

The connection between the accumulation of structural defects caused by proton irradiation and the destruction of the near-surface layer of Li_4SiO_4 – Li_2TiO_3 ceramics

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ABSTRACT

The key problem of using lithium-containing ceramics as materials of breeders for the propagation of tritium in thermonuclear reactors is phase stability, as well as the preservation of strength and thermophysical parameters of ceramics during their operation, which is accompanied by the accumulation of fission products in the near-surface layers, alongside mechanical influences from the outside. Moreover, in contrast to other types of ceramics, the presence of lithium in the composition of the samples under study leads to limitations in the use of classical analysis methods (scanning electron microscopy, energy dispersive analysis or optical spectroscopy) of structural changes caused by the accumulation of radiation damage, which requires the use of more complex methods for the assessment of the defect concentration in the structure, as well as establishing their relationship with the deterioration of strength and thermophysical parameters, playing a key role in determining the stability mechanisms and further exploitation of ceramics for tritium production. In this regard, the aim of the study is to determine the kinetics of changes in the near-surface layer of two-phase Li_4SiO_4 – Li_2TiO_3 ceramics associated with the accumulation of structural distortions caused by irradiation, as well as their relationship with strain embrittlement and disorder. During the studies, it was found that the accumulation of implanted hydrogen in the near-surface layer under high-dose irradiation initiates deformation distortion processes, the intensity of which depends on the ratio of components in the ceramics, according to which the optimal compositions of two-phase ceramics are ratios of components from 0.3 to 0.6. Determination of the type of defects in the composition of the damaged layer, as well as their concentration, was carried out using the electron spin resonance (ESP) method. During the studies, it was found that at low irradiation fluences, the dominant role in the accumulation of structural defects is played by vacancy defects associated with E'-centers, the formation of which is associated with structural distortions, while as the fluence grows, the structure is dominated by deformation disordering caused by the accumulation of Ti^{3+} defects and HC_2 centers (SiO_4^{3-}), the concentrations of which have a clear dependence on the phase composition of the ceramics.

1. Introduction

One of the solutions to global problems related to the shortage of energy resources in the near future, as well as the reduction of harmful emissions in order to reduce the negative impact of the greenhouse

effect, is the development of technologies for the application of nuclear and thermonuclear fusion for energy production [1,2]. These technologies are currently one of the most promising among alternative methods of energy production, due to safety and environmental friendliness, as well as the possibility of obtaining energy for a long time,

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which will solve the issue of shortage of energy resources, both in the short and long term. Expansion of the possibilities of using fusion for energy production is limited by the problem of availability of tritium in the necessary amounts required to support fusion reactions [3–5]. One of the solutions to this problem is the use of lithium-containing ceramics, in which, as a result of nuclear reactions of lithium with neutrons, tritium is formed, as well as other products of nuclear reactions in the form of helium, hydrogen or deuterium, the presence of which in the composition of ceramics at high concentrations leads to destructive changes in the structural and thermophysical properties of ceramics [6, 7]. The accumulation of nuclear reaction products in the near-surface layers of ceramics can lead to the emergence of areas of disorder, the presence of which, in turn, has a negative impact on resistance to external influences, and also prevents the release of tritium from the bulk of the ceramics, since its generation occurs in almost the entire volume of ceramics due to the high penetrating ability of neutrons [8,9]. It is important to highlight that the presence of disorder regions, the formation of which is primarily associated with the accumulation of point defects, oxygen vacancies (V_O), as well as more complex clusters, can have a negative impact on heat transfer processes due to the creation of additional scattering centers with the phonon mechanism of heat transfer [10,11]. In this connection, the research in this direction includes not only a comprehensive study of degradation mechanisms of lithium-containing ceramics as a result of various external influences, but also determination of optimal types of ceramics, the use of which will expand the possibilities of increasing the efficiency of these ceramics for tritium generation for a long time, as well as the possibilities of their use in extreme conditions [12–14].

The most promising types of lithium-containing ceramics among those known today in the field of tritium generation are Li_4SiO_4 ceramics, in which the lithium content is the highest in comparison with other types of ceramics. Moreover, recently, in order to elevate the resistance of these ceramics to external influences, while maintaining a high tritium generation rate, the possibility of using two-phase ceramics of the $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{TiO}_3$ type is being considered [15–17]. In this case, the addition of lithium titanate is usually considered as one of the ways to increase the thermal resistance to cracking, as well as increase the mechanical strength of Li_4SiO_4 ceramics. For example, in the work of Rao, G. Jaya et al. [18], it was shown that the addition of Li_2TiO_3 to the composition of Li_4SiO_4 ceramics results in more than twofold growth in resistance to single compression, and an elevation in resistance to moisture. At the same time, the hardening effect is due to both dimensional factors and the presence of interphase boundaries, the change of which occurs due to a change in the ratio of components in the composition of the ceramics. The addition of lithium titanium to lithium orthosilicate, as a rule, is carried out in small concentrations (no more than 0.1–0.3 mol), which makes it possible to elevate resistance to external influences while maintaining stability in tritium generation due to nuclear reactions. In turn, such modifications of ceramics can be considered as one of the most promising ways to increase the resistance of ceramics to external influences, with the possibility of maintaining the efficiency of tritium generation.

