ceramics

Article

The Influence of Accumulated Radiolysis Products on the Mechanisms of High-Temperature Degradation of Two-Component Lithium-Containing Ceramics

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Abstract

One of the advantages of the EPR spectroscopy method in assessing structural defects caused by irradiation is the fact that using this method it is possible to determine not only the concentration dependences of the defect structure but to also establish their type, which is not possible with methods such as X-ray diffraction or scanning electron microscopy. Based on the data obtained, the role of variation in the ratio of components in Li_4SiO_4–Li_2TiO_3 ceramics on the processes of softening under high-dose irradiation with protons simulating the accumulation of hydrogen in the damaged layer, as well as the concentration of structural defects in the form of oxygen vacancies and radiolysis products on the processes of high-temperature degradation of ceramics, was determined. It was found that the main changes in the defect structure during the prolonged thermal exposure of irradiated samples are associated with the accumulation of oxygen vacancies, the density of which was estimated by the change in the intensity of singlet lithium, characterizing the presence of E-centers. At the same time, it was found that the formation of interphase boundaries in the structure of Li_4SiO_4–Li_2TiO_3 ceramics leads to the inhibition of high-temperature degradation processes in the case of post-radiation thermal exposure for a long time. Also, during the conducted studies, the role of thermal effects on the structural damage accumulation rate in Li_4SiO_4–Li_2TiO_3 ceramics was determined in the case when irradiation is carried out at different temperatures. During the experiments, it was determined that the main contribution of thermal action in the process of proton irradiation at a fluence of 5×10^{17} proton/cm^2 is an increase in the concentration of radiolysis products, described by changes in the intensities of spectral maxima, characterized by the presence of defects such as $\equiv$Si–O, SiO_4^{3-} and Ti^{3+} defects.

Keywords: two-component lithium-containing ceramics; radiolysis products; EPR spectroscopy; radiation damage; degradation; oxygen vacancies

Academic Editors: Gilbert Fantozzi and Vincent Garnier

Received: 31 May 2025
Revised: 22 July 2025
Accepted: 30 July 2025
Published: 3 August 2025

Citation: Kenzhina, I.E.; Askerbekov, S.; Kozlovskiy, A.L.; Tolenova, A.; Piskunov, S.; Popov, A.I. The Influence of Accumulated Radiolysis Products on the Mechanisms of High-Temperature Degradation of Two-Component Lithium-Containing Ceramics. *Ceramics* **2025**, *8*, 99. https://doi.org/10.3390/ceramics8030099

1. Introduction

One of the most promising directions for solving the problem of tritium fuel for thermonuclear reactors is the use of lithium-containing ceramics for its multiplication and subsequent production, the use of which, due to the $^6Li + n \rightarrow {}^3H + {}^4He$ reaction, allows the required amount of tritium to be produced to maintain the operability of thermonuclear reactors [1–3]. At the same time, the existing natural reserves of lithium make it possible to solve this problem for a fairly long period of time (about 100–150 years), which will create the necessary reserve of time for the development of new technologies in the field of energy, as well as reduce the burden on the use of fossil fuels and hydrocarbons in the energy sector [4–6]. In this regard, in recent years, scientific research aimed at study of the prospects for using various lithium-containing ceramics for the purpose of producing tritium, as well as a comprehensive study of the processes of interaction of ceramics with ionizing radiation, including neutrons, protons, alpha particles, the effect of which makes it possible to assess the mechanisms of radiation damage arising in ceramics during irradiation simulating operating conditions, has been actively promoted [7–9]. Also, the use of various types of ionizing radiation, including alpha particles or protons, is usually used to model or simulate the processes of accumulation of nuclear reaction products in the damaged layer, the accumulation of which leads to destabilization and softening of ceramics, which in extreme operating conditions can lead to the rapid failure of ceramics due to loss of strength or thermal overheating. Experiments with neutron irradiation are usually aimed at study of the mechanisms of tritium production due to nuclear reactions with subsequent control of the mechanisms of its release from the volume of ceramics and subsequent transportation [10,11]. Moreover, all experiments related to the impact of various types of ionizing radiation on ceramics lead to the destabilization of the near-surface layers, which is expressed in a decrease in strength and loss of resistance to cracking due to the accumulation of defective inclusions, leading to the partial or complete amorphization of the damaged layer [12–21].

One of the ways to increase the service life of lithium-containing ceramics exposed to high dose loads is to combine two different lithium-containing components, such as lithium titanate, lithium orthosilicate, and lithium metazirconate, allowing the creation of an interphase boundary effect in them that prevents softening processes at high doses of radiation [22–24]. Moreover, the use of lithium titanate and lithium orthosilicate compounds for obtaining two-component ceramics is the most promising ceramic composition, in contrast to γ-$LiAlO_2$ [25], $LiAl_5O_8$ [26], or lithium metazirconate. Interest in Li_4SiO_4–Li_2TiO_3 ceramics is attributed to the possibility of a combination of high tritium production rates, as well as high resistance to mechanical stress and high-temperature effects. However, despite the large number of studies in this area, the search for optimal ratios of lithium-containing ceramics is still ongoing, which expands the possibilities for research groups in this area and stimulates their scientific research [27–30].

Studies on the preservation of the stability of the strength and thermal properties of irradiated samples are of considerable interest due to the possibility to evaluate the effect of the accumulated dose of structural damage on the overall kinetics of degradation [31–33]. In most cases, experiments with irradiated samples are limited to studying the effect of variations in the radiation dose on changes in properties without continuing to study the changes that occur in irradiated samples when exposed to high temperatures or aggressive environments after irradiation. In this case, such studies are of great interest, since accumulated structural damage in samples can significantly accelerate the processes of destruction that arise as a result of external post-radiation effects, and the concentration of structural defects itself leads to the destabilization of the near-surface layers, which also accelerates the corrosion processes of materials. In this paper, we consider the influence of the variation in the ratio of components in the composition of Li_4SiO_4–Li_2TiO_3 ceramics on the resistance to post-radiation thermal effects over a long period of time, simulating the processes of thermal aging and oxidation of samples, as well as identifying the role of changing the ratio of components of ceramics in containing the processes of radiation damage in the case of variation in high-dose irradiation conditions (in this case, variation of the irradiation temperature is considered).

2. Materials and Methods

The objects of the study were Li_4SiO_4–Li_2TiO_3 ceramics obtained using the method of three-stage mechanochemical solid-phase synthesis, carried out with the aim of obtaining two-component ceramics with the possibility of varying the ratio of components, ensuring a change in the strength and thermal physical parameters in the composition of the ceramics. The variation in the ratio of components in the composition of two-component ceramics was carried out by adding Li_2TiO_3 powders in molar fractions from 0.1 to 0.5 M to Li_4SiO_4 powders obtained in the first stage of mechanochemical synthesis, which, upon mixing and subsequent pressing, made it possible to obtain two-component ceramics with different component ratios. A detailed description of the method for obtaining ceramic data, as well as the influence of variation in the ratio of components on the strength and thermal parameters, was presented in [34,35]. Table 1 presents the assessment results of strength parameters (hardness and resistance to cracking), as well as the thermal conductivity coefficient, reflecting the influence of variations in the ratio of components in the composition of ceramics.

