dimensional integration of the peaks was performed, followed by normalization by mass. Formula (1) taken from Ref. [29] was used for the calculations.

$$C_{defects} = \frac{S_x \times N_{ref}}{S_{ref} \times m}, \tag{1}$$

S_x is the area under the absorption curve of the EPR signal, S_{ref} is the area under the absorption curve of the reference sample, N_{ref} is the concentration of unpaired electrons in the reference sample, m is the mass of the sample.

The kinetics of alterations in the thermophysical parameters of ceramics with changes in the irradiation fluence were determined using the method of determination of changes in the stationary longitudinal heat flow in ceramics, the alterations of which is associated with a slowdown in the phonon mechanisms of heat transfer in the damaged layer due to the formation of defective inclusions. The proposed measurement method is based on placing the sample in a special holder equipped with thermocouples fixed on both sides of the sample, after which the sample is heated on one side with temperature changes recorded on both sides, on the basis of which the thermal conductivity coefficient is determined. The measurements were performed on a universal thermal conductivity meter KIT-800 in the temperature range from 25 to 700 °C. Based on the obtained dependencies, the thermal conductivity coefficient was determined, the changes in which are due to an increase in heat loss in the irradiated material.

3. Results and discussion

Fig. 1 reveals the EPR spectroscopy results of 0.5 Li_2ZrO_3 – 0.5 Li_4SiO_4 ceramic samples contingent upon irradiation type in the case of variation in irradiation fluence. In the initial state of the samples not subjected to irradiation, no peaks or bands associated with alterations in the electronic structure, alongside the presence of paramagnetic states associated with structural defects, are observed. In the case of irradiated samples, the observed changes in the EPR spectra can be correlated with three types of defects, the alterations in the concentrations of which indicate the damaged layer degradation rate, and the mechanisms of evolution of structural damage associated with dose dependences. The