Based on the foregoing, the main goal of the study, the results of which are presented in this article, is to determine the influence of variations in the ratio of components in two-phase $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{TiO}_3$ ceramics on the kinetics of changes in structural and thermophysical parameters caused by irradiation with protons. The use of high-dose proton irradiation was chosen to simulate the processes of implantation of hydrogen into a near-surface layer with a thickness of about 20–25 μm , the accumulation of which can lead to the destruction of near-surface layers, as well as have a negative impact on the resistance of ceramics to external influences due to deformation distortion and the formation of point defects, as well as oxygen vacancies. At the same time, simulation of these hydrogenation processes makes it possible to evaluate the degradation kinetics of the ceramic material, in particular, the near-surface layers in which tritium is produced as a result of nuclear

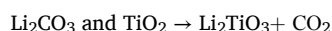
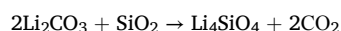
reactions of lithium with neutrons, which in turn results in accumulation of fission products into ceramics, which have high mobility and the ability to agglomerate in voids, with the subsequent formation of gas-filled bubbles. In turn, variation in the ratio of components in the composition of $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{TiO}_3$ ceramics allows not only to change the strength and thermophysical properties of ceramics, but also to increase resistance to radiation-induced damage due to the dispersion effect of hardening, as well as the presence of interphase boundaries and differences in the strength parameters of each ceramic component.

2. Materials and methods

$\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{TiO}_3$ ceramics obtained by solid-phase synthesis and thermal sintering under pressure were chosen as the samples under study. The ceramics manufacturing process was carried out in three stages. The first stage was to obtain single-component Li_4SiO_4 and Li_2TiO_3 powders by mixing Li_2CO_3 and SiO_2 powders to obtain Li_4SiO_4 powder, and Li_2CO_3 and TiO_2 to obtain Li_2TiO_3 powder. Mixing was carried out in a planetary mill at low grinding speeds (no more than 100 rpm) in order to eliminate the processes of cold welding of the samples and obtain a homogeneous consistency and equal distribution of both components in the volume. The second stage consisted of thermal annealing of the ground powders in a muffle furnace at a temperature of 700 °C for 10 h, after which the powders were cooled together with the furnace for 24 h until they cooled completely and reached room temperature. The choice of the annealing temperature of the samples after pressing is based on the need to relax the mechanical stresses arising in the structure of the tablets during pressing, while the annealing temperature should not initiate phase changes in the samples, which imposes restrictions on the upper limit of the annealing temperature of the samples.

The thickness of the samples was monitored using the optical microscopy method, the use of which makes it possible to determine the dimensions of the samples by thickness with high accuracy, as well as to identify inconsistencies if they occur.

Below are the chemical reactions underlying the production of Li_4SiO_4 and Li_2TiO_3 during thermal annealing:



The third stage consisted of mixing the resulting Li_4SiO_4 and Li_2TiO_3 powders in different weight ratios, which varied from 0 to 0.4 M with a step of 0.1 M in order to obtain $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramics. After mixing, the resulting powders were pressed in a special mold to obtain spherical granules with a diameter of about 1 mm. During the pressing process, the mold, being under a pressure of 250 MPa, was subjected to thermal heating to a temperature of 400 °C and was maintained at this temperature for 5 h, which made it possible to reduce the effect of deformation distortion of the structure caused by the mixing processes and subsequent external pressure during pressing. The final product was spherical granules with a size of about 1 mm, which have fairly high resistance to external influences upon single compression, capable of withstanding external pressure of the order of 40–50 N, the Vickers hardness of the samples was about 650–800 HV, depending on the phase ratio in the composition of the pressed ceramics.

Simulation of the hydrogenation processes of the studied ceramics in order to establish the optimal compositions of two-phase ceramics that have the greatest resistance to structural distortions, with associated processes of destruction and reduction of strength and thermophysical parameters, was carried out by irradiating the samples with protons with an energy of the order of 1 MeV and fluences from 10^{14} to 5×10^{17} proton/ cm^2 . Irradiation was carried out at room temperature in a vacuum, which made it possible to exclude the effect of oxidation of the samples during irradiation. According to calculated data, under the selected irradiation conditions, the maximum thickness of the near-

surface layer subject to the accumulation of structural damage is about 20–25 μm , and the choice of high-dose irradiation (above 10^{16} proton/ cm^2) allows simulation of the accumulation processes of structural damage characteristic of deep overlap of defective areas arising as a result of the interaction of protons with the crystal structure of ceramics.

The results of destructive effects associated with the hydrogenation processes of near-surface layers 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 electron spin resonance method. The EPR spectra were

measured at room temperature, the g factor was determined in the range 1.8–2.2, in which, according to a number of studies, the appearance of spectral lines characteristic of the formation of E-centers characteristic of oxygen vacancies, alongside lines, the presence of which is associated with defects such as Ti^{3+} , HC_2 - centers arising as a result of ionization processes of interaction of incident particles with the crystal structure of the damaged layer, is observed. The measurements were carried out on a Bruker BioSpin X-band spectrometer.