Table 1. Data on the strength and thermal parameters of Li_4SiO_4–Li_2TiO_3 ceramics depending on the variation in the ratio of components in the composition.

Parameter	**Concentration of Li_2TiO_3 in Ceramics, M**					
	0	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
Hardness, HV	690 ± 15	715 ± 13	768 ± 14	822 ± 17	803 ± 14	786 ± 16
Crush load, N	42.1 ± 0.2	46.4 ± 0.3	50.2 ± 0.4	57.6 ± 0.3	53.2 ± 0.2	49.3 ± 0.5
Thermal conductivity, W/(m × K)	1.85 ± 0.02	1.87 ± 0.01	1.89 ± 0.02	1.97 ± 0.03	1.88 ± 0.02	1.87 ± 0.01

The strength parameters given in Table 1 were determined using the indentation and single compression methods. Indentation was performed using a Duroline M1 microhardness tester (Metkon, Bursa, Türkiye). A Vickers diamond pyramid was used as an indenter, and the load on the indenter was 100 N. The determination of cracking resistance was carried out using the single compression method implemented on the LFM-L 10kH testing machine (Walter + Bai AG, Löningen, Switzerland). The formation of microcracks was monitored using an extensometer. The maximum pressure value given in Table 1 reflects the load that the ceramics can withstand under compression.

The thermal conductivity of ceramics was determined using the longitudinal heat flow method. Measurements were carried out using a universal thermal conductivity meter KIT-800 (KB Teplofon, Moscow, Russia). The measurements were carried out in the air, with temperature changes being monitored using thermocouples. During the measurement of the thermal conductivity of the irradiated samples, the effects of structural changes, as well as the associated anisotropic effects of degradation of the damaged layer, were considered.

According to the data presented in Table 1, the addition of Li_2TiO_3 powder to the composition of Li_4SiO_4 ceramics at concentrations of 0.1–0.3 M leads to an increase in strength (hardness and resistance to cracking) and thermal conductivity, while at concentrations of 0.4–0.5 M, a slight decrease in these parameters is observed due to changes in the structural features of the ceramics. The observed change in strength parameters in this case is due to dispersion hardening, which occurs as a result of combining two types of lithium-containing powders, the variation of which leads to the formation of barrier effects that have a hardening effect in the structure of ceramics, and also increase thermal conductivity, which has a positive effect on the properties of lithium-containing ceramics.

The simulation of the processes of hydrogenation and destabilization of the near-surface layer was carried out by the irradiation of the studied ceramics with protons with an energy of 1.0 MeV. The irradiation fluence was 5×10^{17} proton/cm^2, and the beam current was about 25 μA. The proton penetration depth was about 20–25 μm. In this case, the selected irradiation fluence, according to the results of work [35], leads to the appearance in the structure of the damaged layer of both oxygen vacancies and radiolysis products, the density of which depends on the ratio of components in the composition of the ceramics. Irradiation was carried out on special ceramic targets equipped with heating elements, allowing irradiation to be carried out at a constant specified temperature. Control over maintaining the sample temperature during the entire irradiation period was carried out using thermocouples.

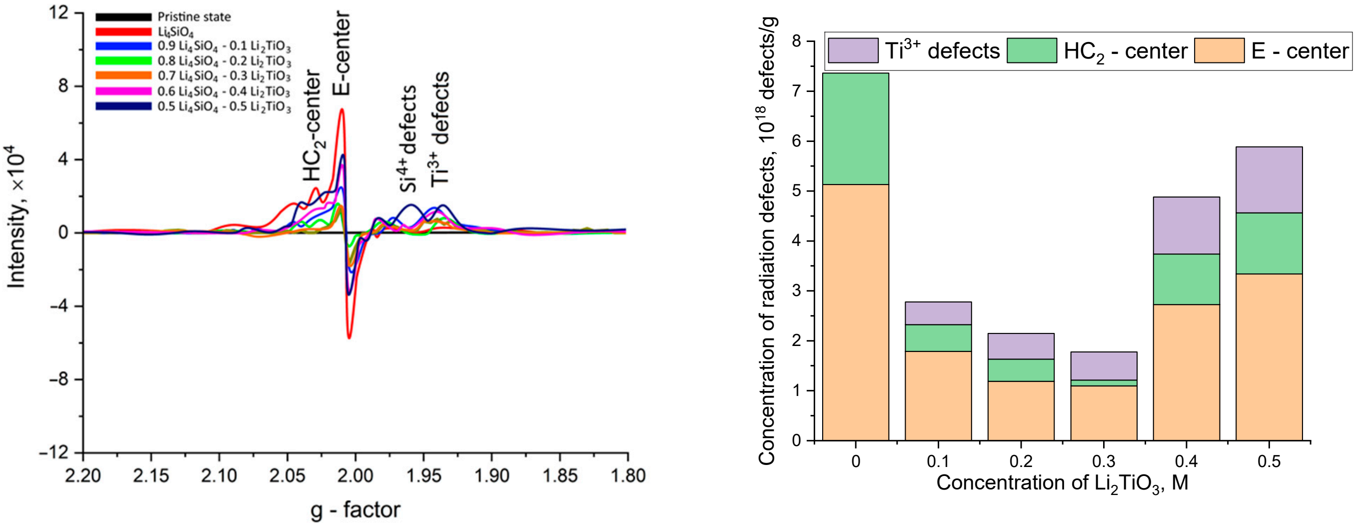
The influence of temperature factors on the rate of accumulation of defects in the structure of the damaged layer in Li_4SiO_4–Li_2TiO_3 ceramics in the case of high-dose proton irradiation was assessed by irradiating ceramic samples at different temperatures of 300 K, 700 K, and 1000 K, the choice of which was determined by the possibilities of simulating the processes of ceramic degradation under conditions as close as possible to real operating conditions. The basis for conducting such experiments were the results of a number of experimental works [36,37], which showed the difference in the mechanisms of accumulation of structural damage in ceramics in the case of irradiation at high temperatures. Such effects are explained by the more accelerated diffusion of structural defects arising as a result of irradiation, which leads to more intensive degradation of the damaged layer. To determine the mechanisms of destructive changes in the damaged layer depending on the irradiation temperature, the EPR spectroscopy method was used, which makes it possible to evaluate not only the general changes in structural properties, expressed in the accumulation of defects in the damaged layer, but to also determine the type of defects that arise when the irradiation conditions vary.

