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The Influence of High-Temperature Tests on the Resistance to Degradation and Reduction in Strength Properties of Lithium-Containing Ceramics Used as Blanket Materials for Tritium Breeding

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Abstract: Conducting high-temperature tests on ceramics-containing lithium, which are employed as tritium breeding materials, plays a crucial role in comprehending their ability to withstand degradation and maintain their strength properties throughout operation. From the standpoint of fusion research, it is imperative to grasp these phenomena in order to guarantee the safety and effectiveness of reactors. Additionally, these factors could impact the choice of particular materials and designs for blanket materials. The primary objective of this research is to evaluate alterations in the strength characteristics of ceramics-containing lithium when subjected to high-temperature thermal stability tests, while also preserving the hardness stability and resistance to cracking in ceramics subjected to cyclic tests. Lithium-containing ceramics based on lithium titanate (Li_2TiO_3), lithium orthosilicate (Li_4SiO_4), and lithium methacyrconate (Li_2ZrO_3), having a high structural ordering degree and good strength properties, were chosen as objects for assessing resistance to high-temperature degradation. During the studies, it was discovered that the presence of interphase boundaries in the composition of ceramics linked to the development of impurity phases results in crack resistance growth during long-term high-temperature tests simulating the stress effect on the material. At the same time, an assessment of high-temperature aging as a result of modeling destruction processes showed that ceramics based on lithium metazirconate are the most resistant to degradation of strength properties. By simulating high-temperature aging processes, it became feasible to establish connections between structural alterations resulting from the thermal expansion of the crystal lattice and oxygen migration phenomena occurring at elevated temperatures. These factors collectively contribute to a detrimental reduction in the strength properties of ceramics-containing lithium.

Keywords: Li_2ZrO_3 ceramics; high temperature tests; tritium breeding; degradation; strength characteristics

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1. Introduction

In recent years, the advancement of the energy sector in developed nations has become more closely tied to nuclear and thermonuclear energy technologies [1,2]. This shift is driven by several factors, with the primary ones being the move away from extensive reliance on hydrocarbon resources, the imperative to decrease carbon dioxide emissions into the atmosphere, and a growing demand for increased power consumption [3].

Lithium-containing ceramic materials are one of the potential candidates for the role of blanket materials for the propagation of tritium in thermonuclear reactors [4,5]. At the same

time, blank materials are subjected to significant temperature loads as well as high levels of neutron radiation, which can cause degradation and a decrease in the strength properties of these materials. Typically, lithium ceramics and structural materials are exposed to high temperatures and radiation loads during reactor operation [6–8]. High-temperature testing can markedly affect the degradation resistance and strength properties of lithium-containing ceramics, which are used as blanket materials for tritium breeding in fusion reactors [9]. Two primary factors that could be influenced are the thermal stability [10,11] and radiation resistance [12,13] of materials. In the elevated temperatures characteristic of a fusion reactor, materials undergo thermal stress, which can result in phase transformations, thermal expansion, and potential cracking within the material [14,15]. Such alterations can diminish the ceramic's strength properties and raise the risk of degradation. Additionally, lithium-containing ceramic materials are exposed to radiation as part of the tritium multiplication process. Radiation-induced damage can introduce supplementary defects into the material's structure, subsequently diminishing its mechanical strength and resistance to deterioration [16,17]. The precise impact of subjecting lithium-containing ceramic materials to high-temperature testing will hinge on various factors, such as the material's specific chemistry, the ceramic's structure, and the operational conditions. Therefore, comprehensive testing and analysis are indispensable for guaranteeing the safety and effectiveness of deploying these materials in fusion reactors [18–20]. In the realm of thermonuclear fusion [21,22], a pivotal undertaking is the exploration and advancement of blanket materials that can endure high temperatures and withstand elevated radiation levels without degradation while maintaining their strength properties. The execution of high-temperature tests serves as a crucial means to assess the performance of these materials within a fusion reactor. In particular, such testing may identify potential problems related to thermal degradation, matrix stability, lithium diffusion, mechanical, and radiation resistance. Investigating these and other potential problems is a key step toward creating efficient and sustainable blanket materials for fusion reactors.

The primary aim of this work is to determine the destruction kinetics of the strength characteristics of lithium-containing ceramics during tests for thermal stability and resistance to thermal heating and rapid cooling. These experimental results will enable the identification of the most efficient ceramic type, along with the kinetics of high-temperature degradation of the strength and crack resistance of ceramics. The choice of Li_2TiO_3, Li_4SiO_4, and Li_2ZrO_3 ceramics as objects of study is due to their prospects as the main candidate materials for tritium breeding, since these ceramics have the most suitable set of properties (structural, strength, and thermophysical parameters) capable of withstanding long-term exposure to radiation damage (as a result of nuclear fission reactions of lithium during interaction with neutrons) [23–26], as well as high levels of resistance to mechanical stress (compression when volume changes as a result of thermal effects and the radiation damage accumulation). There is considerable interest not only in this type of ceramic used for tritium propagation but also in the methods of their production, since developments in this area of research will make it possible to solve a number of important problems in the field of thermonuclear energy associated with the accumulation of tritium, which is one of the key types of fuel for thermonuclear installations. Moreover, in recent years, not only methods for producing such ceramics (mechanochemical grinding, hydrothermal synthesis, and sol–gel technology) but also a comprehensive study of their properties have been considered, in particular determining resistance to external influences, including temperature aging, comparable to the actual operating conditions of these materials in reactors.

Lithium-containing ceramics are promising materials for use as blanket materials in fusion reactors for tritium breeding. However, before they can be used in such conditions, it is necessary to carefully study their resistance to degradation and changes in strength properties under the influence of high temperatures and radiation loads.

High-temperature testing can have the following effects on lithium-containing ceramic materials: thermal degradation, fracture and cracking, ion diffusion, and chemical reactions.

High temperatures can cause thermal degradation of the material, including changes in its structure and chemical composition. This can lead to a decrease in strength properties and degradation resistance. Heating and subsequent cooling can cause thermal stress, which can result in cracking and eventual failure of the material. At high temperatures, ions, including lithium ions, can diffuse through the material, which can cause changes in its structure and properties. So, for example, a number of studies [27,28] have shown that an increase in operating time at elevated temperatures leads to a decrease in resistance to mechanical stress as well as a deterioration in strength parameters. These effects have been studied quite well for lithium-ion batteries based on lithium-containing ceramics [28–31], but for blanket materials, there are practically no such studies. However, high temperatures can accelerate chemical reactions, including oxidation and other processes that can change the properties and composition of the material. A reduction in the strength characteristics in this case can result in accelerated embrittlement and destruction of ceramics, which can adversely affect service life. The most effective way to assess the effect of thermal heating on changes in strength characteristics and to determine thermal stability to temperature changes is to conduct experiments on heating and subsequent sharp cooling of samples, which makes it possible to simulate the processes of thermal shocks that occur during operation in the event of critical or emergency situations. Through these experiments, the examined structures undergo temperature variations that can induce alterations in the extent of thermal atomic vibrations within the crystal lattice. Additionally, they enhance the mobility of oxygen through energy transfer, resulting in the emergence of oxygen vacancies and the reconfiguration of oxygen within the ceramic composition, potentially leading to oxidation processes. A set of such alterations can contribute to the destruction of ceramics by reducing their strength characteristics as well as their resistance to cracking or embrittlement. Hence, the study of such processes and the determination of their effect on alterations in the strength properties of ceramics are very important to determine their potential for use as blanket materials, which, in addition to exposure to high temperatures during operation, will also be subject to radiation exposure.