Determination of the stability of defective inclusions formed as a result of irradiation to thermal effects was carried out by heating the

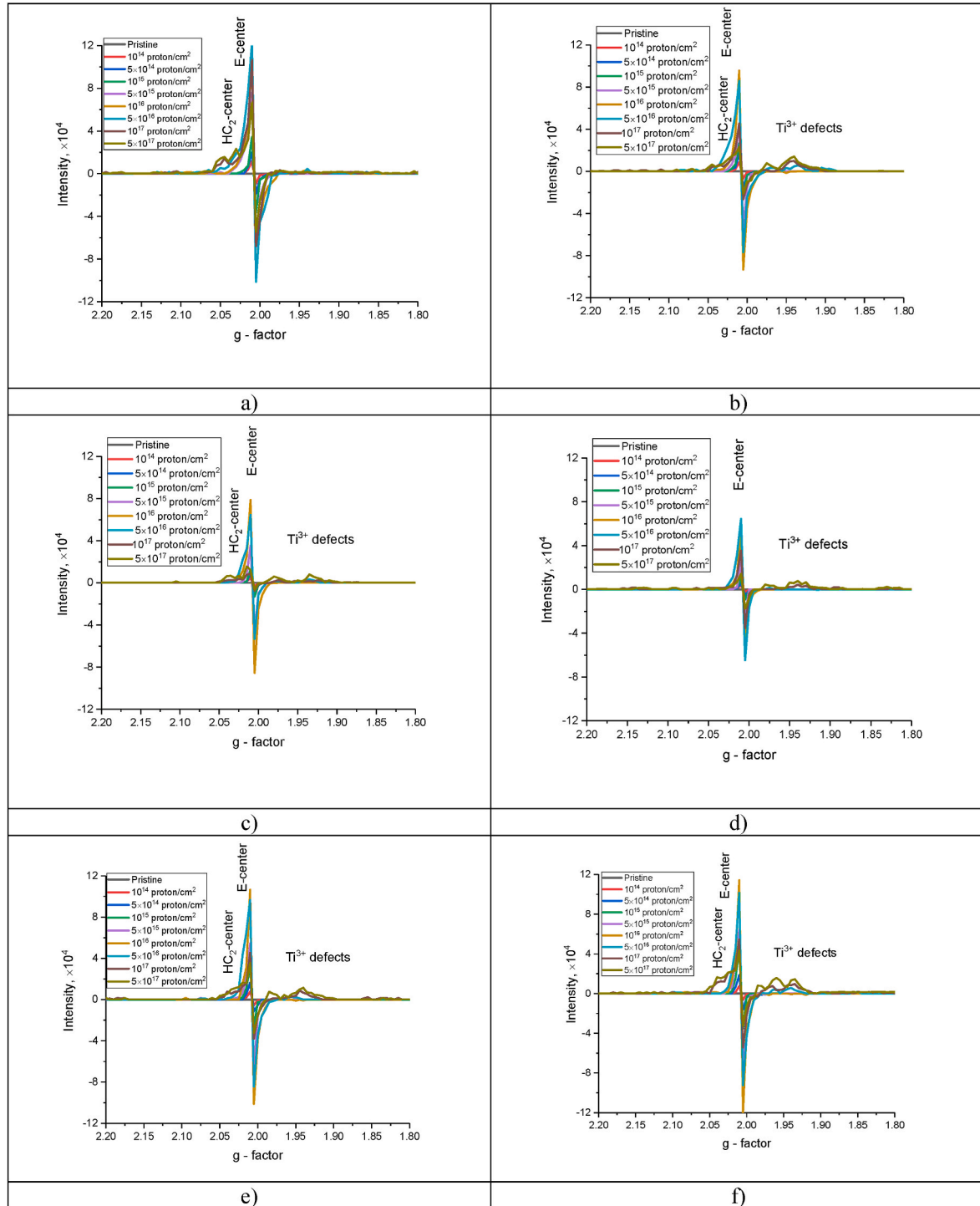


Fig. 1. Results of ESR spectroscopy of the studied $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramics depending on the ratio of components in the composition: a) Li_4SiO_4 ; b) 0.9 M $\text{Li}_4\text{SiO}_4 - 0.1$ M Li_2TiO_3 ; c) 0.8 M $\text{Li}_4\text{SiO}_4 - 0.2$ M Li_2TiO_3 ; d) 0.7 M $\text{Li}_4\text{SiO}_4 - 0.3$ M Li_2TiO_3 ; e) 0.6 M $\text{Li}_4\text{SiO}_4 - 0.4$ M Li_2TiO_3 ; f) 0.5 M $\text{Li}_4\text{SiO}_4 - 0.5$ M Li_2TiO_3 .

samples to a temperature of 700 °C and holding the samples at this temperature for 10 h. Changes in the concentration of defects were carried out by comparative analysis of EPR spectra based on alterations in the values of spectral lines characteristic of various types of defects arising as a result of the accumulation of structural changes in the samples.

Determination of the influence of the concentration of defective inclusions, and their types, caused by irradiation and subsequent hydrogenation processes, on thermophysical properties was assessed using a method for determining the thermal conductivity coefficient based on the use of the mode for determining a stationary longitudinal heat flow. For measurements, a universal thermal conductivity meter KIT-800 was used. The thermal conductivity coefficient was measured in the temperature range from 25 to 700 °C, which made it possible to assess the change in the thermal conductivity coefficient, alongside its resistance to changes associated with the heating temperature.