The influence of accumulated radiation structural damage in ceramics on changes in thermal properties was studied by assessing changes in the thermal conductivity coefficient of ceramics depending on the conditions of external influences. Measurements were carried out using the KIT-800 device in the temperature range from 25 to 800 °C, which made it possible to establish the dependences of the influence of the concentration of structural defects on the slowdown of heat transfer processes associated with phonon heat transfer in samples. The data presented in Table 1 on the change in the thermal conductivity coefficient of the studied Li_4SiO_4–Li_2TiO_3 ceramics depending on the variation in the ratio of components in the composition of the ceramics showed that the addition of Li_2TiO_3 to the composition of the ceramics leads to an increase in thermal conductivity, the change in which in this case is due to the structural features and thermophysical properties of lithium titanate. Moreover, in the case of high concentrations of Li_2TiO_3 in the composition of ceramics (more than 0.3 M), a slight decrease in thermal conductivity associated with the structural changes caused by variations in the ratio of components in the composition of ceramics is observed.

Experiments on the simulation of the processes of post-radiation thermal aging caused by long-term exposure to high temperatures on the studied samples, pre-irradiated, were carried out by placing ceramic samples in a muffle furnace and then holding the samples for 1000 h at a temperature of 1000 K. After 500 h, the samples were subjected to intermediate measurements of the EPR spectra and thermal conductivity coefficient in order to establish changes caused by oxidation processes under thermal influence.

3. Results and Discussion

Figure 1a reveals the EPR spectra of the studied samples after irradiation with protons with a fluence of 5 × 10^{17} proton/cm^2, reflecting the influence of the variation in the ratio of components in Li_4SiO_4–Li_2TiO_3 ceramics on the density of defects formed as a result of irradiation. An analysis of the EPR spectra with an interpretation of the main absorption centers is given in Table 2.



(**a**)

(**b**)

Figure 1. (**a**) EPR spectra of the studied Li_4SiO_4–Li_2TiO_3 ceramics after irradiation with protons with a fluence of 5 × 10^{17} proton/cm^2. (**b**) Diagram of the dependence of the change in the concentration of defects depending on the ratio of components in the composition of ceramics.

Table 2. EPR spectroscopy data.

Parameter	**Concentration of Li_2TiO_3 in Ceramics, M**					
	0	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
E-center (g-factor~2.002–2.005)	Oxygen vacancies; the intensity of the singlet band is quite large.	The decrease in the intensity of the singlet band is due to the increase in the stability of two-component ceramics to disordering processes caused by irradiation.				
HC_2-center (g-factor~2.020–2.025)		The weakening of the signals of HC_2 centers is due to the higher stability of TiO_6 octahedra to radiation damage and the higher radiation resistance of titanates compared to silicates.				
Ti^{3+} defects (g-factor~~1.94–1.98)	none	The intensity increases as Li_2TiO_3 concentration grows in the ceramics′ composition.				
Si^{4+}-defects (g-factor~~2.01–2.015)	Oxygen vacancies in SiO_4-tetrahedra	As the Li_2TiO_3 concentration in the ceramics grows, the intensity of the spectral band characteristic of this type of defect reduces, which indicates an increase in the stability of the ceramics to radiation damage.				

A general analysis of the EPR spectra showed the presence of spectral lines characteristic of the formation of oxygen vacancies (E-centers), defects of the ≡Si–O or SiO_4^{3-} (HC_2 centers) type, and Ti^{3+} defects, the formation of which causes the accumulation of radiolysis products in the damaged layer. The presence of oxygen vacancies (V_O), described by the formation of a singlet line at g = 2.002–2.005 (E-center), is due to ballistic mechanisms of defect formation during the knocking out of lithium or oxygen atoms from the nodes of the crystal lattice, as a result of which V_O is formed. At the same time, the observed values of the g-factor are in good agreement with the results of the works [38,39]. It should be noted that the broadening of the singlet line indicates the formation of defects in the structure with broken ≡Si– bonds associated with oxygen vacancies. Similar defects were found in the works [40,41]. The formation of the spectral maximum with g = 2.020–2.025 is associated with the formation of HC_2-centers, which are holes associated with oxygen atoms in tetrahedra. The results obtained agree with the results of the works of Zarins A. et al. [42,43], who are actively engaged in the study of orthosilicate ceramics, considered as blanket materials. It should be noted that the highest intensity of this spectral band is observed for single-component Li_4SiO_4 ceramics. The addition of Li_2TiO_3 to the composition of ceramics leads to a decrease in the intensity of this band, the weakening of which is due to the higher stability of TiO_6 octahedra to radiation damage and the higher radiation resistance of titanates compared to silicates. Also, the formation of HC_2-centers in the composition of ceramics can be caused by the accumulation of radiolysis products during high-dose irradiation. The observed Si^{4+}-related defects ($g \approx 2.01–2.015$), the presence of which was established in the EPR spectra of single-component Li_4SiO_4 ceramics samples, are in good agreement with the results of [44,45].

In the case of two-component Li_4SiO_4–Li_2TiO_3 ceramics, the addition of Li_2TiO_3 to the composition leads to the formation of Ti^{3+} defects associated with the $Ti^{4+} + e^- \rightarrow Ti^{3+}$ type reactions, characteristic of radiolysis processes that occur during high-dose irradiation [46,47]. It should be noted that variation in the ratio of components in the composition of Li_4SiO_4–Li_2TiO_3 ceramics leads to a change in the concentration of defects in the damaged layer, according to calculations carried out using Formula (1), based on an assessment of the areas of the absorption curves of EPR signals (S_x) in comparison with reference samples (S_{ref}), alongside the concentration of unpaired electrons (N_{ref}) and the mass of the sample (m) [28]. Non-irradiated samples were used as a standard, a comparison with which made it possible to evaluate the change in the concentration of defects in the structure caused by irradiation.