2. Materials and Methods

2.1. Objects of Research

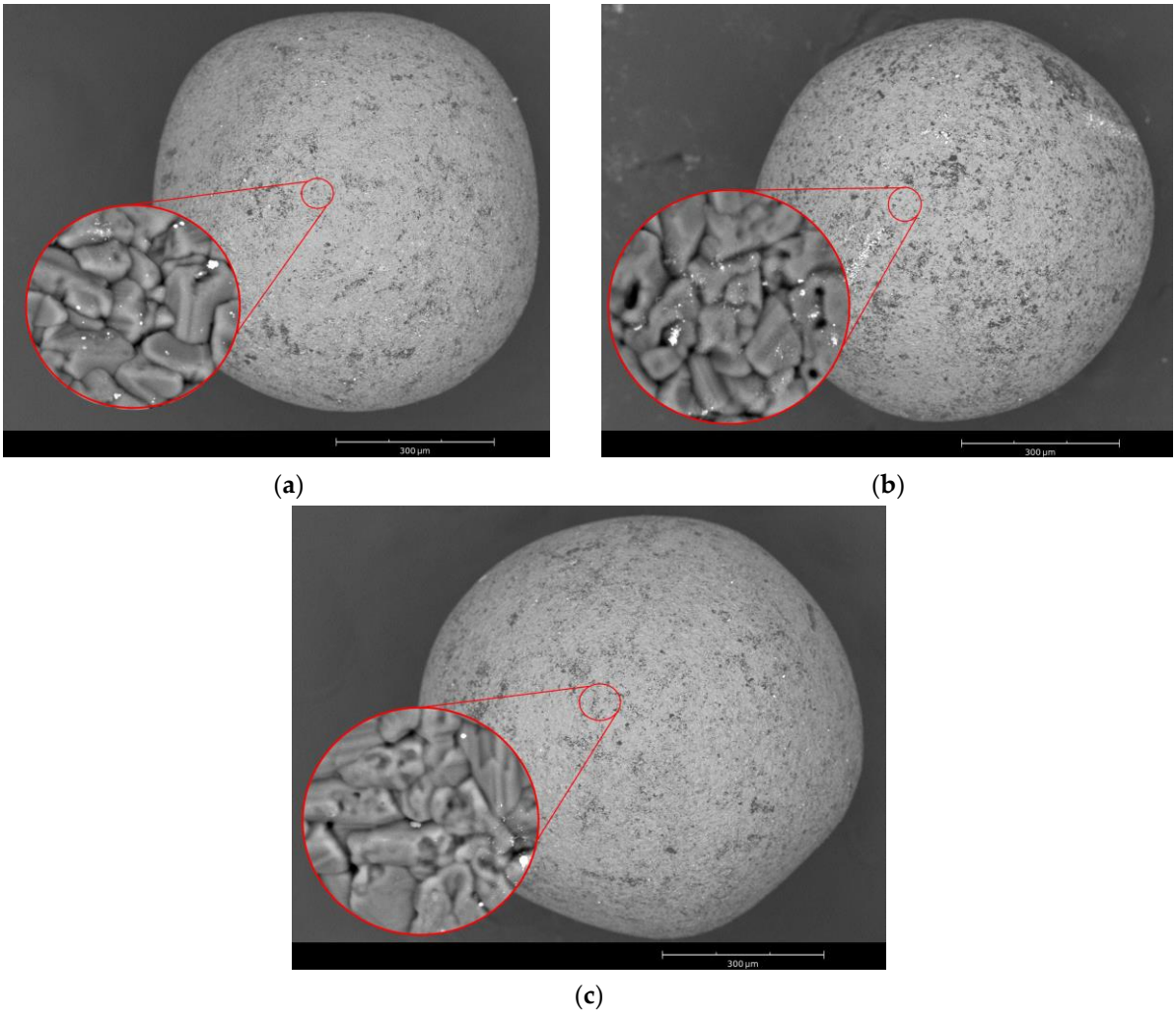
Lithium-containing ceramics based on lithium titanate (Li_2TiO_3), lithium orthosilicate (Li_4SiO_4), and lithium metazirconate (Li_2ZrO_3) were selected as objects for assessing resistance to high-temperature degradation. According to X-ray phase analysis data, it was observed that the ceramics under study have a monoclinic crystal structure type with a high structural ordering degree.

The production of these ceramics involved a process of mechanochemical solid-phase synthesis, followed by thermal sintering at 1000 °C. $LiClO_4 \times 3H_2O$ and oxide components such as TiO_2, SiO_2, and ZrO_2 were chosen as the initial components for the manufacture of lithium-containing ceramics. To obtain the samples, the stoichiometric ratio of the components was 50:50%. Grinding was carried out in a planetary mill of a PULVERISETTE 6 classic line mill (Fritsch, Berlin, Germany) at a rotation speed of 400 rpm, and the grinding time was about 1 h. For grinding, a special glass made of tungsten carbide was used; tungsten carbide balls with a diameter of 10 mm were used as grinding bodies. The choice of tungsten carbide material was determined by the need to exclude any impurities from the grinding media during grinding. The choice of grinding conditions is determined by the need to obtain a powder of uniform composition, which is subsequently annealed in a muffle furnace. Thermal annealing of the samples was carried out in a RUS-universal muffle furnace (RUS-universal, Moscow, Russia) at a temperature of 1000 °C for 8 h, at a heating rate of 20 °C/min. After holding the samples for 8 h, the samples were cooled to room temperature within 24 h. Annealing was carried out in an oxygen-containing atmosphere. To produce the samples under study in the form of spheres, a special mold was used, which made it possible to obtain high-density spheres with a diameter of 1–1.5 mm. The samples were pressed at a pressure of 250 MPa for 30 min, after which

the resulting samples were removed from the press and annealed at a temperature of 400 °C for 10 h to relieve mechanical stresses arising during pressing. The choice of the annealing temperature of the samples after pressing was determined by an a priori method, according to which, under the selected heat treatment conditions, the maximum efficiency of relieving structural stresses in the samples is achieved. The selection of these particular samples for research stems from their potential use as materials for tritium multiplication and subsequent extraction from the ceramics, a crucial step in sustaining thermonuclear reactions for energy production.