3. Results and discussion

Fig. 1 reveals the results of the ESR spectra of the ceramic samples under study depending on the proton irradiation fluence. Data are also presented for ceramics in the initial state, for which the results of irradiated samples were compared, which made it possible to conclude that the observed peak at $g = 2.003$ (singlet), the formation of which occurs at an irradiation fluence of 10^{14} proton/cm², corresponds to the appearance of E-centers in the structure, associated with oxygen vacancies, the occurrence of which is due to ionization effects resulting from the interaction of protons with the crystal structure of ceramics. Moreover, according to the data presented, an alteration in the irradiation fluence leads to an elevation in the intensity of this peak and its broadening, which indicates an increase in the concentration of these defects in the structure of ceramics caused by irradiation. In the case of Li₄SiO₄ ceramics, a rise in the irradiation fluence above 10^{16} proton/cm², in addition to the main peak characteristic of the accumulation of E-centers in the composition, the formation of peaks in the region of 2.001–2.05 is observed. The latter is characteristic of the formation of defects, the occurrence of which in the composition of ceramics indicates the initialization of radiolysis processes characteristic of high-dose irradiation, and as a consequence, high concentrations of structural changes caused by irradiation. It should also be noted that the broadening of the main peak with the formation of an additional maximum with $g = 2.01$ can be explained by the formation of HC₂ - centers representing $\equiv \text{Si}-\text{O}$ or SiO_3^{4-} , i.e. a hole associated with oxygen atoms in SiO₄ tetrahedra. At the same time, assessing the change in the intensity of the peak characteristic of E-centers at fluences above 10^{16} proton/cm² in comparison with the intensity of the peaks characteristic of HC₂ - centers, it can be concluded that at high irradiation fluences, the main structural changes in Li₄SiO₄ ceramics are associated with radiolysis processes, which result in the formation of structural distortions leading to destabilization of the structural ceramics. Thus, it can be concluded that at low irradiation fluences (below 10^{16} proton/cm²), processes associated with the formation of point defects and oxygen vacancies play a key role in structural changes. While at fluences above 10^{16} proton/cm², the dominant role in structural changes is played by defects associated with radiolysis processes, which result in the accumulation of defective inclusions, which are various complexes such as SiO_3^{4-} , $\equiv \text{Si}-\text{O}-\text{O}$, and small Li_n particles, the formation of which is due to physicochemical processes of radiolysis initiated by irradiation processes.

The addition of 0.1Li₂TiO₃ to the composition of Li₄SiO₄ ceramics, according to the data presented in Fig. 1b, leads to a decrease in the intensity of the singlet signal characteristic of E-centers at low irradiation fluences (below 10^{16} proton/cm²), as well as lower intensities of the peaks characteristic of HC₂ - centers, which indicates the positive effect of the Li₂TiO₃ additive on the resistance to the formation of radiation defects in the structure. At the same time, at fluences above 10^{16} proton/cm²,

the formation of broadened peaks in the region of $g = 1.98\text{--}1.95$ is observed, which can be characterized by the formation of Ti³⁺ defects, the occurrence of which is associated with the disordering of Li₂TiO₃ inclusions as a result of initiated radiolysis processes. The formation of Ti³⁺ centers can be explained by the following process $\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+}$ associated with electron capture by Ti⁴⁺ ions, as well as differences in the crystal structure of the environment of titanium ions in the samples [19]. It should be noted that the intensity of the peaks characteristic of Ti³⁺ centers, along with the intensities of HC₂ - centers, increases with increasing fluence, while the intensity of the singlet of E-centers reduces, which indicates the dominance in the structure of ceramics at high irradiation fluences of processes characteristic of the physicochemical stage of radiolysis, which results in the formation of complex defects [20,21].

Similar changes due to a decrease in the intensities of E-centers (at irradiation fluences below 10^{16} proton/cm²) and also HC₂ - centers (at fluences above 10^{16} proton/cm²) in comparison with one-component Li₄SiO₄ ceramics are observed for samples 0.8 M Li₄SiO₄ – 0.2 M Li₂TiO₃ and 0.7 M Li₄SiO₄ – 0.3 M Li₂TiO₃ ceramics, from which it follows that an increase in the Li₂TiO₃ content from 0.1 M to 0.2–0.3 M leads to a growth in the stability of two-phase ceramics, radiation damage processes associated with the formation of vacancy defects, and physicochemical processes of radiolysis. At the same time, it should be noted that for samples of 0.7 M Li₄SiO₄ – 0.3 M Li₂TiO₃ ceramics, the intensities of the peaks characteristic of HC₂ - centers and Ti³⁺ - centers at fluences of 10^{17} – 5×10^{17} proton/cm² are minimal, which indicates that the addition of 0.3 M Li₂TiO₃ to the ceramic composition results in inhibition of radiation damage processes, which results in the ceramics degradation rate reduction.

The Li₂TiO₃ concentration growth to 0.4–0.5 M, in the case of high-dose irradiation (above 10^{16} proton/cm²), leads to an elevation in the intensities of the peaks characteristic of Ti³⁺ centers, along with fairly high singlet intensities characteristic of E-centers, which indicates that at high contents of Li₂TiO₃ in the composition, radiolysis processes occur more intensely due to the formation of Ti³⁺ centers, which are caused by the structural features of these ceramics associated with distortion of the crystal structure.