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

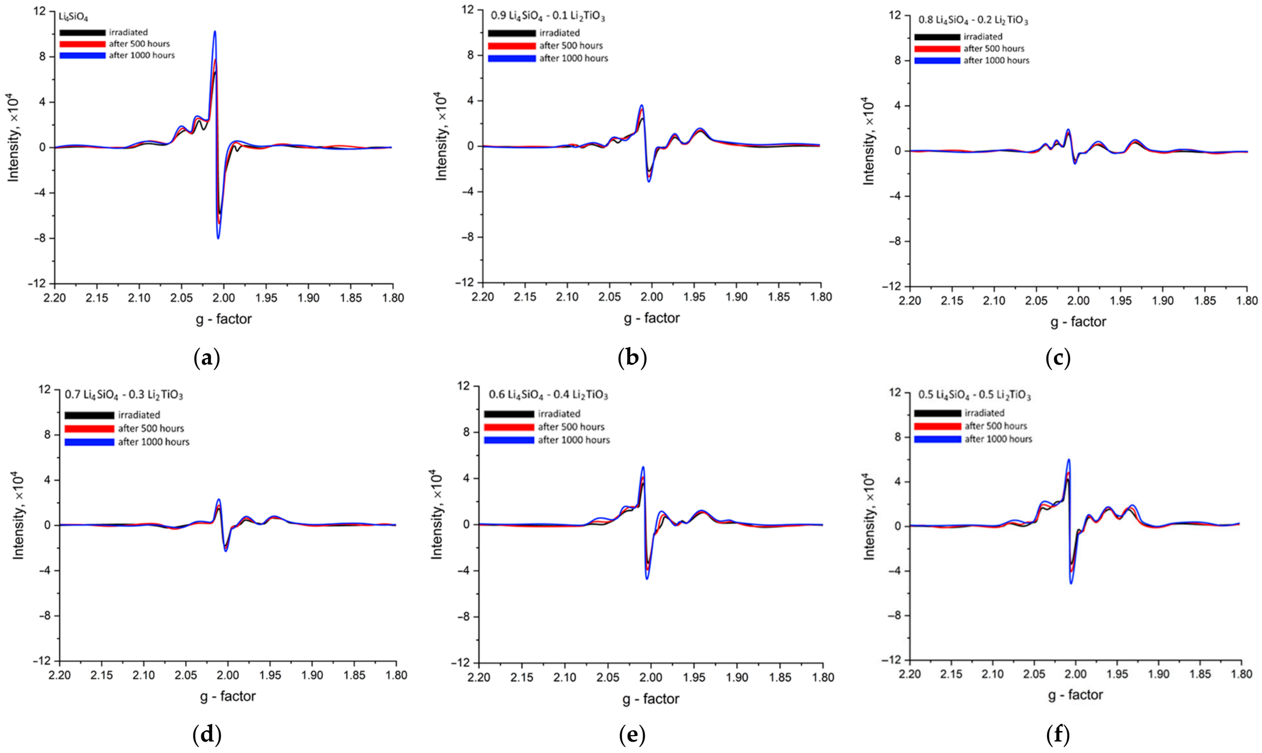
The assessment results are shown in Figure 1b as a comparative diagram reflecting the contribution of each type of defect found in the structure of the damaged layer. According to the presented data, the dominant role in the defect structure is played by oxygen vacancies, the contribution of which ranges from 55% (for 0.7 Li_4SiO_4–0.3 Li_2TiO_3 ceramics) to 70% (for Li_4SiO_4 ceramics). In this case, the contribution of HC_2 centers and Ti^{3+} defects, depending on the ratio of components in the composition of Li_4SiO_4–Li_2TiO_3 ceramics, varies from 7% to 21% (for HC_2 centers) and from 16% to 32% (for Ti^{3+} defects). It should also be noted that the addition of 0.1–0.3 M Li_2TiO_3 to the composition of Li_4SiO_4 ceramics leads to a decrease in the overall concentration of defects by more than 2.5–3.5 times, from which it follows that the presence of interphase boundaries leads to an increase in the stability of ceramics and an increase in resistance to defect formation processes under high-dose irradiation.

According to the obtained data of EPR spectra analysis, it can be noted that the variation in the component ratio in the composition of Li_4SiO_4–Li_2TiO_3 ceramics leads to a slowdown in degradation processes. This effect is due to the formation of interphase boundaries in the composition of ceramics, which results in hardening and increased resistance to disordering processes. Similar effects of radiation damage resistance growth due to the presence of interphase boundaries have been studied in several studies [48,49], in which ceramics were subjected to neutron irradiation. The hardening effect in this case is due to the creation of barriers for migrating vacancy defects and radiolysis products formed as a result of high-dose irradiation, which leads to a slowdown in diffusion and the inhibition of agglomeration. The presence of such barriers associated with the variation in component concentration in Li_4SiO_4–Li_2TiO_3 ceramics makes it possible to reduce the effect of gas swelling during high-dose irradiation with protons or helium [34,35], alongside restraining the processes of accumulation of radiolysis products during neutron irradiation [48,49]. The variation of components in the composition of ceramics also plays an important role in the alteration of strength characteristics [50] and the production of tritium [51].

It should also be noted that in the case of two-component ceramics, variation in the ratio of the Li_4SiO_4 and Li_2TiO_3 components in the composition leads not only to an increase in resistance to structural disorder caused by the accumulation of defects in the damaged layer but also to a decrease in the contribution of oxygen vacancies, which determine the main role in the mechanisms of defect formation in the damaged layer during irradiation. Moreover, as was shown in works [35,36], the accumulation of radiolysis products in the case of high-dose irradiation has a direct dependence on the concentration of oxygen vacancies in the damaged layer, the achievement of a critical concentration of which leads to the formation of complex defects that contribute to the acceleration of the physical and chemical processes of accumulation of radiolysis products. The accumulation of structural changes caused by proton irradiation, as well as the inhibition of the processes of accumulation of radiolysis products due to the change in the ratio of components in the composition of ceramics, are in good agreement with the reactor experiments conducted by the research group Zarins A. et al. in several works [42–45]. In this case, the selection of the optimal ratio of components in the composition of Li_4SiO_4–Li_2TiO_3 ceramics allows us to not only reduce the overall concentration of structural defects by more than 1.5–3.5 times but also slow down the accumulation of radiolysis products, which allows us to further extend the life of lithium-containing ceramics.

The effect of high-temperature degradation resulting from long-term exposure to high temperatures on irradiated lithium-containing ceramics was assessed by comparative analysis of changes in the EPR spectra of samples after 500 and 1000 h of sequential heating at a temperature of 1000 K. The choice of these experimental conditions aimed at stimulating the processes of high-temperature corrosion of the irradiated samples under study is determined by the potential operating modes in which the samples can be subjected to prolonged thermal heating, which leads to the initialization of oxidation and degradation processes. The most accurate method for the assessment of degradation processes in this case is the EPR spectroscopy method, the use of which allows one to assess the concentration of structural defects and their type as a result of external high-temperature effects based on changes in spectral lines. The results of changes in the EPR spectra are presented in Figure 2. To compare the changes caused by thermal exposure with different time intervals, EPR spectra of samples after irradiation are given for each studied ceramic depending on the variation in the ratio of components in the composition. It should be noted that the main changes observed in the EPR spectra of irradiated ceramic samples, presented in the form of two spectra of samples after 500 and 1000 h of temperature exposure, are associated with a change in the intensities of the main observed spectral lines, as follows: a singlet characteristic of E-centers (oxygen vacancies), HC_2-centers, and Ti^{3+} defects (for two-component ceramics). At the same time, no new spectral lines were found in the

EPR spectra of irradiated samples subjected to thermal effects, and the observed changes, including a slight broadening of the spectral lines for HC_2 centers and Ti^{3+} defects, can be explained by a change in the density of these defects associated with oxidation processes during thermal heating, as well as the diffusion of oxygen from the outside into the damaged layer. The observed change in the intensity of the singlet line describing the change in the concentration of oxygen vacancies in the damaged layer may be due to the processes of diffusion of oxygen and vacancies in the damaged layer as a result of oxidative embrittlement of the damaged layer, as well as the occurrence of internal oxidative stresses arising as a result of chemical oxidation processes due to the uneven oxygen saturation of the damaged layer.