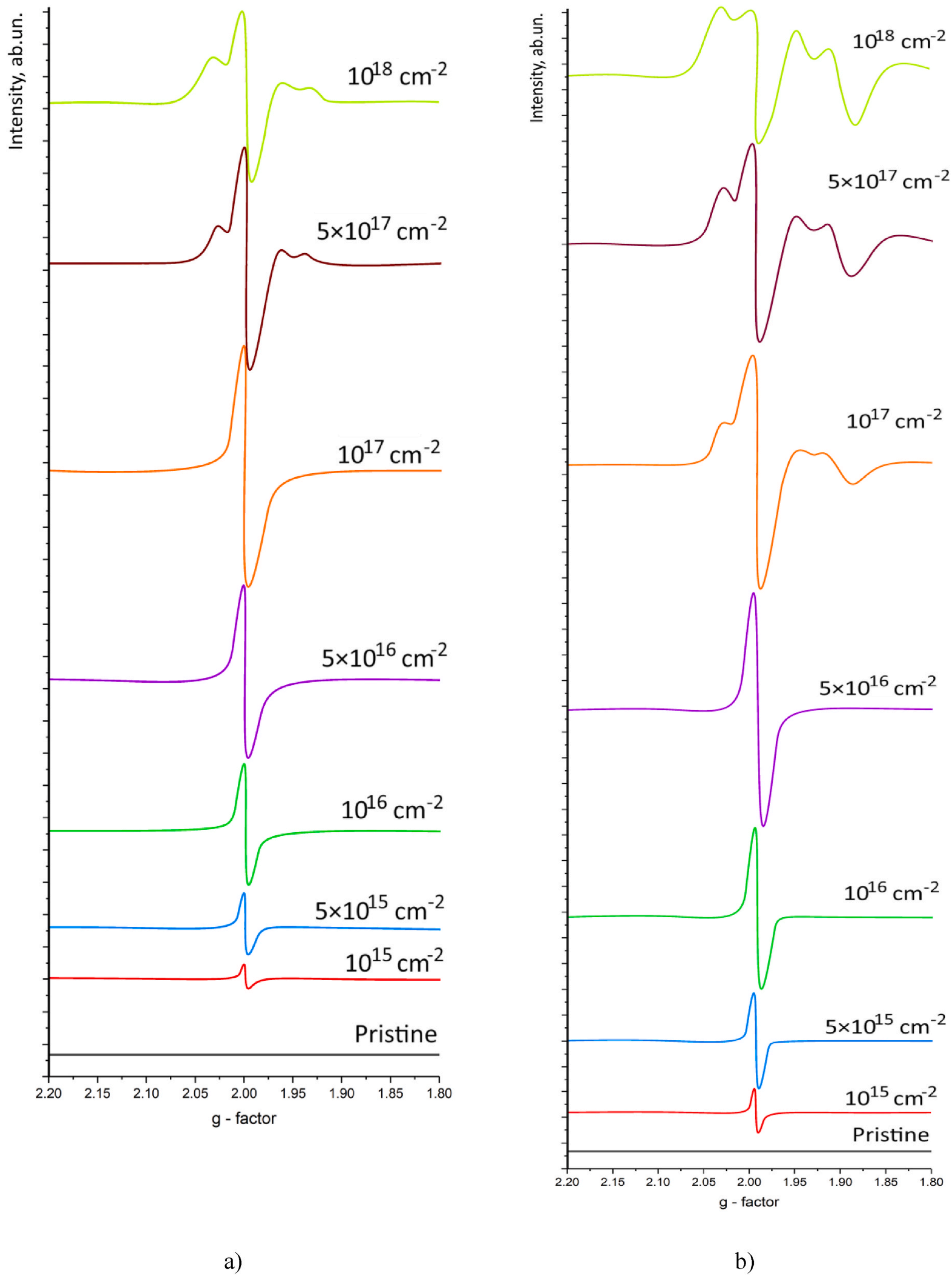
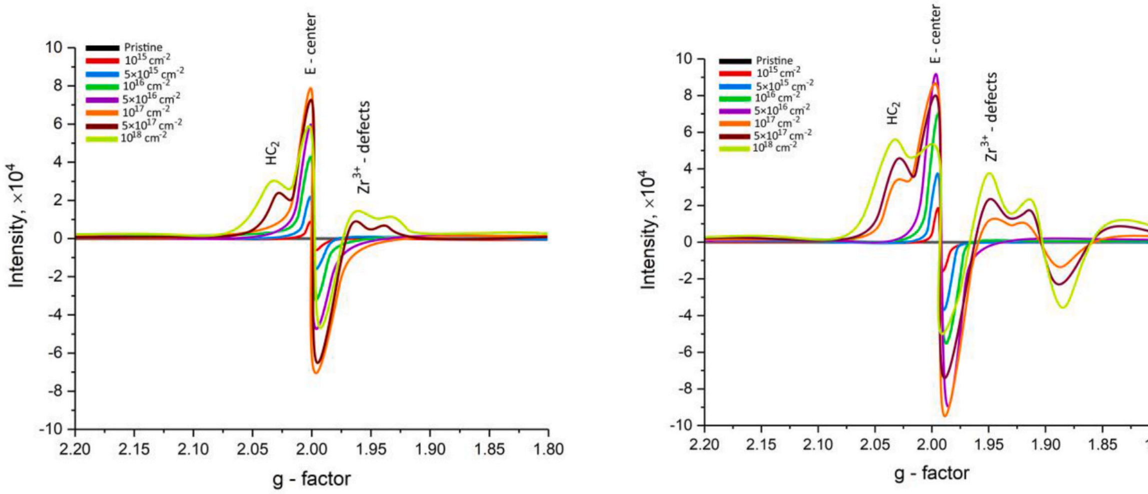


Fig. 1. EPR spectra of ceramics depending on the irradiation fluence: a) proton irradiation; b) He^{2+} ion irradiation.

main changes observed in the EPR spectra are due to the presence of a singlet line with g = 2.001–2.003, which characterizes the formation of oxygen vacancies in the structure of the damaged layer, the presence of which causes the main structural changes at fluences of 10^{15} - 10^{17} cm^{-2} in the case of proton irradiation, and fluences of 10^{15} - 5×10^{16} cm^{-2} when irradiated with He^{2+} ions. The observed lines at irradiation fluences above 5×10^{16} - 10^{17} cm^{-2} at g = 2.01–2.03 are characteristic of structural defects of the HC2 type – centers, the formation of which is caused by structural defects of the ≡ Si–O or SiO_4^{3-} type, i.e. a hole associated with oxygen atoms in SiO_4 tetrahedra. Also, the observed bands with g = 1.96–1.93 can be associated with Zr^{3+} defects, which were established in Refs. [30–32]. Moreover, comparing the changes in