The use of electron spin resonance methods to determine structural changes in lithium-containing ceramics associated with the effects of accumulation of radiation-induced defects caused by irradiation is one of the most promising research methods for a number of reasons. Firstly, unlike the X-ray diffraction method, the ESR method makes it possible to accurately determine the type of defects that arise as a result of deformation of the crystal structure, due to the difference in the g-factor values, and by intensity it is possible to determine the concentration of various defects in the structure of ceramics with a high probability degree. In the case of the X-ray diffraction method, the analysis of X-ray diffraction patterns allows one to establish only the total concentration of structural distortions recorded on the basis of changes in the position of the shape and intensity of the diffraction lines. Secondly, the capabilities of ESR make it possible to determine the influence of various factors on the concentration dependences of formed defects, as well as to establish the kinetics of their changes, including the reversibility of structural distortions associated with the accumulation of vacancy defects under external thermal influences, including post-radiation thermal influences. The influence of structural effects associated with changes in the grain sizes of lithium-containing ceramics on the resistance to radiation defects when irradiated with He⁺ ions (280 keV, 10^{16} He⁺/cm²) was considered in Ref. [22]. According to the data presented, a decrease in grain size in ceramics leads to a rise in the stability of the crystal structure of ceramics to deformation distortions associated with the accumulation of vacancy and interstitial defects. In turn, it was shown in Ref. [23] that a change in the type of ions during irradiation from He⁺ to O⁺ leads to a change in the concentration of defects associated with oxygen vacancies (characteristic of He⁺ irradiation) and Ti³⁺ defects, the appearance of which occurs during irradiation with O⁺

ions. The differences in the types of defects formed in this case are associated both with the type of incident ions and their energy. According to the analyses, the authors found that irradiation with He^+ ions with an energy of 2 MeV and fluences of the order of $10^{16} - 2 \times 10^{17} \text{ He}^+/\text{cm}^2$ results in less pronounced structural changes associated with disordering of the crystal structure, the change of which is associated with the appearance of defective inclusions in the damaged layer area. In turn, the role of structural defects, in particular, E' -centers associated with oxygen vacancies, in the processes of tritium release from lithium-containing ceramics was studied in Ref. [24], where it was shown that in the case of Li_2ZrO_3 ceramics subjected to neutron irradiation, the resulting concentrations of E-centers play an important role in the processes of tritium release, as well as in the annihilation of defects formed as a result of irradiation.

Fig. 2 demonstrates the assessment results of defects formed as a result of irradiation in $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramics depending on the irradiation fluence, as well as the type of ceramics. The concentration of defects, as well as radiolysis products (Ti^{3+} - centers, HC_2 - centers) was assessed using formula (1) [25]:

$$C_{\text{defects}} = \frac{S_x \times N_{\text{ref}}}{S_{\text{ref}} \times m}, \quad (1)$$

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.

As is evident from the data presented, in the case of irradiation fluences below $10^{16} \text{ proton}/\text{cm}^2$, the main changes in the concentrations of defects are associated with the accumulation of vacancy and point defects, the concentration of which was determined from changes in the peaks of the $g = 2.003$ singlet. Moreover, the addition of Li_2TiO_3 to a concentration of 0.3 M in the ceramic composition leads to a decrease in the concentration of vacancy and point defects by more than 1.5–2.0 times in comparison with the results of the concentration of defects for single-component Li_4SiO_4 ceramics. Such changes indicate a growth in the resistance of two-component ceramics to the formation of vacancy and point defects during irradiation, alongside inhibition of the degradation mechanisms of ceramics at low irradiation fluences (below $10^{16} \text{ proton}/\text{cm}^2$). It should also be noted that the analysis of radiolysis products (by changes in peaks characteristic of HC_2 - centers and Ti^{3+} - centers) for ceramic samples with Li_2TiO_3 concentrations equal to 0.1–0.3 M indicates a positive effect of the presence of inclusions of the Li_2TiO_3 phase on increase in the degradation resistance of ceramics under high-dose irradiation. In the case of ceramics in which the concentration of Li_2TiO_3 is 0.4–0.5 M, with high-dose proton irradiation, a smaller number of defects associated with HC_2 - centers is observed, however, the concentration of defects caused by the formation of Ti^{3+} - centers increases in comparison with other samples, which can be explained by the high concentrations of Li_2TiO_3 in the composition of two-component ceramics, which results in more pronounced radiolysis

processes in Li_2TiO_3 than in Li_4SiO_4 .

Thus, analyzing the data on changes in ESR spectra, as well as concentration dependences, we can conclude that the most optimal ratios for obtaining ceramics with high radiation stability to high-dose irradiation are $0.8\text{Li}_4\text{SiO}_4 - 0.2\text{Li}_2\text{TiO}_3$ and $0.7\text{Li}_4\text{SiO}_4 - 0.3\text{Li}_2\text{TiO}_3$. For these samples, in the case of low irradiation fluences (below $10^{16} \text{ proton}/\text{cm}^2$), inhibition of degradation processes associated with the formation of oxygen vacancies and point defects is observed. In the case of high-dose irradiation (above $10^{16} \text{ proton}/\text{cm}^2$), the accumulation of radiolysis products associated with the formation of HC_2 - and Ti^{3+} - centers is less pronounced than for single-component Li_4SiO_4 ceramics. From the data presented it can be concluded that the addition of 0.2–0.3 M Li_2TiO_3 to Li_4SiO_4 ceramics during their mechanochemical solid-phase synthesis makes it possible to obtain highly stable ceramics that are resistant to the accumulation of radiation damage and radiolysis products at high radiation doses.

An important role in the selection of lithium-containing ceramics for use as blanket materials is played by their thermophysical properties, in particular, thermal conductivity and its stability during the accumulation of radiation damage.