(**a**) (**b**) (**c**)

(**d**) (**e**) (**f**)

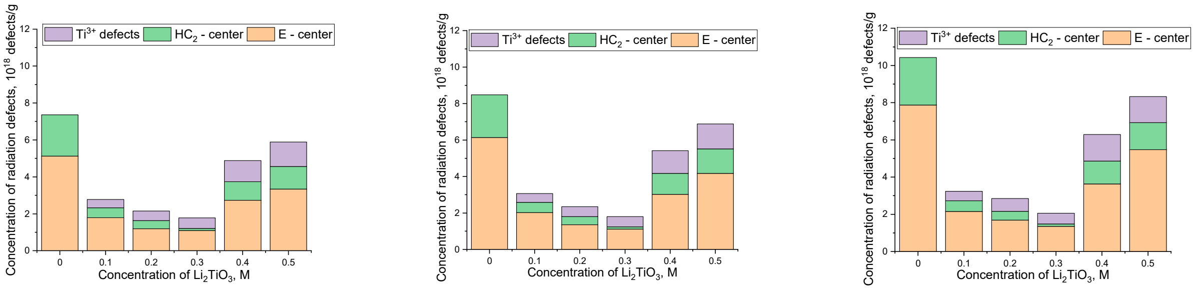
Figure 2. EPR spectra of the studied lithium-containing ceramics depending on the thermal heating time (500 and 1000 h): (**a**) Li_4SiO_4; (**b**) 0.9 Li_4SiO_4–0.1 Li_2TiO_3; (**c**) 0.8 Li_4SiO_4–0.2 Li_2TiO_3; (**d**) 0.7 Li_4SiO_4–0.3 Li_2TiO_3; (**e**) 0.6 Li_4SiO_4–0.4 Li_2TiO_3; and (**f**) 0.5 Li_4SiO_4–0.5 Li_2TiO_3.

The resulting oxygen vacancies, as well as metal ions Ti^{3+} or Si^{4+} as a result of irradiation, can promote reverse oxidation processes as a result of prolonged thermal heating. Moreover, these processes can be accompanied by the release of energy in a small local volume, which, together with the uneven oxygen saturation of the near-surface layer under thermal influence, can lead to the formation of additional structural stresses that have a destabilizing effect on the damaged layer. In turn, chemical oxidation processes during prolonged thermal exposure are capable of initiating the processes of formation of new phases, the result of which is a change in the chemical composition due to the mechanisms of oxidative embrittlement, leading to a decrease in thermophysical parameters and softening of irradiated ceramics. The observed increase in the intensity of spectral lines characteristic of HC_2 centers can be explained by the slow occurrence of oxidation processes in the damaged layer, which are accompanied by the formation of peroxide groups of the $\equiv$Si–O–O type [42–44]. These groups are metastable, and as a result, they can disintegrate under prolonged heating, which leads to the formation of additional oxygen inside the damaged layer, which leads to internal oxidation and the destabilization of the damaged layer.

According to the presented EPR spectra, in the case of variation in the component ratio in Li_4SiO_4–Li_2TiO_3 ceramics, the observed change in the intensities of the spectral lines indicates the inhibition of oxidation processes that occur as a result of long-term thermal exposure. In this case, the observed changes indicate a positive effect of variation in the component ratio on enhancement of the stability of two-component ceramics, not only to high doses of irradiation but also to subsequent long-term thermal exposure. At the same time, the observed effects of changes in the intensities of spectral lines of ceramic samples subjected to long-term thermal exposure are in good agreement with the results of studies [52–54], according to which, the accumulation of structural defects in the case of small doses when exposed to high temperatures can compete with the processes of annihilation (partial relaxation), and in the case of high-dose irradiation, accelerate the processes of destabilization of the damaged layer.

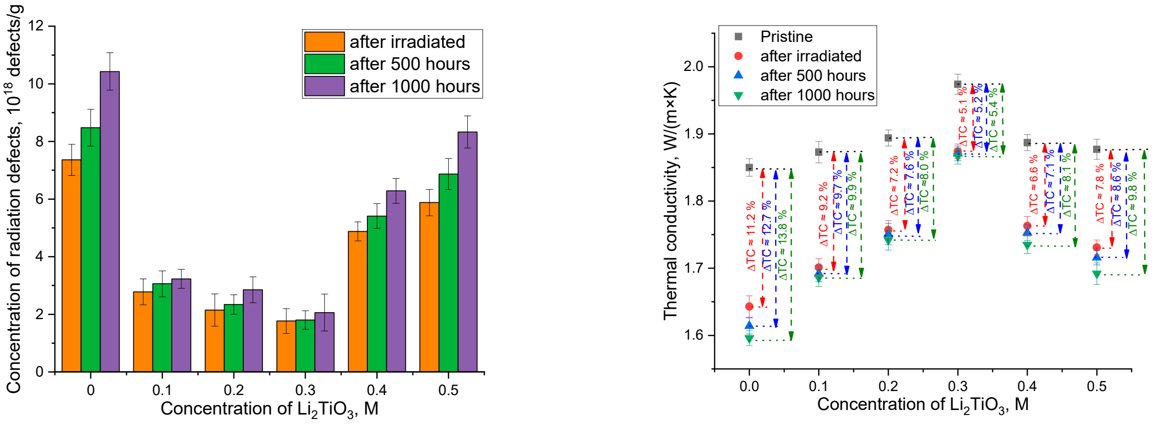
The diagrams shown in Figure 3 reflect the change in defect concentration depending on the time of the thermal impact on irradiated samples. The data in the diagrams are presented in the form of columns reflecting the contribution of each established type of defect in the structure of the damaged ceramic layer, and for comparative analysis, all data are presented on a single scale with the purpose of clearly demonstrating the observed changes in defect concentration caused by thermal impact. The data shown in the diagrams in Figure 3 reflect oxidation processes that occur as a result of prolonged thermal exposure, which is accompanied by the penetration of oxygen from the surface into the depths of the sample, followed by the initialization of oxidation processes of the damaged layer. At the same time, the observed increase in the change in the concentration of structural defects in comparison with the initial values clearly demonstrates the time dependence of oxidation processes, as well as the role of the influence of changes in the ratio of components in the composition of ceramics on the resistance to the growth of defective inclusions in the damaged layer. In the case of single-component Li_4SiO_4 ceramics, the main changes caused by long-term thermal exposure are associated, according to the analysis of EPR spectra, with a change in the concentration of oxygen vacancies in the damaged layer, the growth of which has a time dependence, and an increase in the time of exposure to high temperatures results in more intense oxidation due to an increase in the contribution of structural stresses during the diffusion of oxygen into the sample, leading to destabilization of the damaged layer and more intense oxidation. In the case of Li_4SiO_4–Li_2TiO_3 ceramics, the presence of interphase boundaries leads to the inhibition of oxidation processes, which are expressed in small changes in the concentration of defective inclusions both after 500 h and after 1000 h, while the most resistant to destructive high-temperature oxidation processes are ceramics with a component ratio of 0.7 Li_4SiO_4–0.3 Li_2TiO_3. At the same time, a growth in the proportion of Li_2TiO_3 in the composition of two-component ceramics above 0.3 M results in the destabilization of the crystalline structure of the damaged layer due to the processes of lithium titanate destabilization.