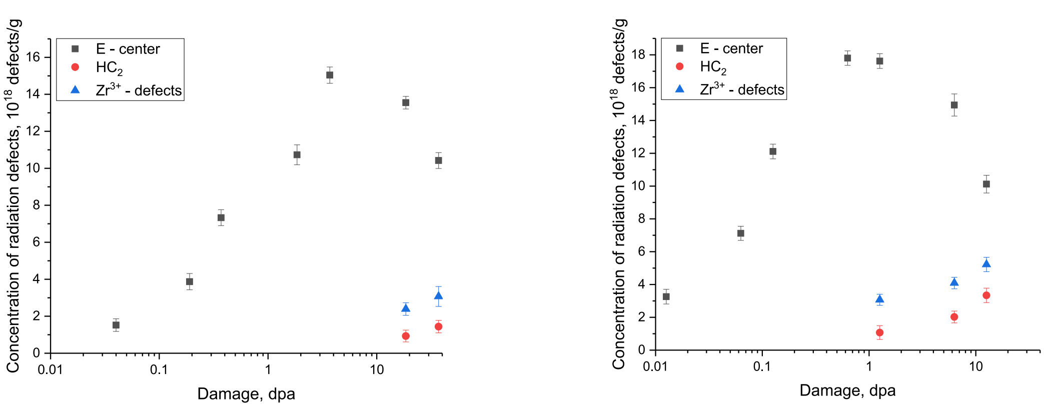
a) b)

Fig. 2. Comparative analysis results of alterations in the intensities of the EPR spectra of the studied ceramics depending on the type of irradiation, reflecting the damaged layer degradation kinetics: a) proton irradiation; b) He^{2+} ion irradiation.

band intensities (see data in Figs. 1 and 2), it can be concluded that the rate of formation of oxygen vacancies, as well as more complex defects such as HC_2 centers and Zr^{3+} defects, is different for irradiation with protons and He^{2+} ions, but the main mechanisms of defect accumulation and their evolution are of a similar nature. The main defect formation mechanisms in the case of irradiation with protons and helium ions are ionization losses of energy of incident particles upon collision with the crystal structure, which occur along the trajectory of particle movement in the material. It should also be noted that in the works [33–35] it was shown that in the structure of lithium-containing ceramics it is a very complex task due to the possible overlap of signals, which requires a sufficiently accurate understanding of the possible types of structural defects arising as a result of irradiation, as well as a clear separation of spectral lines during their processing.

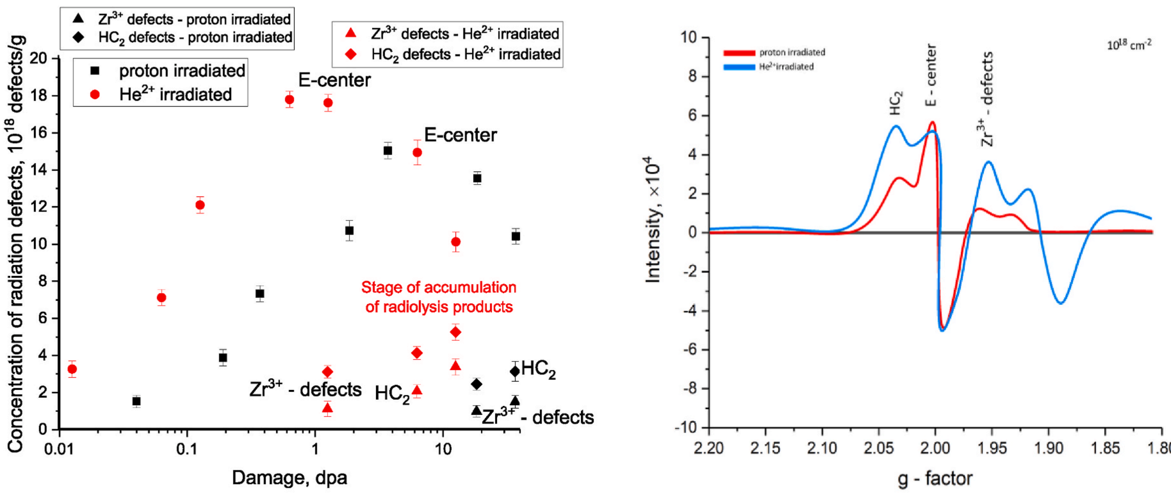
Fig. 2 illustrates the comparative analysis results of the obtained EPR spectra, reflecting the kinetics of changes in structural damage associated with the accumulation of oxygen vacancies, characterized by a change in the intensity of the singlet line, characteristic of E-centers, alongside the formation of bands for HC_2 and Zr^{3+} defects, characteristic of the formation of radiolysis products in the structure associated with the occurrence of physicochemical processes in the damaged layer. An analysis of the comparison of the kinetics of changes in the EPR spectra indicates that, under proton irradiation, the degradation processes associated with the accumulation of HC_2 and Zr^{3+} defects (radiolysis products) are less pronounced than in the case of irradiation with He^{2+} ions, for which, at high fluences of 10^{17}–10^{18} cm^{-2}, a clearly expressed growth in the contribution of HC_2 and Zr^{3+} defects in the damaged layer is observed (according to a comparative analysis of the intensities of these spectral lines).