2.2. Methods for Characterizing the Studied Samples

Figure 1 demonstrates images of the ceramic samples under study obtained via the scanning electron microscopy (SEM) method. Images were taken using a Hitachi TM3030 scanning electron microscope (Hitachi, Tokyo, Japan).



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

(**c**)

Figure 1. SEM images of the ceramic samples under study: (**a**) Li_2TiO_3, (**b**) Li_4SiO_4, and (**c**) Li_2ZrO_3.

As evident from the SEM image data provided, the synthesized ceramics are spherical particles measuring 1.0–1.5 mm in diameter, composed of closely arranged grains with rhombic or oblong shapes, approximately sized at 100–120 nm. Concurrently, upon examining the morphological characteristics, it becomes apparent that Li_2ZrO_3 ceramics demonstrate the densest packing. The presence of such dense packing may result in elevated levels of hardness and resistance to cracking within the ceramics, in addition to ensuring stability during high-temperature tests.

Figure 2 reveals the results of X-ray diffraction of the studied ceramic samples in their initial state, not subjected to thermal heating, which reflect the phase composition of the studied ceramics as well as the degree of structural ordering. X-ray diffraction patterns of ceramic samples were obtained on a D8 Advance ECO diffractometer (Bruker, Berlin, Germany).

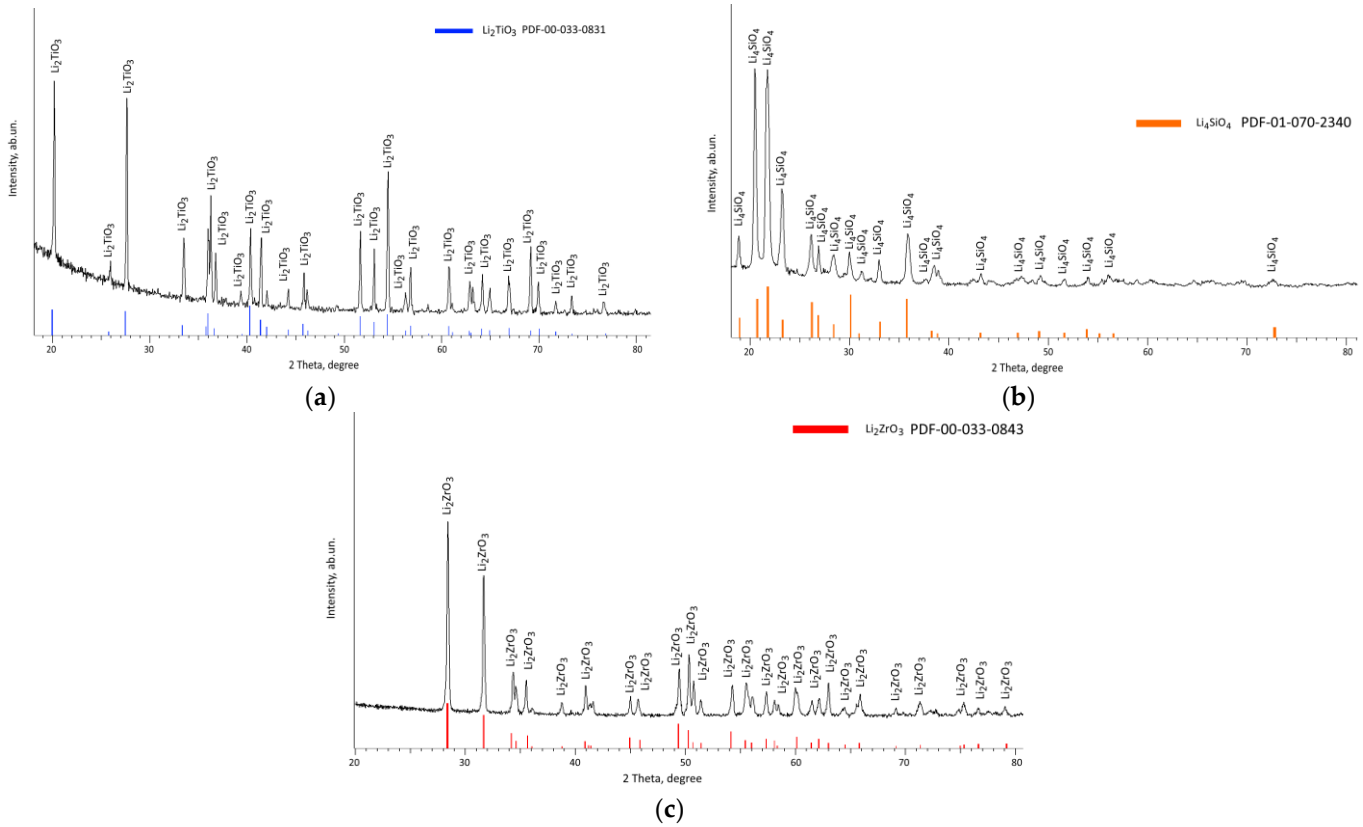


Figure 2. X-ray diffraction results of the ceramic samples under study: (**a**) Li_2TiO_3, (**b**) Li_4SiO_4, and (**c**) Li_2ZrO_3 (in the figures, dashed colored lines (blue, orange, and red) indicate the reference positions of diffraction reflection phases established during X-ray phase analysis).

The use of the method of comparing the position of diffraction reflections with reference values from the PDF-2 (2016) database indicates the presence of only one phase in the structure of each ceramic, without the presence of any impurity inclusions. Data on crystal lattice parameters for all studied samples are presented in Table 1. According to the obtained data presented in Figure 2, the ceramics under study are single-phase ceramics (no reflections that do not correspond to the main established phases are identified in the diffraction patterns) with a monoclinic type of crystal structure characteristic of this type of ceramic.

Table 1. Data on the structural parameters of the ceramic samples under study.