Figure 4a shows the results of a comparative analysis of changes in the concentration of structural defects, including oxygen vacancies and radiolysis products in the form of ≡Si–O, SiO_4^{3-}, and Ti^{3+} defects, calculated using Formula (1) based on the obtained EPR spectra and the data shown in Figures 2 and 3. This diagram clearly demonstrates the influence of the time of temperature exposure on irradiated samples, as well as the role of structural changes caused by variations in the ratio of components in the composition of ceramics, a change in which leads to an increase in resistance to softening and degradation as a result of prolonged thermal heating. In the case of Li_4SiO_4 ceramics, thermal heating from 500 to 1000 h leads to an increase in the growth rate of the concentration of defective inclusions, which is associated with both an increase in the concentration of oxygen vacancies and HC_2 centers responsible for the accumulation of radiolysis products. In this case, prolonged thermal exposure to ceramics leads not only to a growth in oxygen vacancies caused by structural changes during the penetration of oxygen from the outside and its subsequent diffusion but also the acceleration of chemical oxidation processes, the result of which is the accumulation of radiolysis products. The addition of Li_2TiO_3 to the ceramic composition at concentrations of 0.1–0.3 M allows us to minimize the thermal effects and associated oxidation processes; however, with prolonged exposure, the acceleration of defect accumulation processes in the damaged layer is also observed, albeit at a lower rate.



(**a**) (**b**) (**c**)

Figure 3. Results of changes in defect concentration in ceramics after high-temperature exposure: (**a**) after irradiation; (**b**) after 500 h; and (**c**) after 1000 h.



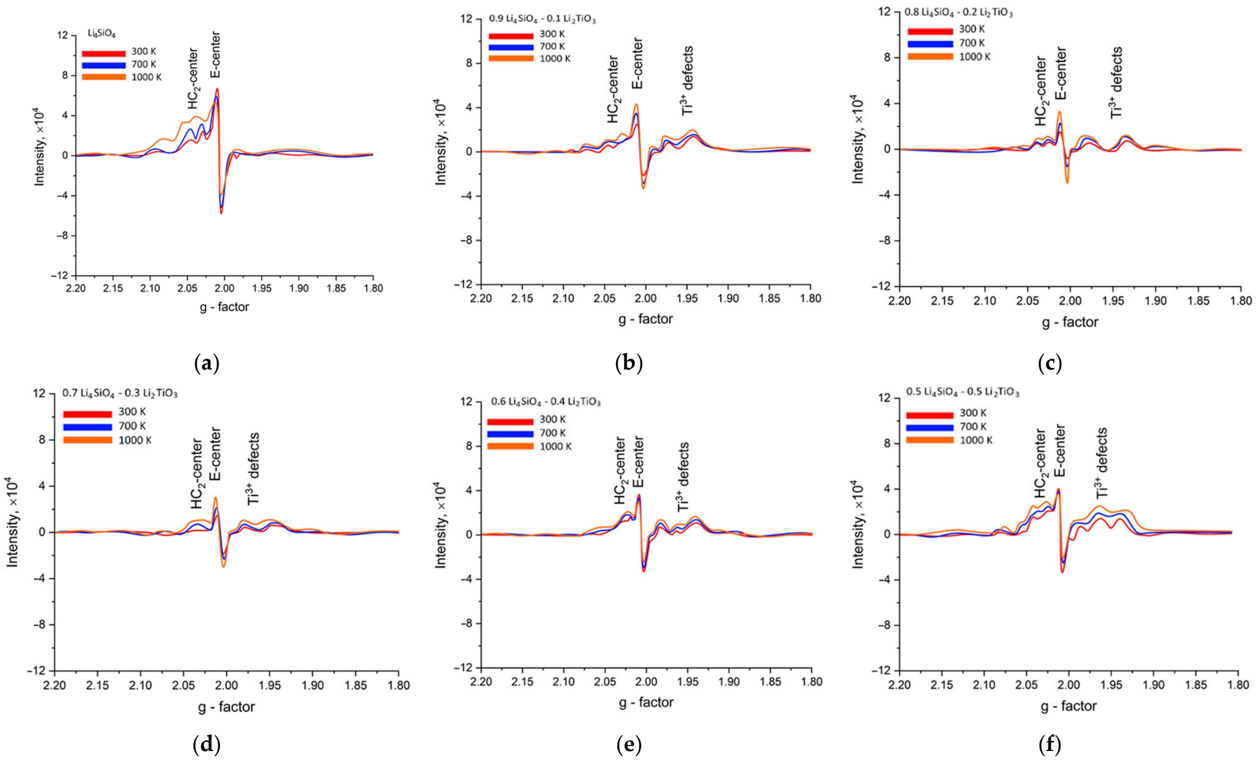
(**a**) (**b**)

Figure 4. (**a**) Results of a comparative analysis of changes in the concentration of defects in the structure of ceramics after proton irradiation and thermal exposure for 500 and 1000 h, reflecting the influence of temperature exposure on the processes of degradation and disordering. (**b**) Assessment results of the change in the thermal conductivity coefficient of the studied lithium-containing ceramics depending on the time of exposure to thermal heating simulating thermal aging of ceramic samples.

Figure 4b shows the results of a comparative analysis of changes in the thermal conductivity coefficient of Li_4SiO_4–Li_2TiO_3 ceramics subjected to proton irradiation and subsequent thermal heating over a long exposure time (about 500 and 1000 h of heating). These changes, shown in Figure 4b, reflect the general trend of the influence of accumulated structural damage caused by irradiation and subsequent thermal exposure on the thermophysical parameters and their degradation, caused by the slowdown of heat transfer processes due to structural defects in the damaged layer. The obtained results of changes in the thermal conductivity coefficient of Li_4SiO_4–Li_2TiO_3 ceramics samples after irradiation with protons with a fluence of 5×10^{17} proton/cm^2 in comparison with the results of the thermal conductivity coefficient of the original ceramic samples (not subjected to irradiation) reflect a positive tendency of variation in the ratio of components in two-component ceramics on resistance to degradation under irradiation. The formation of interphase boundaries in the structure that prevent the processes of deterioration of the crystalline structure, expressed in a change in the concentration dependences of the defective fraction in the damaged layer (see the data shown in Figures 3a–c and 4a) in the case of two-component ceramics, leads to a rise in resistance not only to a general change in the thermophysical parameters, but this also leads to an increase in resistance to the high-temperature degradation of the thermal conductivity coefficient, the changes in which in the case of two-component ceramics after 500 and 1000 h of thermal exposure are of the order of less than 1.0%, while for Li_4SiO_4 ceramics the change in the value of ΔTC after 1000 h of thermal exposure is more than 2.5%. Analyzing the data obtained, it can be concluded that the boundary effects have a positive effect, restraining the diffusion penetration of oxygen deep into the samples during thermal exposure. The observed decrease in the thermophysical parameters of irradiated ceramics depending on the time of thermal post-radiation exposure indicates that oxidation processes have a clearly expressed dependence on the degree of structural disorder, expressed in changes in the concentration of structural defects caused by irradiation. In the case of low concentrations of structural defects, the inhibition of the formation of which is associated with changes in the ratio of components in the composition of ceramics (the presence of interphase boundary effects), the increased resistance of ceramics to prolonged thermal exposure accompanied by oxidation processes is observed.