Fig. 3 demonstrates the assessment results of the concentration of defects, the calculation of which was carried out according to the method specified in the work [36], which provides a fairly detailed description of the method for determination of the concentration of various defects and the method for calculating them based on EPR spectra. The general form of the presented dependences of the change in concentrations has a clearly bell-shaped form for the change in the concentration of E-centers, the reduction in the concentration of which is observed during the formation of contributions to the structure of HC_2 and Zr^{3+} defects associated with the accumulation of radiolysis products, which are recorded at values of the order of more than 10 dpa in the case of irradiation with protons, and more than 1 dpa when irradiated with He^{2+} ions.



a) b)

Fig. 3. Assessment results of the concentration of various defects in the damaged layer depending on the irradiation type: a) proton irradiation; b) He^{2+} ion irradiation.



a) b)

Fig. 4. Results of comparative analysis of defect structure: a) Comparison of kinetics of change in concentration of various defects from the damage degree, expressed in atomic displacements for two types of irradiation; b) Comparison of EPR spectra of ceramic samples irradiated with a maximum fluence of 10^{18} cm^{-2}, reflecting differences in the degree of the damaged layer degradation, caused by a change in the concentration of defects, and an elevation in the contribution of radiolysis products to the degradation degree.

Fig. 4a reveals the comparative analysis results of changes in the concentration of various types of defects in 0.5 Li_2ZrO_3 – 0.5 Li_4SiO_4 ceramics under proton and helium irradiation, which clearly reflect the relationship between the irradiation type (and, as a consequence, the ionization losses of incident particles during interaction with electron and nuclear shells), and the radiation damage degree. In the case of proton irradiation, the value of $dE/dx_{electron}$ is about 8–11 keV/nm, while for He^{2+} ions, the value of $dE/dx_{electron}$ is about 15–16 keV/nm. At the same time, due to the low energies of He^{2+} ions, during high-dose irradiation, it is necessary to consider the factor of influence of ionization losses $dE/dx_{nuclear}$, which are an order of magnitude greater ($dE/dx_{nuclear}$ - 0.3–0.4 keV/nm) than similar values of $dE/dx_{nuclear}$ for protons, the value of which is about 0.009–0.014 keV/nm. In this case, the contribution of ionization losses during collisions with nuclei plays a role in the defect formation processes, the result of which is the earlier formation of radiolysis products in the case of irradiation with He^{2+} ions. At the same time, the difference in the concentration of oxygen vacancies is due to differences in the values of ionization losses, in which the number of collisions in the case of He^{2+} ions results in large changes in the electron density, the result of which is the formation of a larger number of oxygen vacancies (V_O) with smaller atomic displacement values. In this case, the achievement of a critical concentration of oxygen vacancies in the structure of the damaged layer in combination with structural changes caused by the interaction of ions with nuclei and subsequent effects associated with athermal deformation processes lead to the formation of radiolysis products and their subsequent accumulation, which results in the damaged layer destruction at high irradiation fluences.

Fig. 4b shows a comparison of the EPR spectra of samples irradiated at the maximum fluence (10^{18} cm^{-2}), reflecting the differences in the degradation degree of ceramics with variations in the type of irradiation (in the case of irradiation with protons and He^{2+} ions). In this case, the presence of a deviation from the baseline spectrum of a ceramic sample irradiated with He^{2+} ions with a fluence of 10^{18} cm^{-2} is associated with structural distortions caused by the accumulation of radiolysis products, as well as deformation of the crystal structure as a result of high-dose irradiation. As can be seen from the data presented, in the case of irradiation with He^{2+} ions at maximum fluence, an almost equally probable ratio of the intensities of the lines characteristic of HC_2 – and Zr^{3+} -defects and oxygen vacancies (E – centers) is observed, while with irradiation with protons, the main contribution at maximum fluence to the changes in the EPR spectrum is associated with the intensity of the singlet line characteristic of E – centers, and the bands of HC_2 – and Zr^{3+} -defects are less pronounced than in the case of irradiation with He^{2+} ions.