Fig. 3a illustrates the assessment results of the thermal conductivity coefficient of the studied $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramics contingent upon the concentration of Li_2TiO_3 in the composition, reflecting the influence of this phase on the thermophysical parameters. A comparison of the values of the thermal conductivity coefficient (TC) was carried out with single-component Li_4SiO_4 ceramics, which made it possible to determine the effect of the inclusion of lithium titanate in the ceramic composition on changes in heat transfer mechanisms. It is important to highlight that a reduction in the thermal conductivity coefficient is observed at an irradiation fluence above $10^{16} \text{ proton}/\text{cm}^2$ for all samples, which indicates that the main mechanisms of thermal conductivity degradation are due to the accumulation of structural distortions caused by irradiation, but the concentration of these distortions affects the degradation degree of thermophysical parameters. The general appearance of the presented dependence indicates that an increase in the content of the Li_2TiO_3 phase in the composition from 0.1 to 0.3 M leads to the most effective changes in TC, which indicates a positive dynamics of thermal conductivity growth. At the same time, a growth in the Li_2TiO_3 concentration in the ceramic composition above 0.3 M results in reduction in the growth efficiency of δTC , which is about 2 % and 1.5 % for Li_2TiO_3 concentrations equal to 0.4 M and 0.5 M, respectively. The maximum increase in δTC for the ceramics under study is about 6.7 % for samples containing 0.3 M Li_2TiO_3 . The observed decrease in the efficiency of δTC for samples with a high content of Li_2TiO_3 in the composition can be explained by an elevation in the contribution of this phase, as well as the creation of a large number of interphase boundaries that interfere with the mechanisms of phonon heat transfer due to additional scattering of phonons that transfer heat. Analyzing the general changes, we can conclude that the most optimal composition of ceramics from the point of view of the greatest efficiency of changes in

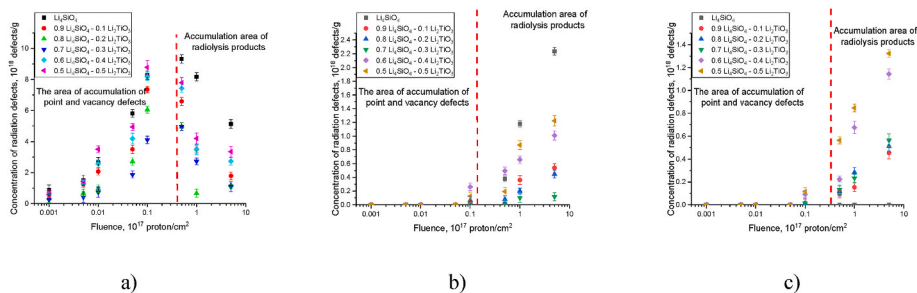


Fig. 2. Assessment results of changes in the concentration of defects in ceramics contingent upon the irradiation fluence, determined based on changes in certain peaks (the dotted line delimits the areas of formation of point defects and accumulation of radiolysis products): a) concentration of E - centers; b) concentration of HC_2 - centers; c) concentration of Ti^{3+} - centers.

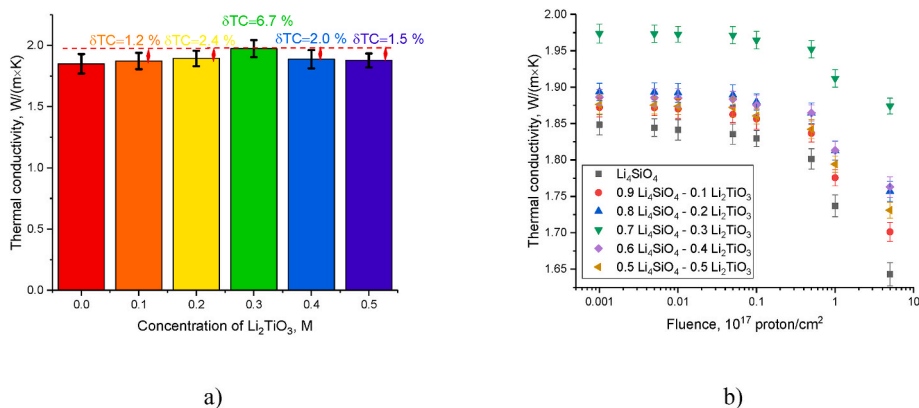


Fig. 3. a) Diagram of comparison of the thermal conductivity coefficient of the studied $xLi_4SiO_4 - (1-x)Li_2TiO_3$ ceramics in the initial (non-irradiated) state, reflecting the influence of variations in the ratio of components on the thermophysical properties (the dotted red line marks the boundary for comparing the value of δTC of two-component ceramics in comparison with Li_4SiO_4 ceramics); b) Results of a comparative analysis of changes in the thermal conductivity coefficient of the studied $xLi_4SiO_4 - (1-x)Li_2TiO_3$ ceramics depending on the proton irradiation fluence, reflecting the degradation of the thermal conductivity properties of the ceramics. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

δTC are ceramics containing a Li_2TiO_3 content of 0.3 M. It should be noted that for all two-phase ceramics the thermal conductivity coefficient is higher than for single-phase Li_4SiO_4 ceramics, which indicates a positive effect of the addition of Li_2TiO_3 on the change in thermophysical properties.