Figure 5 reveals the results of experiments aimed at studying the effect of irradiation temperature on the mechanisms of defect formation in the damaged layer, as well as the determination of the role of temperature factors on the rate and degree of disordering of the damaged layer in Li_4SiO_4–Li_2TiO_3 ceramics in the case of variations in the ratio of components in the composition of the ceramics. In this case, the presented EPR spectra were obtained on samples irradiated at different temperatures (under irradiation conditions from 300 to 1000 K), with strict maintenance of the irradiation fluence of 5×10^{17} proton/cm^2 in order to exclude factors associated with differences in the irradiation dose. The observed alterations in the EPR spectra reflect the effect of the sample heating temperature during irradiation, from which it follows that the observed differences in the spectral line intensities are associated with the thermal effect on the defect formation mechanisms during irradiation. In the case of the irradiation temperature growth from 300 to 700 and 1000 K, a change in the ratio of spectral line intensities, reflecting a change in the defect formation mechanisms caused by thermal action, is observed.

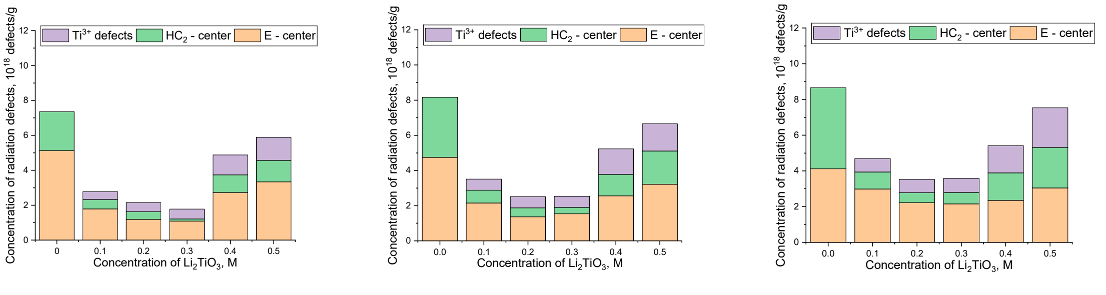
The assessment results of the change in the defect concentration in the damaged ceramic layer in the case of a change in the irradiation temperature are shown in Figure 6 in the form of comparative diagrams reflecting the contribution of each type of defect in the damaged layer. The data were calculated using Equation (1) and are presented on a single scale to clearly demonstrate the changes associated with the temperature effect on the crystalline structure during irradiation of ceramic samples. The calculations were carried out by assessing the areas and intensities of the spectral lines shown in Figure 5. Analysis of the observed changes in the concentration dependences presented for samples irradiated at different temperatures showed that an increase in the irradiation temperature leads to an increase in radiolysis products in the form of ≡Si–O, SiO_4^{3-}, and Ti^{3+} defects. Moreover, the growth of radiolysis products is most pronounced for single-component Li_4SiO_4 ceramics, from which it can be concluded that thermal heating during irradiation leads to thermal expansion of the crystal lattice, as a result of which the processes of diffusion of structural defects become more intense, which leads to the acceleration of the processes of destabilization of the damaged layer due to the formation of complex defects, as well as the migration of defects to a greater depth [55]. Such effects can be restrained by barrier boundaries arising from the mixing of two different phases, which not only slows down the defect formation processes but also prevents defect migration near grain boundaries. Moreover, as was shown in works [56–59], high-dose irradiation of ceramic materials at high temperatures can lead to the formation of blisters (gas-filled inclusions) in the damaged layer, which contributes to the destabilization of the crystalline structure and its embrittlement. Thus, the observed trends in the change in the concentration of defects in ceramic samples, which have a clearly expressed tendency from the ratio of components in the composition of ceramics, indicate a positive effect of inhibiting thermally stimulated processes of radiation swelling, which makes it possible to increase the service life of two-component ceramics under extreme conditions.



(**a**) (**b**) (**c**)

(**d**) (**e**) (**f**)

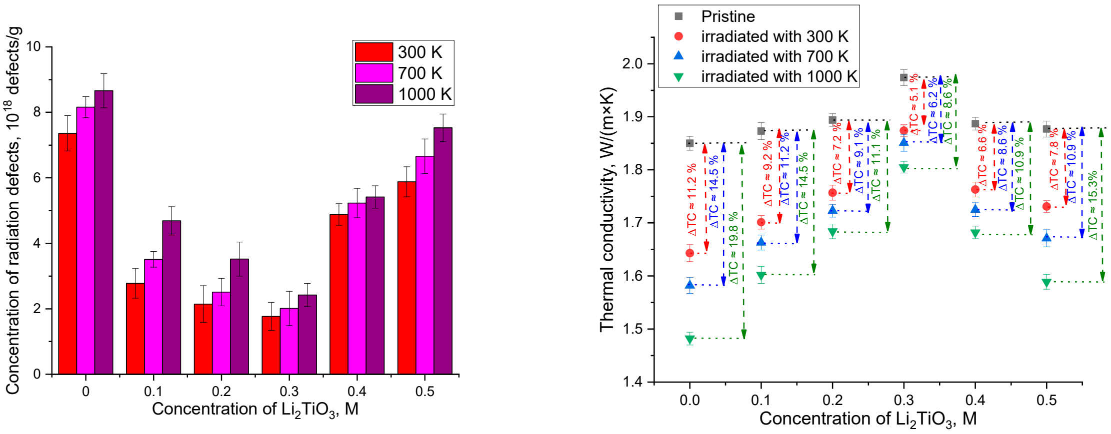
Figure 5. Results of changes in the EPR spectra of ceramic samples exposed to proton irradiation at different temperatures, reflecting the influence of the irradiation temperature on the change in the mechanisms of defect formation in the damaged layer of ceramics: (**a**) Li_4SiO_4; (**b**) 0.9 Li_4SiO_4–0.1 Li_2TiO_3; (**c**) 0.8 Li_4SiO_4–0.2 Li_2TiO_3; (**d**) 0.7 Li_4SiO_4–0.3 Li_2TiO_3; (**e**) 0.6 Li_4SiO_4–0.4 Li_2TiO_3; and (**f**) 0.5 Li_4SiO_4–0.5 Li_2TiO_3.