Fig. 5 demonstrates comparative diagrams of the assessment of the weight contributions of the concentration of various defects in the damaged layer structure, determined on the basis of the assessment results of the concentrations of defects under different irradiation conditions. The general trend of alterations in the contributions of defects is that in the case of irradiation with He^{2+} ions at an irradiation fluence of 10^{17} cm^{-2}, the formation of the HC_2 – and Zr^{3+} -type defects, characteristic of the accumulation of radiolysis products, the proportion of which is about 20 % and grows almost by 2.3–2.4 times with an elevation in fluence to 10^{18} cm^{-2}, is observed. At the same time, for samples irradiated with protons, the formation of HC_2 – and Zr^{3+} -defects is observed at a fluence of 5×10^{17} cm^{-2}, and it should be noted that the weight contribution of HC_2 – and Zr^{3+} -defects is also approximately 20 %, and in the case of a fluence of 10^{18} cm^{-2}, the proportion rises to 30 %, which is comparable with the concentration of HC_2 – and Zr^{3+} -defects in the case of irradiation with He^{2+} ions at a fluence of 5×10^{17} cm^{-2}. From the presented dependencies, it can be concluded that the mechanisms of accumulation of radiolysis products are comparable in the case of high-dose irradiation, however, when irradiated with protons, the formation of radiolysis products occurs at high irradiation fluences, with a difference of approximately 5×10^{16} cm^{-2}.

Fig. 6 illustrates the results of a comparative analysis of changes in the thermal parameters of the studied 0.5 Li_2ZrO_3 – 0.5 Li_4SiO_4 ceramics when irradiated with protons and He^{2+} ions in the case of irradiation fluence variation. The data are presented as a dependence of the change in the thermal conductivity coefficient on the atomic displacement value in the case of different types of irradiation.

The general trend of changes in the thermal conductivity coefficient depending on the type of irradiation (in the case of irradiation with protons or He^{2+} ions) can be divided into two characteristic sections, described by differences in the degree of deterioration of thermal conductivity. At atomic displacement values of up to 1 dpa, for which, according to EPR spectroscopy data for both types of irradiation, structural

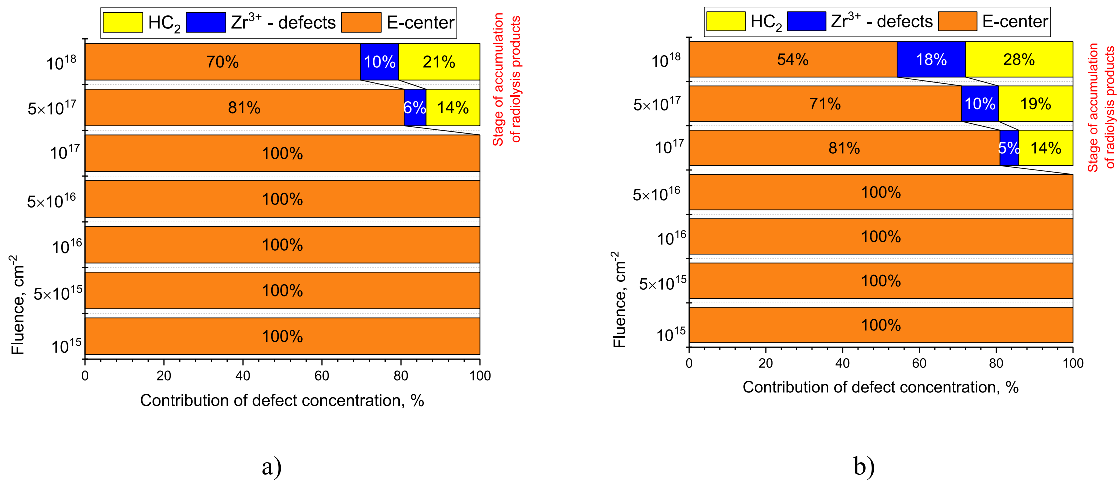


Fig. 5. Assessment results of the weight contributions of various defects in the damaged layer depending on the irradiation fluence in the case of irradiation of ceramics with different radiation types: a) proton irradiation; b) He^{2+} ion irradiation.