Fig. 3b reveals the measurement results of the thermal conductivity coefficient of the studied $xLi_4SiO_4 - (1-x)Li_2TiO_3$ ceramics contingent upon the proton irradiation fluence, which reflect the deterioration of the thermal conductivity of the ceramics due to the accumulation of structural damage associated with ionization processes, alongside deformation distortions of the crystal structure. The general trend of observed changes in the thermal conductivity coefficient indicates a two-stage change in the thermal conductivity of ceramics, which have a clear dependence on the concentration of accumulated damage, as well as on their type, which was determined using the ESR method. In the case when, in the composition of ceramics, when irradiated with protons with a fluence of 10^{14} – 10^{16} proton/cm^2 , the main structural changes are associated with a change in the concentration of oxygen vacancies, the decrease in thermal conductivity is no more than 1 %, and a decreasing trend with increasing fluence appears only at a fluence of 10^{16} proton/cm^2 . In turn, when radiolysis products (Ti^{3+} - defects, HC_2 - centers), characteristic of high-dose irradiation (above 10^{16} proton/cm^2), begin to form in the ceramics, the decline in the thermal conductivity coefficient becomes more pronounced. It should also be noted that in this case, the ratio of components in the composition of the ceramics plays a large role in the stability of the thermophysical properties of ceramics. In the case when the Li_2TiO_3 content in the ceramic composition is 0.3–0.4 M, the decrease in the thermal conductivity coefficient is no more than 5–6.5 % of the initial value at an irradiation fluence of 5×10^{17} proton/cm^2 , while for single-component Li_4SiO_4 ceramics the maximum reduction in the thermal conductivity coefficient at a similar irradiation fluence is more than 11 % (compared to the initial value). It should also be noted that for 0.7 $Li_4SiO_4 - 0.3 Li_2TiO_3$ samples, the trend towards a reduction in the thermal conductivity coefficient at irradiation fluences above 10^{16} proton/cm^2 is less pronounced than in the case of other samples, which indicates higher stability of the thermophysical properties of ceramics to effects associated with high-dose irradiation. Analysis of the established trends in changes in thermophysical properties depending on the irradiation fluence allows us to conclude that the observed effects of an increase in resistance to degradation of thermophysical properties are associated primarily with the presence of the second component, an alteration in the concentration of which not only leads to a change in the thermal conductivity coefficient in the initial state, but also has a positive effect on the degradation resistance

associated with structural changes caused by the accumulation of defect concentrations.

Fig. 4 demonstrates the assessment results of the EPR spectra of the ceramics under study after thermal annealing at a temperature of 700 °C for 10 h, in order to determine the thermal stability of the formed defects in the ceramic composition.

The results of study of the effect of thermal annealing of irradiated samples on changes in the concentrations of structural and vacancy defects revealed that in the case of low irradiation doses, for which the main changes are associated with the formation of E-centers, almost complete relaxation of oxygen vacancies is observed, due to the registration of weak signals of the intensity of spectral lines characteristic of E-centers. In the case of samples irradiated with fluences above 10^{16} proton/cm^2 , for which, according to the data presented in Fig. 1, the formation of HC_2 centers is characteristic, thermal annealing leads to a reduction in the intensities of the peaks characteristic of HC_2 centers, however, the decline in intensities is less pronounced than in the case of the intensities of singlets of E – centers. From the obtained dependences it can be concluded that when in the studied samples at low irradiation fluences (below 10^{16} proton/cm^2), the resulting oxygen vacancies and point defects are in a metastable state, the relaxation of which occurs under thermal influence on the samples. At the same time, the formed radiolysis products at high irradiation fluences are less susceptible to thermal relaxation than vacancy defects, which indicates a small effect of post-irradiation treatment of lithium-containing ceramics exposed to high-dose irradiation. It should be noted that in the case of samples of 0.8 $Li_4SiO_4 - 0.2 Li_2TiO_3$ and 0.7 $Li_4SiO_4 - 0.3 Li_2TiO_3$ ceramics, heat treatment results in crystal structure stabilization due to the relaxation of radiation damage, which indicates the possibility of using the method of post-irradiation heat treatment to stabilize and restore the crystalline structure of ceramics.

4. Conclusion

The paper presents the assessment results of the influence of the phase composition of $xLi_4SiO_4 - (1-x)Li_2TiO_3$ ceramics on changes in resistance to radiation damage caused by high-dose irradiation with protons, the use of which made it possible to simulate the hydrogenation processes of near-surface layers of lithium-containing ceramics, considered as promising materials for tritium generation.

During assessment of EPR spectra in order to determine the kinetics of changes in structural defects, as well as radiolysis products, a two-stage mechanism for the accumulation of radiation damage, which is directly dependent on the irradiation fluence, was determined. At the