(**a**) (**b**) (**c**)

Figure 6. Results of a comparative analysis of changes in the concentration of defects in the damaged layer of lithium-containing ceramics, reflecting the influence of temperature factors on the mechanisms of defect formation during irradiation: (**a**) at an irradiation temperature of 300 K; (**b**) at an irradiation temperature of 700 K; and (**c**) at an irradiation temperature of 1000 K.

Figure 7a illustrates the results of a comparative analysis of changes in the concentration of defects in the structure of the damaged layer in Li_4SiO_4–Li_2TiO_3 ceramics in the case of variations in irradiation conditions associated with a change in irradiation temperature, leading to an acceleration of the processes of destabilization of the damaged layer. According to the presented data on changes in the concentration of defective inclusions in the damaged layer of ceramics, it can be concluded that the effect of temperature during irradiation contributes to an increase in the destructive disordering of damaged layers in ceramics due to the acceleration of diffusion processes and subsequent agglomeration of defects, which contributes to an increase in the density of defects in ceramics. The observed inhibition of defect formation mechanisms, according to the general analysis, also has a clear dependence on the irradiation temperature, from which it follows that an increase in temperature from 700 to 1000 K leads to a more pronounced softening of the damaged layer in ceramics with a concentration of 0.9–0.8 M Li_2TiO_3, due to an increase in the concentration of oxygen vacancies formed as a result of irradiation.



(**a**) (**b**)

Figure 7. (**a**) Results of changes in the concentration of defects in the structure of the damaged layer, determined on the basis of the analysis of EPR spectra depending on the irradiation temperature, reflecting the role of temperature effects on defect formation processes. (**b**) Results of changes in the thermal conductivity coefficient of the studied ceramics depending on the irradiation temperature (for comparison, data are provided for the initial values of the thermal conductivity coefficient, reflecting the influence of the variation in the ratio of components on the thermophysical parameters of the ceramics).

Figure 7b demonstrates the assessment results of changes in the thermal conductivity coefficient of the studied Li_4SiO_4–Li_2TiO_3 ceramics subjected to proton irradiation with a fluence of 5×10^{17} proton/cm^2 at different temperatures. The data are presented in comparison with the results of the thermal conductivity coefficient of the studied ceramics in the initial state, and the dotted lines indicate the difference ΔTC, reflecting the magnitude of the decrease in the thermal conductivity coefficient caused by irradiation under different conditions. According to the presented data, an increase in the irradiation temperature has a negative effect on the change in the thermal conductivity of ceramics, expressed in an increase in the difference ΔTC, reflecting the degree of degradation of thermal conductivity due to the accumulation of structural damage. An elevation in the irradiation temperature, which, according to the assessment of structural changes using the EPR spectroscopy method, leads to a more intensive growth in the concentration of defective inclusions in the damaged layer. In particular, an increase in the concentration of radiolysis products in the form of ≡Si–O, SiO_4^{3-}, and Ti^{3+} defects results in the more pronounced destabilization of the damaged layer, which as a consequence leads to a decrease in thermal conductivity. The accumulation of structural damage, especially radiolysis products in the damaged layer, leads to a slowdown in heat exchange processes, resulting in a decrease in thermal conductivity, and therefore, the formation of local areas of overheating may occur. An increase in resistance to the formation of structural defects due to variations in the ratio of components in the composition of ceramics, consequently, leads to less pronounced changes in the thermal conductivity coefficient, which correlates well with the proposed hypothesis about the formation of hardening and stabilizing factors due to interphase boundaries that prevent disordering and a decrease in thermal conductivity during high-dose irradiation. According to the presented dependencies in Figure 7a,b, it can be concluded that there is a direct correlation between the concentration of structural damage associated with the formation of defects in the damaged layer and the degradation of thermal conductivity. Suppression of disordering mechanisms due to the presence of interphase boundaries increases not only resistance to defect formation processes, in particular, to slowing down the formation and accumulation of radiolysis products in the form of $\equiv$Si–O, $SiO_4{}^{3-}$, and Ti^{3+} defects, but also increases stability and preserves the thermal properties of ceramics exposed to irradiation.

4. Conclusions

The paper presents the results of experimental studies aimed at studying the mechanisms of the effect of temperature factors during proton irradiation simulating the effect of hydrogen on the near-surface layers of ceramics, as well as identifying the role of the component ratio alteration in the composition of ceramics to inhibit the mechanisms of defect formation and subsequent high-temperature degradation. The main types of structural defects arising as a result of high-dose proton irradiation are determined. The mechanisms of high-temperature degradation under prolonged exposure to high temperature on irradiated samples of lithium-containing ceramics were studied. It was found that prolonged exposure to temperature on irradiated samples leads to an increase in the density of oxygen vacancies, the change in which has a clearly expressed dependence on the composition of the ceramics. Using the EPR method, the main mechanisms of defect formation depending on the conditions of proton irradiation, during which it was established that variation in the ratio of components in the composition of Li_4SiO_4–Li_2TiO_3 ceramics leads to inhibition of the processes of accumulation of radiolysis products that occur during high-dose irradiation in the case of high-temperature irradiation, were determined. During the work, the role of irradiation temperature on the processes and mechanisms of defect formation in lithium-containing ceramics was determined. According to the data of the analysis of the EPR spectra of Li_4SiO_4–Li_2TiO_3 ceramics samples irradiated at different temperatures, it was found that an elevation in temperature during irradiation leads to an increase in radiolysis products, the accumulation of which is associated with the acceleration of the diffusion of structural defects and more intense disordering of the crystalline structure. Moreover, in the course of the experimental work, a relationship between changes in the ratio of components in the composition of ceramics and resistance to disorder caused by the inhibition of the diffusion of oxygen vacancies was established.

Author Contributions: Conceptualization, I.E.K. and S.A.; methodology, I.E.K.; software, S.A.; validation, I.E.K., S.A., A.L.K., A.T., S.P., and A.I.P.; investigation, I.E.K., S.A., A.L.K., A.T., S.P. and A.I.P.; writing—original draft preparation, I.E.K. and S.A.; writing—review and editing, I.E.K., S.A., A.L.K. and A.I.P.; data curation, I.E.K., S.A., A.L.K., A.T., S.P. and A.I.P.; project administration, I.E.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (No. AP19679905). In addition, A.I.P. was supported by EUROfusion Enabling Research Project ENR-MAT.02.ISSP-UL—"New dielectric functional materials and interfaces (DFMI)—Theoretical and Experimental analysis". This work has been carried out within the framework of the EUROfusion Consortium, funded by the European Union via the Euratom Research and Training Programme (Grant Agreement No 101052200—EUROfusion). Views and opinions expressed are, however, those of the authors alone and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

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