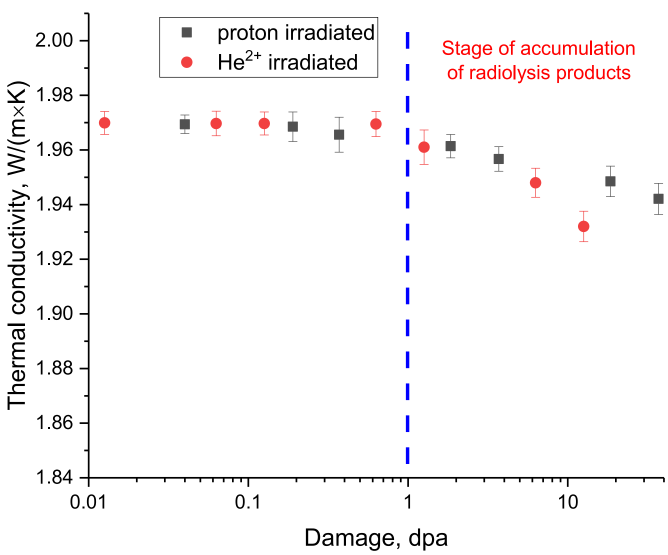


Fig. 6. Results of comparative analysis of alterations in the thermal conductivity coefficient of the studied ceramics when irradiated with protons and He^{2+} ions.

defects associated with oxygen vacancies dominate, changes in the thermal conductivity coefficient are minimal and are within the permissible error limits. At damage values greater than 1 dpa, the observed change in the trend of thermal conductivity coefficient reduction may be due to a greater degree of structural disorder associated with the formation and accumulation of radiolysis products in the damaged layer structure. It should be noted that in the case of proton irradiation, according to EPR spectroscopy data, the accumulation of radiolysis products is observed at fluences of the order of 5×10^{17} cm^{-2} (more than 10 dpa), however, the observed reduction in the thermal conductivity coefficient at fluences of 5×10^{16}–10^{17} cm^{-2} is due to the high concentration of oxygen vacancies, the presence of which leads to an elevation in the scattering of phonons during heat transfer, thereby reducing thermal conductivity.

A growth in the degradation of the thermal characteristics of ceramics depending on the increase in irradiation fluence may be due to the occurrence of heterogeneities in the structure of the damaged layer associated with an elevation in the concentration of absorbing centers associated with the accumulation of radiolysis products during high-dose irradiation. It should be noted that in the case where oxygen vacancies dominate as the main defects in the structure of ceramics, the change in the thermophysical properties of ceramics is minimal and is within the limits of measurement error. In the case of formation of structural damage in ceramics associated with the accumulation of HC_2 centers and Zr^{3+} defects in the structure, the thermal conductivity reduction is caused by phonon scattering processes, the number of acts of which grows due to interaction with defective inclusions, which results in a slowdown in heat transfer processes and, consequently, a decline in thermal conductivity.

To determine the temperature effect on the kinetics of radiation damage accumulation associated with radiolysis products during high-dose irradiation, a series of experiments in which samples were irradiated with protons and helium ions with a fluence of 10^{17} cm^{-2} (at which the initialization of the processes of accumulation of radiolysis products is observed during irradiation with helium ions) at various temperatures, varying in the range from 300 K to 1000 K, was conducted. The key objective of these experiments was to determine the mechanisms of temperature effects on diffusion processes that can result in accelerated degradation due to thermal effects associated with both thermal expansion of the crystal structure and a growth in the point and vacancy defect mobility rate, which can subsequently result in more pronounced agglomeration and degradation processes. The results of comparison of the EPR spectra of ceramics irradiated with protons and helium ions at a fluence of 10^{17} cm^{-2} with variations in the irradiation temperature are shown in Fig. 7.

The general trend of the observed changes in the EPR spectra, regardless of irradiation type, indicates an adverse impact of the irradiation temperature on the change in defect concentrations in the damaged layer, which has a clearly expressed dependence on the irradiation temperature. The obtained results of alterations indicate a change in the defect formation rates at the same fluence, and a decrease in the damage resistance of ceramics, expressed in more pronounced alterations in the intensities of spectral lines characteristic of HC_2 centers and Zr^{3+} defects associated with radiolysis products. In the case of proton irradiation, alteration of the irradiation temperature from 300 K to 500 K leads to the singlet line intensity growth, indicating an elevation in the concentration of vacancy defects in the structure with a change in the irradiation temperature, as well as the formation of a band characteristic of HC_2 centers, the intensity of which rises with a change in the irradiation temperature to 700 and 1000 K. Also, at temperatures of 700 and 1000 K, the spectra record bands characteristic of Zr^{3+} defects, which indicates that under high-temperature irradiation (above 500 K), the process of accumulation of radiolysis products in the form of