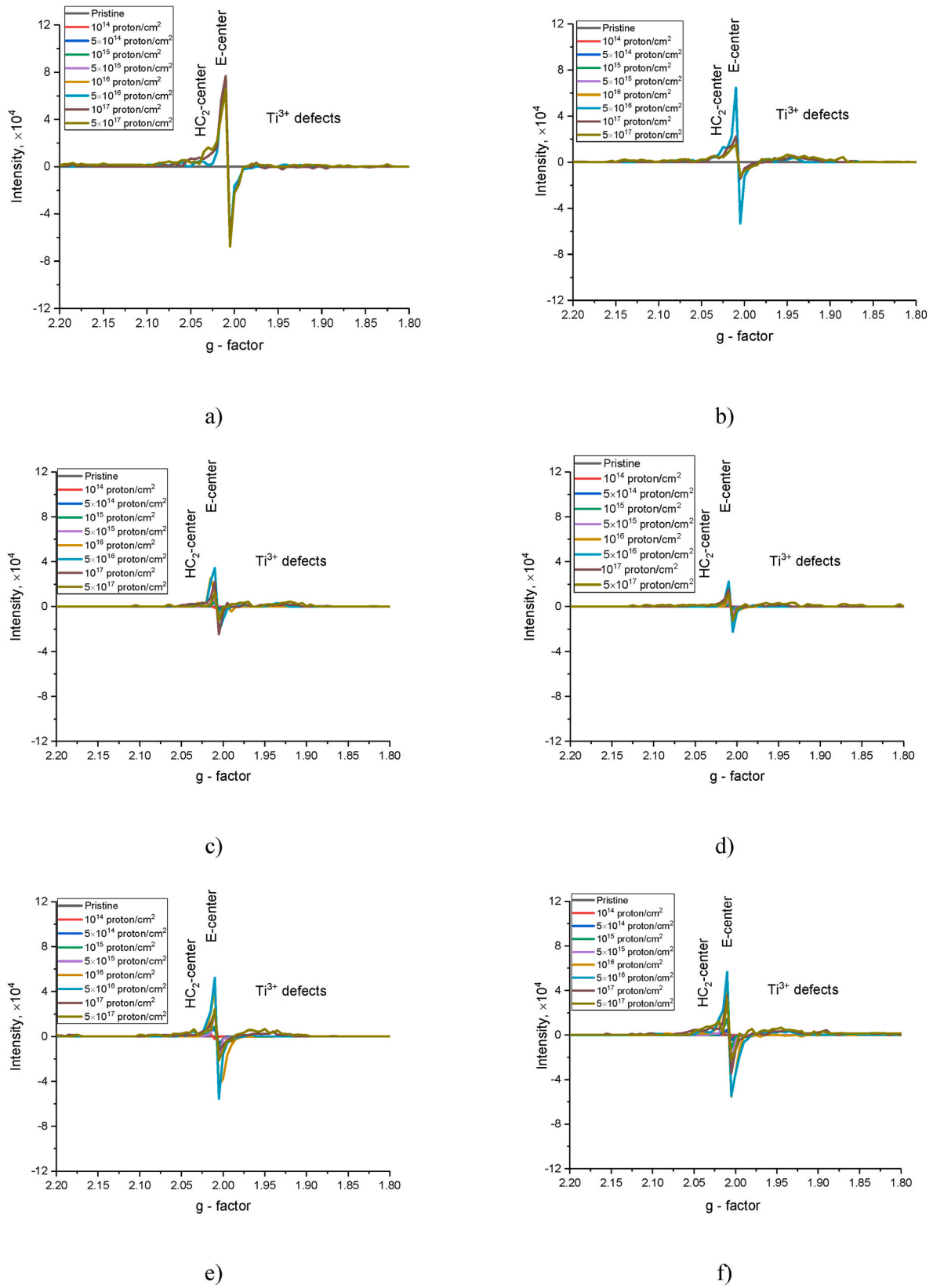


Fig. 4. Results of ESR spectroscopy of the studied $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramics after thermal annealing at a temperature of 700 °C for 10 h, depending on the ratio of components in the composition: a) Li_4SiO_4 ; b) 0.9 M $\text{Li}_4\text{SiO}_4 - 0.1$ M Li_2TiO_3 ; c) 0.8 M $\text{Li}_4\text{SiO}_4 - 0.2$ M Li_2TiO_3 ; d) 0.7 M $\text{Li}_4\text{SiO}_4 - 0.3$ M Li_2TiO_3 ; e) 0.6 M $\text{Li}_4\text{SiO}_4 - 0.4$ M Li_2TiO_3 ; f) 0.5 M $\text{Li}_4\text{SiO}_4 - 0.5$ M Li_2TiO_3 .

same time, the key mechanism for inhibiting the radiation damage formation in ceramic samples was an elevation in the concentration of Li_2TiO_3 in the ceramic composition, as a result of which a reduction in the concentration of oxygen vacancies and point defects, and radiolysis products under high-dose irradiation, was observed.

Analysis of alterations in the thermal conductivity coefficient of the $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramics under study, caused by changes in the variation of components in the composition, as well as the radiation damage accumulation, indicates the positive effect of the addition of Li_2TiO_3 , which consists not only in thermal conductivity growth, but also in more pronounced degradation resistance of thermophysical properties associated with radiation damage.

In the case of the applicability assessment of post-radiation thermal annealing of $x\text{Li}_4\text{SiO}_4 - (1-x)\text{Li}_2\text{TiO}_3$ ceramic samples in order to reduce the concentration of defective inclusions in the damaged layer, it was found that with prolonged temperature exposure (at a temperature of 700 °C), at low concentrations of vacancy and point defects, almost complete relaxation is observed, while the presence of radiolysis products in the structure results in inhibition of relaxation processes and less pronounced structural relaxations associated with a reduction in the concentration of defects.

Further prospects for the use of lithium-containing ceramics as tritium breeding materials will consist in detailing the mechanisms of tritium extraction from ceramics as a result of nuclear reactions of lithium with neutrons, as well as determining the effect of the accumulation of structural distortions and degradation on the processes of tritium generation and its extraction. It should be noted that the most promising direction in this study is the expansion of the possibilities of using two-phase ceramics, which, as the results of this study showed, are the most resistant to external influences.

CRediT authorship contribution statement

Inesh E. Kenzhina: Writing – original draft, Visualization, Investigation, Funding acquisition, Data curation, Conceptualization. **Artem L. Kozlovskiy:** Writing – review & editing, Writing – original draft, Project administration, Investigation, Formal analysis, Data curation, Conceptualization. **Aktolkyn Tolenova:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Meiram Begentayev:** Visualization, Supervision, Investigation, Formal analysis, Data curation, Conceptualization. **Saulet Askerbekov:** Supervision, Investigation, Funding acquisition, 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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