Phase	Li_2TiO_3	Li_4SiO_4	Li_2ZrO_3
Lattice parameter	a = 5.05409 ± 0.00018 Å, b = 8.76622 ± 0.00014 Å, c = 9.73412 ± 0.00032 Å, β = 100.141°, V = 424.54 Å3	a = 11.54015 ± 0.00042 Å, b = 6.07448 ± 0.00053 Å, c = 16.60257 ± 0.00024 Å, β = 99.285°, V = 1147.60 Å3	a = 5.39574 ± 0.00017 Å, b = 8.98502 ± 0.00018 Å, c = 5.38123 ± 0.00031 Å, β = 113.132°, V = 239.91 Å3

Moreover, for all the studied samples, according to X-ray phase analysis data, no impurity inclusions in the form of oxides or any other compounds are observed, which

indicates the possibility of obtaining highly ordered single-phase ceramics and also the fact that during mechanochemical grinding and subsequent thermal annealing, contamination of ceramic samples with impurities does not occur. At the same time, studies of the ratio of the areas of diffraction reflections and the area characterizing the background radiation (amorphous component) found that for all three ceramics, the degree of structural ordering is more than 90%, which, in turn, indicates a high degree of ordering of ceramics, which can be achieved by mechanochemical grinding and subsequent thermal annealing and is used for phase formation and stabilization of the crystal structure. Structural differences in monoclinic-type ceramics lie only in the parameters of the crystal lattice (different values are due to the sizes of the ionic radii of titanium, silicon, and zirconium, as well as their location in lattice positions). Moreover, for all three types of ceramics, according to the presented diffraction patterns, there are selected texture orientations (reflections with maximum intensity), which indicates that during phase formation during thermal annealing, the formation of grains has a preferred orientation, characteristic of the monoclinic type of crystal lattices. Also, analysis of the shape of reflections (determining their symmetry relative to the maximum) indicates a small number of structural deformation distortions, which confirms that the selected thermal annealing conditions lead not only to phase formation processes but also to structural stabilization of the crystal structure and the removal of most deformation distortions in the crystal lattice.

2.3. Thermal Stability Tests

The thermal resistance study was conducted by heating ceramic samples in a muffle furnace at temperatures of 700, 900, and 1000 °C for one hour, followed by rapid cooling of the samples by removing them to the air. This procedure was executed over five consecutive cycles; after each cycle, the hardness values of these ceramics and their crack resistance under single compression were measured.

The hardness of the ceramics was determined using the indentation method, implemented using a LECO LM700 microhardness tester (LECO, Tokyo, Japan). A Vickers diamond pyramid was used as an indenter; the applied pressure during indentation was 1 kN. The indentation process involved pressing the indenter against the sample with a predetermined pressure for 30 s, subsequently yielding indentations, an assessment of the size of which allowed for the determination of hardness values. Indentation at a given load (1 kN) was observed for all samples. The number of measurements needed to collect statistics, determine the measurement error, and calculate the standard deviation was about 30. For the calculations, a standard technique was used to determine the hardness along the diagonals of the indenter print, considering that a Vickers pyramid was used as an indenter. Moreover, in order to avoid overlapping of the indenter prints, each subsequent measurement was performed at a distance of at least 10–15 μm from the previous print. The amount of decrease in resistance to high-temperature corrosion (softening value) for ceramic samples was calculated by comparing the hardness data of the samples after testing with the data of the initial values (samples not subjected to long-term thermal exposure).

The determination of the resistance of ceramics to cracking with increasing single compression force was carried out using an LFM-1 testing machine (Walter + Bai AG, Löhningen, Switzerland). Crack resistance (stress cracking) measurements were carried out by placing samples between two holders, one of which was fixed and the other subjected to a load at a speed of 1 mm/s. The destruction of the sample was monitored using an extensometer, which was used to determine the stage of the onset of cracking of the samples during compression and loading of the sample. At the same time, at the moment of cracking of the sample, the maximum value of the force (crush load) at which the sample begins to collapse was recorded.

The influence of thermal heating during thermal stability tests on alterations in the crystal structure was established by determining the crystal lattice swelling of the samples and calculating the coefficients of thermal expansion.

3. Results and Discussion

3.1. Results of Strength Characteristics Measurements

Figure 3 shows the cyclic dependence of the change in hardness of the ceramics under study before and after thermal stability tests at different test temperatures. Hardness measurements were carried out using the method of indentation in various places on the surface of ceramic samples and the subsequent determination of the average hardness value. Analysis of the hardness values of ceramics in the initial state showed that ceramics based on Li_2ZrO_3 have the highest hardness, for which the hardness value is 752 HV, which is 10% higher than the hardness of Li_2TiO_3 ceramics and 2.5% higher than the hardness values of Li_4SiO_4 ceramics. This difference in the initial hardness values is due to the higher strength characteristics of zirconium in contrast to titanium and silicon, which makes this type of ceramic one of the most promising among lithium-containing ceramics for blanket materials. As is evident from the presented data on the alterations in hardness values during cyclic tests for thermal stability, the smallest changes are observed at a test temperature of 700 °C, for which the maximum reduction in hardness is no more than 1% in the case of Li_2TiO_3 ceramics and less than 0.3% for Li_4SiO_4 and Li_2ZrO_3 ceramics after five consecutive cycles of heating and cooling tests. Moreover, a hardness reduction becomes apparent during cyclic tests at 700 °C only after three consecutive cycles, signifying the considerable resistance of the ceramics to the stressful temperature effects.

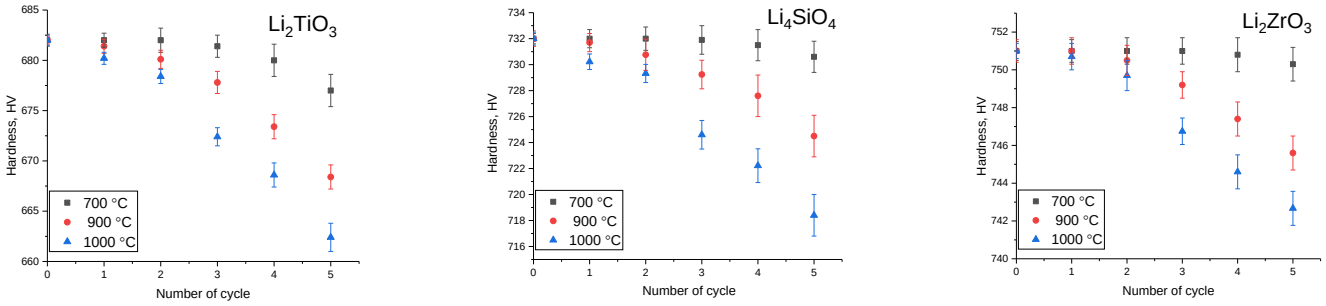


Figure 3. The assessment results of the alteration in ceramic hardness before and after heat resistance tests as a function of the test temperature and the number of cycles: (**a**) Li_2TiO_3, (**b**) Li_4SiO_4, and (**c**) Li_2ZrO_3.

At a testing temperature of 900 °C, the shift in hardness values becomes more noticeable, indicating that the degradation processes exhibit a marked correlation with the exposure temperature. This temperature factor plays a pivotal role in altering the thermal vibrations of the crystal lattice. Conversely, alterations linked to softening (reduction in hardness) are detected after just 1–2 cycles. In contrast, when conducting tests at 700 °C, softening was observed after a greater number of testing cycles.