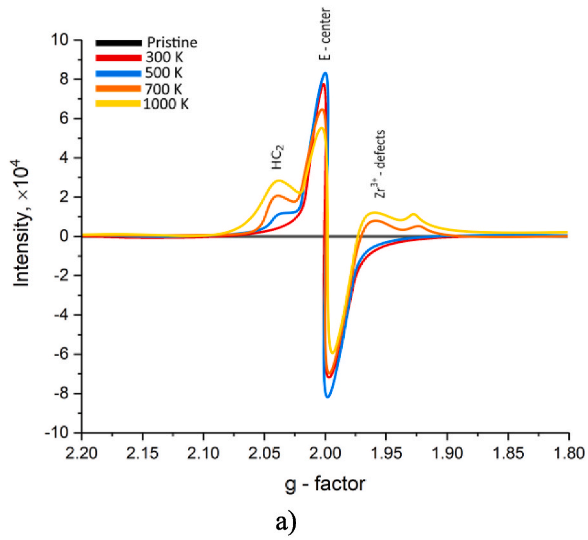


Fig. 7. Results of EPR spectroscopy of the studied ceramic samples exposed to irradiation at a fluence of 10^{17} cm^{-2} with a change in irradiation temperature: a) proton irradiation; b) He^{2+} ion irradiation.

HC_2 centers and Zr^{3+} defects in the damaged layer during proton irradiation proceeds more intensely, and the accumulation of radiolysis products is recorded at lower irradiation fluences, which indicates a reduction in the radiation resistance of ceramics to radiation damage processes with an elevation in the irradiation temperature.

In the case of samples irradiated with He^{2+} ions, the main alterations in the EPR spectra of the irradiated samples with an elevation in irradiation temperature are associated with a growth in the intensity of the spectral lines of HC_2 centers and Zr^{3+} defects, which indicates more intense accumulation processes of radiolysis products and degradation of the damaged ceramic layer.

Based on the obtained EPR spectra, an assessment of the change in the concentration of defects in the damaged layer, the results of which are presented in Fig. 8 in the form of diagrams reflecting the weight contributions of various defects in the damaged layer, was made.

The acceleration of the degradation processes of the damaged layer in both cases of irradiation with an elevation in the irradiation temperature can be explained by the following factors associated both with the effects of thermal expansion and the processes of thermally stimulated diffusion of vacancy defects in the damaged layer. In the case of two-phase ceramics, as has been shown in a number of studies [37,38], one of the key factors that determines higher radiation resistance values in comparison with single-phase ceramics is the effect of dislocation or dispersion hardening associated with the presence of grains of different sizes, as well as interphase boundaries, which in this case serve as barriers that restrain the diffusion of point and vacancy defects, and also reduce the likelihood of defect agglomeration due to the formation of the V_O – He or V_O – H type complexes. Moreover, as has been shown in several studies [39–41], reduction of the grain size even in the case of single-phase ceramics is one of the most promising methods for enhancement of resistance to radiation-induced gas swelling, the effect of which is due to the creation of additional restraining centers for the agglomeration of products of nuclear reactions of neutrons with lithium, alongside radiolysis products. In the case of thermal exposure, thermal expansion of the crystal structure due to a change in the amplitude of thermal vibrations can result in partial relaxation of point and dislocation defects, which, in combination with an alteration in the diffusion rate of vacancy defects and implanted hydrogen or helium, results in more pronounced processes of migration and subsequent agglomeration, which, as can be seen from the presented data of the EPR spectra analysis, leads to a rise in the weight contributions of defects associated with the accumulation of radiolysis products. In this case, the processes of thermally stimulated diffusion of vacancy defects, as well as implanted helium or hydrogen ions, lead to the acceleration of

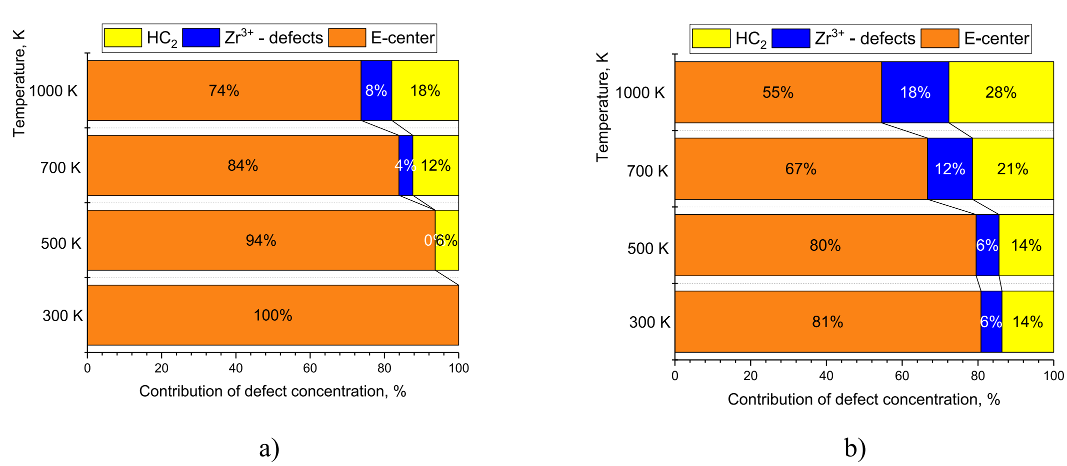


Fig. 8. Assessment results of the weight contributions of different types of defects in the damaged layer depending on the irradiation temperature, characterizing the change in the degradation kinetics due to thermally stimulated diffusion of radiation defects: a) proton irradiation; b) He^{2+} ion irradiation.