When subjected to a temperature of 1000 °C, the decline in hardness linked to softening is noticeable after just one cycle and becomes notably pronounced after five cycles (with a reduction exceeding 1.5–2.5%). The most substantial variations in hardness, as indicated by the provided data, occur in the case of Li_2TiO_3 ceramic samples. These results reveal that Li_2TiO_3 ceramics are the least resistant to temperature-induced aging and the subsequent decline in strength properties. Regarding high-temperature tests, Li_4SiO_4 and Li_2ZrO_3 ceramic samples demonstrated greater stability when contrasted with Li_2TiO_3 ceramics.

Figure 4 illustrates the assessment outcomes of the softening factor in ceramics as a function of the conditions of thermal stability tests in the case of variations in test temperature. These findings were derived through a comparative analysis of the alterations in ceramic hardness before and after testing. The softening factor value, as depicted in Figure 4, signifies a reduction in the resistance of ceramics to external influences during indentation and the determination of the hardness of ceramics.

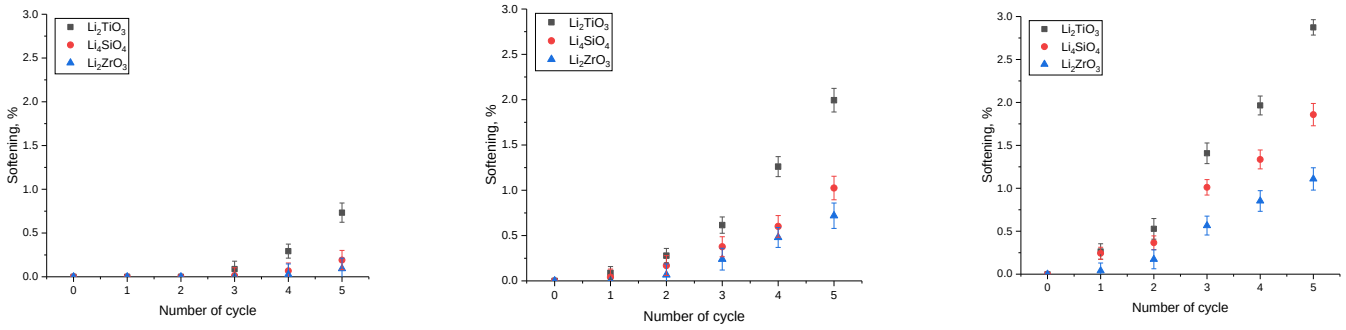
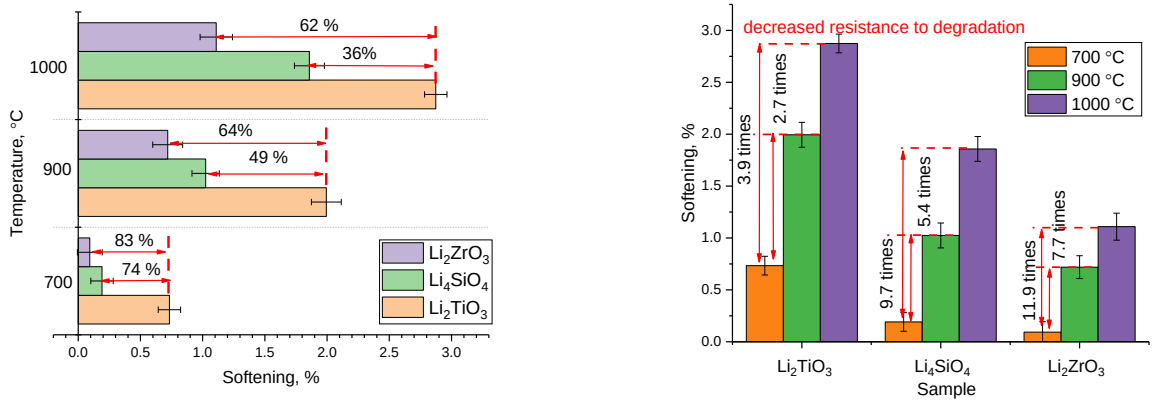


Figure 4. The assessment results of the softening factor of ceramics depending on the number of cycles for thermal stability with varying test temperatures: (**a**) 700 °C, (**b**) 900 °C, and (**c**) 1000 °C.

The ceramics' softening, as deduced from alterations in their hardness values in relation to the number of thermal stability test cycles, exhibits a distinct correlation with both the test temperature (with a rise in temperature from 700 °C to 900–1000 °C, more than 3–5 times softening in percentage terms is observed) and the quantity of test cycles, as per the gathered data. Furthermore, in the instance of Li_2ZrO_3 ceramics, these alterations are comparatively milder than those observed in the other two ceramic types, signifying their greater resistance against cracking and surface degradation. Analysis of the obtained dependences of changes in resistance to softening at different temperatures depending on the number of cycles showed that during long-term operation of samples with increasing temperatures of thermal tests, the stability of strength parameters decreases, which results in cracking and accelerated degradation. Moreover, for different types of ceramics under study, these mechanisms have different destruction degrees; however, a significant decrease in strength parameters is observed after two consecutive cycles for all ceramics under study. In this case, such alterations may be associated with the accelerated destruction of samples and their embrittlement due to thermal expansion of the crystal lattice.

The results of a comparative analysis of changes in the softening factor with the maximum number of test cycles for the thermal stability of ceramics depending on the test temperature are presented in Figure 5a. The overall pattern of the presented dependences on the change in the softening factor for different types of ceramics at the same test temperature suggests that Li_2ZrO_3 ceramics are more resistant to high-temperature degradation during stress tests. At the same time, the stability of Li_2ZrO_3 ceramics, in comparison with Li_4SiO_4 ceramics, is more than 35–50%, while in comparison with Li_2TiO_3 ceramics, the resistance to destruction after five successive test cycles is more than 60–80%, depending on the test temperature. It is important to highlight that Li_2TiO_3 ceramics proved to be the least resistant to thermal stress tests, the degradation of which can be explained by the migration effects of oxygen in the crystal structure of the ceramics.

Figure 5b reflects the change in the value of degradation of strength properties for each type of ceramics depending on the temperature of thermal stability tests, which makes it possible to determine the resistance to degradation of the hardness and strength of ceramics with a growing test temperature. The depicted relationships evidently illustrate the impact of elevating the heating temperature on diminishing the resistance of strength characteristics, where minor alterations noted at a test temperature of 700 °C suggest strong resistance to degradation in Li_2ZrO_3 and Li_4SiO_4 ceramics. However, the test temperature growth results in a more noticeable escalation in degradation.

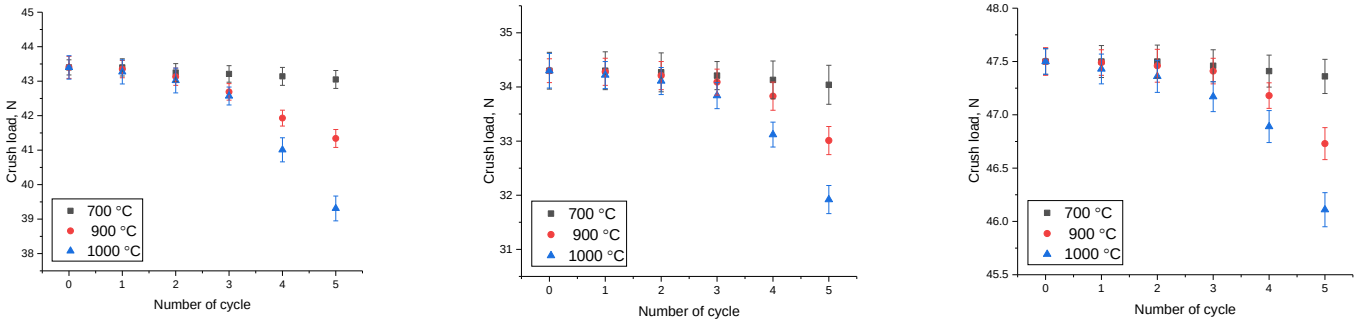


(**a**) (**b**)

Figure 5. The results of alterations in the softening factor: (**a**) dependence of variations in the softening factor on temperature for the ceramics under study and (**b**) comparative diagram of the variations in the softening factor for the studied ceramics.

3.2. Single Compression Measurements

Figure 6 demonstrates the assessment test results of ceramics for crack resistance and cracking under single compression at a constant speed (0.1 mm/min) before and after thermal stability tests. The obtained dependencies reflect changes in resistance to external loads as well as the preservation of their strength characteristics under variable loads.



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

Figure 6. The assessment results of the maximum pressure value that ceramics can withstand during a single compression of samples subjected to thermal stability tests: (**a**) Li_2TiO_3, (**b**) Li_4SiO_4, and (**c**) Li_2ZrO_3.

The general appearance of the data presented in Figure 6 is similar to the data on changes in the hardness of ceramics, which also indicates the adverse effect of thermal heating and rapid cooling on the resistance to cracking and destruction of ceramics. Based on the obtained dependences of the change in the maximum load that ceramics can withstand during compression, the values of resistance to cracking and its reduction were determined depending on the number of test cycles. To calculate this value (as a percentage), the analysis was conducted using the values of the maximum load leading to cracking of the samples in the initial state. The calculation results are illustrated in Figure 7.

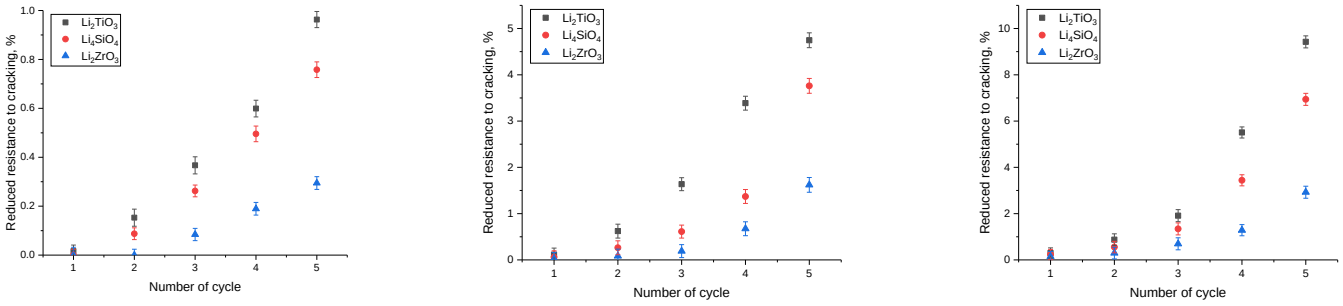


Figure 7. The assessment results of the variation in the crack resistance of ceramics as a function of the number of thermal stability test cycles with temperature variations: (**a**) 700 °C, (**b**) 900 °C, and (**c**) 1000 °C.

Analysis of changes in the crack resistance value indicates a rather low resistance to cracking of Li_2TiO_3 ceramics at temperatures of 900–1000 °C, the value of which was more than 5–10% after five successive test cycles. At the same time, Li_2ZrO_3 and Li_4SiO_4 ceramics showed higher stability to cracking both at temperatures of 700 °C and at high temperatures of 900–1000 °C. The differences in softening values, which varied by less than 3% after five cycles, and crack resistance, which varied from 5 to 10% after five cycles, can be explained by the following factors: In the case of compression, the impact occurs throughout the entire volume of spherical ceramics, which leads to the initialization of accelerated deformation inside the ceramics associated with the accumulation of structural distortions and deformations during thermal heating and rapid cooling. In this case, many structural distortions in the volume lead to the formation of microcracks and chips inside the ceramic, which in turn, under external influence and increasing load, leads to the rapid propagation of cracks, thereby accelerating the destruction process. During indentation, the impact process occurs under a constant load in one place of the surface layer, which leads to a local impact on the ceramics.

3.3. Determination of Swelling of the Crystal Structure as a Result of Thermal Tests

One of the key factors influencing alterations in crack resistance and strength reduction is thermal broadening of the crystal structure, caused by an elevation in the mobility of atoms in the nodes of the crystal lattice due to changes in the magnitude of thermal vibrations under external influences, along with the initialization of migration processes under the influence of thermal heating of points and vacancy defects in the structure. Also, in the case of stressful situations that arise during rapid heating and cooling, oxidation processes associated with diffusion processes in the structure of ceramics can occur. All this can cause deformation swelling of the crystal lattice, which will result in a variation in its volume (ΔV). To determine the dynamics of alterations in the crystal lattice swelling value most accurately, a series of X-ray diffraction patterns of the studied samples were taken before and after thermal stability tests (after each test cycle), which made it possible to determine changes in the crystal lattice parameters and, accordingly, its volume. The results of a comparative analysis of changes in the volume of the crystal lattice of samples subjected to thermal stability tests depending on the number of cycles are presented in Figure 8. The crystal lattice volume of ceramics in their initial state (not subjected to thermal stability tests) was used as the initial value (V_0) for calculations. As is evident from the data presented, the most pronounced alterations in the crystal lattice volume, linked to its increase, indicating the accumulation of deformation tensile stresses, are observed at test temperatures of 900–1000 °C. In the case of a test temperature of 700 °C, the maximum rise in ΔV is less than 0.2%, which implies small structural distortions caused by thermal heating.