agglomeration processes due to the formation of the V_O – He or V_O – H type complexes, an elevation in the concentration of which results in destabilization of the damaged layer and deterioration of its structural ordering (according to the data of the assessment of structural parameters in the case of high-temperature irradiation, the degree of volumetric structural swelling is more pronounced than in the case of irradiation at room temperature).

It should also be noted that in the case of high-dose irradiation, which is usually accompanied by the accumulation of a large number of structural defects in the damaged layer, standard methods such as X-ray diffraction do not allow determining the type of point defects, but only their concentration, which excludes the possibility of a full analysis of the kinetics of structural damage. At the same time, for understanding the evolution of structural damage, as well as predicting possible mechanisms of destruction, the most suitable methods are EPR spectroscopy and Raman spectroscopy, the use of which allows with high accuracy to determine the types of structural defects arising from irradiation or as a result of nuclear fission reactions. For example, a number of studies [42–46] have shown that the use of Raman spectroscopy and EPR spectroscopy methods allows for a detailed description of the types of point defects that arise as a result of irradiation, as well as for determining the kinetics of subsequent changes in the structural and optical properties of ceramic materials, which in turn is very important both from a practical point of view and from a fundamental point of view, related to the expansion of ideas about the kinetics of radiation damage in ceramics used in nuclear and thermonuclear energy.

4. Conclusion

According to the analysis of the structural damage accumulation kinetics in the case of irradiation with protons and He^{2+} ions in the near-surface layer of 0.5 Li_2ZrO_3 – 0.5 Li_4SiO_4 ceramics, it was found that at low irradiation fluences (10^{15} - 10^{17} cm^{-2}), the dominant role in structural changes is played by the concentration dependences of oxygen vacancies, the change of which results in small alterations in thermal conductivity, while at fluences above 10^{17} cm^{-2}, the contribution to the changes in the destruction of the near-surface layer is made by radiolysis products (HC_2 – and Zr^{3+} - defects), the accumulation of which is more pronounced in the case of irradiation with He^{2+} ions. It has been established that the main mechanisms of formation of oxygen vacancies are associated with the values of electron ionization losses of incident particles, while the accumulation of radiolysis products is significantly influenced by nuclear ionization losses, as well as the associated athermal deformation effects.

During conducted experimental works, on determination of the influence of the irradiation temperature on the change of weight contributions of different types of defects in the damaged layer, as well as the change of the mechanisms of their formation, the following was established. In the case of proton irradiation, the temperature growth results in more intensive processes of structural damage accumulation, which leads to the initialization of accumulation of radiolysis products at lower fluences than in the case of irradiation at room temperature. In the case of irradiation with He^{2+} ions, the obtained dependences indicate an acceleration of the intensity of accumulation of radiolysis products and a more pronounced degradation of the damaged layer. Based on the data obtained, it can be concluded that the temperature effect during irradiation has an adverse effect on the resistance of ceramics to radiation damage and accumulation of radiolysis products, which must be taken into account during assessment of the prospects for application of these ceramics as materials for tritium breeding, in the case of their operation under elevated temperatures. The main mechanisms that cause accelerated degradation of the damaged layer in the case of high-temperature irradiation are thermally stimulated diffusion of vacancy defects, alongside their agglomeration into complexes, leading to the formation of gas-filled inclusions in the near-surface damaged layer.

The results of the studies conducted can be further used to determine the potential for application of the proposed ceramic compositions as materials for tritium breeding, as well as to assess the prospects for application of two-component ceramics as a basis for blanket materials that have higher stability indicators compared to one-component ceramics.

CRediT authorship contribution statement

Dmitriy I. Shlimas: Writing – original draft, Software, Resources, Formal analysis, Data curation, Conceptualization. **Daryn B. Borgekov:** Resources, Project administration, Investigation, Formal analysis, Data curation, Conceptualization. **Artem L. Kozlovskiy:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

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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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