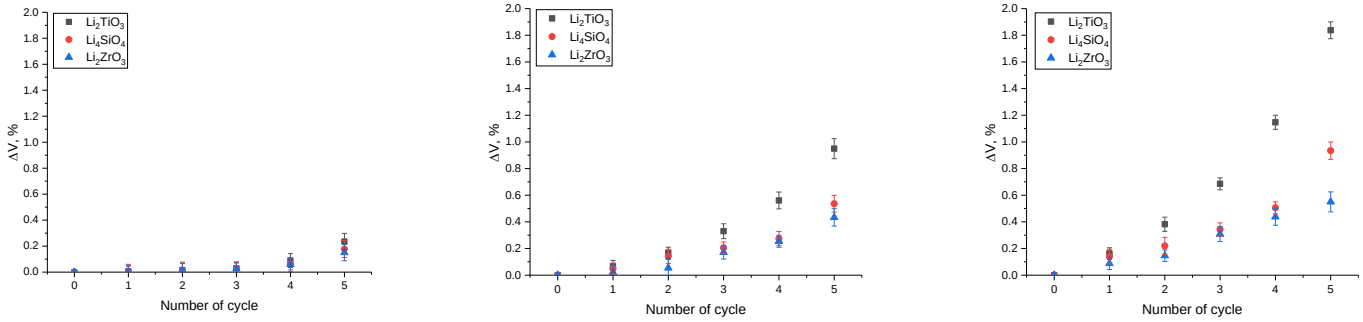


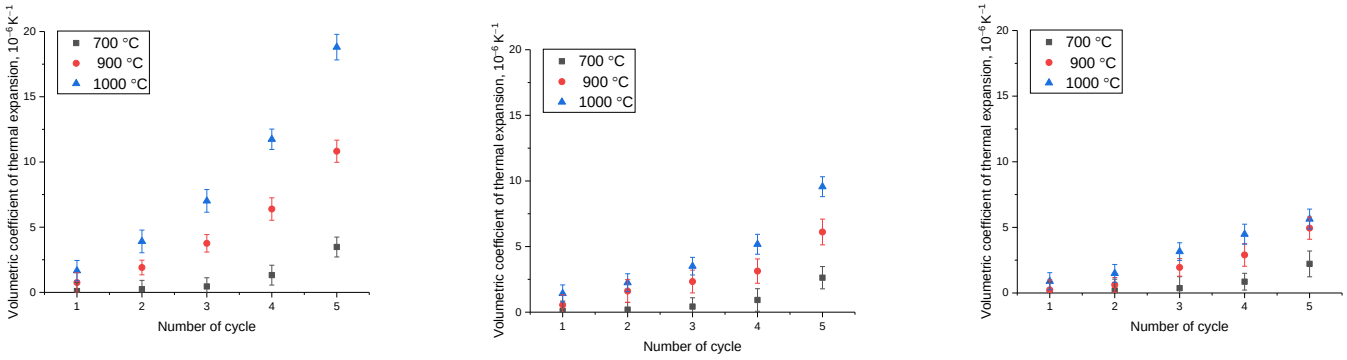
Figure 8. The assessment results of the change in the crystal lattice volume of the studied samples as a function of the number of cycles for thermal stability and test temperature: (**a**) 700 °C, (**b**) 900 °C, and (**c**) 1000 °C.

The alteration in the crystal lattice volume, resulting from thermal exposure and subsequent cooling, primarily arises from the mechanisms of oxygen migration. The enhanced mobility of oxygen is a consequence of thermal effects. In this scenario, oxygen migration, along with its diffusion from the surface into the material's interior, can induce deformation distortion of the crystal lattice due to penetration into nodes and interstices, along with the formation of oxygen vacancies. Oxygen diffusion can also occur by acquiring the energy necessary for movement in the event of an increase in thermal vibrations of the crystal lattice, which in turn leads to the formation of vacancies and voids. In this case, vacancy and structural defects (associated with the replacement of atoms of other elements by oxygen in the nodes of the crystal lattice) can initiate the formation of microcracks, resulting in the destruction of the structure under mechanical loads. Analysis of X-ray diffraction data showed the absence of any inclusions of new impurity phases associated with oxidation processes, which indicates the absence of corrosion processes linked to the formation of oxide inclusions. The absence of new inclusions in the form of oxide phases or impurities indicates that the change in the volume of the crystal lattice, as well as the decrease in strength characteristics, is primarily due to deformation distortions associated with the migration processes of oxygen in the structure of ceramics [32,33].

3.4. Determination of Thermal Expansion Factors of the Crystal Lattice of Ceramics during High-Temperature Heating

One of the factors influencing changes in strength characteristics, as well as a decrease in resistance to cracking under mechanical loads, may be crystallographic thermal volumetric expansion. The occurrence of such effects in the structure can lead to anisotropic distortions (especially for non-cubic crystal lattices), which in turn leads to a deterioration in the properties of materials [34]. At the same time, the most pronounced effect influencing the variation in the properties of ceramics subject to heating is the formation factor of tensile deformation distortions associated with changes in the volume of the crystal lattice as a result of thermal effects. Figure 9 demonstrates the results of alterations in the value of the coefficient of volumetric thermal expansion ($\beta_V(T)$), which characterizes the influence of external influences on the deformation of the crystal structure under thermal influence [35]. To calculate the volumetric coefficient of thermal expansion, Formula (1) was used:

$$\beta_V(T) = \frac{1}{V_{initial}} \frac{\Delta V}{\Delta T}, \quad (1)$$

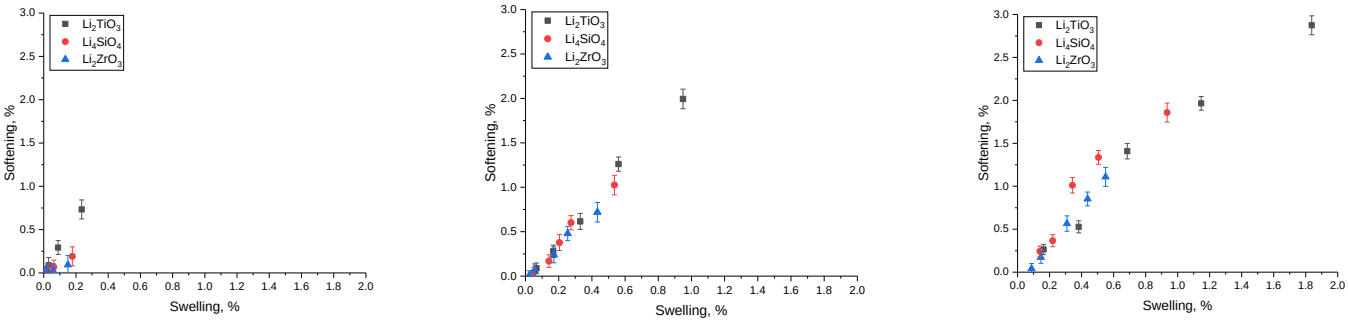


(**a**) (**b**) (**c**)

Figure 9. The assessment results of the alteration in the volumetric coefficient of thermal expansion of the ceramics under study as a result of thermal stability test evaluation: (**a**) Li_2TiO_3, (**b**) Li_4SiO_4, and (**c**) Li_2ZrO_3.

The presented evaluation results of alterations in the volumetric coefficient of thermal expansion for each type of ceramic under study depending on the annealing temperature can be divided into two characteristic types of changes. The first type is associated with the acceleration of degradation processes in ceramics with a rise in the number of cycles of successive tests, which is most pronounced for Li_2TiO_3 ceramics and less pronounced for Li_2ZrO_3 ceramics. The second type is associated with a change in the value of $\beta_V(T)$ in the case of a change in the thermal effect temperature during one cycle. In this case, Li_2ZrO_3 ceramics proved to be the most resistant to volumetric thermal expansion as well as to deformation distortion of the crystal structure, for which the value of $\beta_V(T)$ changes insignificantly both with a growth in the exposure temperature and the number of test cycles.

Figure 10 reveals the results of a comparison of softening values with data on volumetric swelling of the crystal lattice for all studied ceramics, which reflects the connection between strength degradation and crystal lattice deformation. The overall appearance of the obtained dependencies demonstrates a direct correlation between the swelling and softening of ceramics as a result of a rise in the number of thermal test cycles.



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

Figure 10. The results of a comparative analysis of the softening and swelling values of the crystal lattice of ceramics at different temperatures of thermal stability tests: (**a**) 700 °C, (**b**) 900 °C, and (**c**) 1000 °C.

3.5. Morphological Features of Ceramic Degradation

Figure 11 reveals, as an example, the results of the morphological features of the ceramics under study after high-temperature tests for thermal stability at a temperature of 1000 °C after five consecutive cycles.

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

Figure 11. The results of morphological studies of ceramic surfaces after 5 test cycles: (**a**) Li_2TiO_3, (**b**) Li_4SiO_4, and (**c**) Li_2ZrO_3.

As evident from the SEM images presented, the degradation of Li_2TiO_3 ceramics tested at a temperature of 1000 °C for five consecutive cycles results in cracking through the formation of longitudinal microcracks and the formation of buildups on the surface, the presence of which is linked to degradation processes of the near-surface layer of ceramics as a result of thermal tests. In the case of Li_4SiO_4 and Li_2ZrO_3 ceramics subjected to thermal heating at 1000 °C for five consecutive cycles, microcracks are not observed on the surface, and the main changes are related to the formation of small inclusions associated with surface corrosion. Moreover, these inclusions may be caused by oxide buildups, the formation of which occurs only on the surface, since X-ray diffraction data did not establish the presence of any impurities in the samples. The impurities observed on the surface of the samples after high-temperature aging tests were observed only on the surface and were not registered by X-ray phase analysis due to their small quantity. When analyzing the observed inclusions using mapping methods, it was assumed that these inclusions could be presented in the form of silicon oxide compounds for Li_4SiO_4 ceramics. In the case of Li_2TiO_3 ceramics, the resulting growths contain a large amount of oxygen, which may also indicate the formation of oxide inclusions, but their quantitative analysis (weight content) could not be reliably performed. In the case of Li_2ZrO_3 ceramics, the amount of impurities is quite small, which did not allow them to be reliably identified.

The higher resistance to softening of Li_4SiO_4 and Li_2ZrO_3 ceramics is due to several factors that were identified as a result of the experiments. First, according to the obtained data, Li_4SiO_4 and Li_2ZrO_3 ceramics in the initial state have higher strength characteristics (hardness values for Li_2TiO_3 were 682 HV, while for Li_4SiO_4 and Li_2ZrO_3 ceramics, these values were 732 HV and 751 HV, respectively). At the same time, for Li_4SiO_4 and Li_2ZrO_3 ceramics, according to the morphological features, a more dense packing of grains is observed, which in turn creates additional obstacles to the propagation of microcracks and chips and also prevents the processes of thermal destruction. This difference results in higher resistance to external influences under mechanical compression and external load on the sample, which was clearly demonstrated by measuring hardness and resistance to single compression during testing.

By analyzing the data on changes in the volume of the crystal lattice as well as the coefficients of thermal expansion for the ceramics under study, it was determined that the least stable ceramics to thermal expansion are Li_2TiO_3 ceramics, for which, especially at high temperatures of 900–1000 °C, the value of $\beta V(T)$ increases several times with an increasing number of test cycles. This change indicates the low stability of the crystal lattice of Li_2TiO_3 ceramics to volumetric expansion, which is due to an increase in the amplitude of thermal vibrations, leading to accelerated destruction during high-temperature tests. In the case of Li_4SiO_4 and Li_2ZrO_3 ceramics, the volumetric thermal expansion of the crystal structure is less pronounced, which leads to higher stability and resistance to external influences and high-temperature degradation processes. Small changes in the coefficient

βV(T) for Li_4SiO_4 and Li_2ZrO_3 ceramics are also due to their structural features, according to which these types of ceramics are more resistant to temperature influences and the effects of thermal expansion.

4. Conclusions

In conclusion, it is possible to summarize the results of the experiments as follows:

1. Simulation of high-temperature aging processes enabled establishing the connections between structural changes caused by thermal expansion of the crystal lattice and oxygen migration processes at high temperatures, leading to a destructive reduction in the strength properties of lithium-containing ceramics.

2. Based on the data acquired from temperature-dependent assessments of changes in ceramics' strength properties under thermal stress conditions, it was determined that even after undergoing five consecutive cycles at 700 °C, alterations in strength and structural attributes remain minimal. This observation underscores the ceramics' robust resistance to external influences and high temperatures. In this scenario, when ceramics are operated at temperatures of 700 °C and below, adverse effects such as embrittlement, reduced strength, and hardness degradation can be prevented. This is because degradation processes are relatively mild at these temperatures.

3. In the case of operating conditions in which emergency situations with heating of samples to temperatures of 900–1000 °C are possible, the use of Li_2TiO_3 ceramics can lead to accelerated degradation due to a decrease in strength and the formation of microcracks, which can adversely affect the purity of the plasma in the case of ceramic embrittlement and the formation of small scales on the surface of the ceramics. Simultaneously, Li_2ZrO_3 ceramics, among the materials investigated, displayed exceptional stability in terms of strength characteristics during high-temperature degradation tests. They also exhibited remarkable resistance to deformation swelling when subjected to extended thermal exposure.

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