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INFLUENCE OF PHASE FORMATION PROCESSES IN LITHIUM ZIRCONATE CERAMICS ON STRENGTH AND THERMAL PROPERTIES

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The article is devoted to the study of the properties of lithium zirconate ceramics obtained by solid-phase synthesis. The choice of lithium zirconate ceramics as objects of study is due to the great prospects for their use as materials for tritium propagation. Results of a study of the influence of the $LiO/ZrO_2/Li_2ZrO_3 \rightarrow LiO/Li_2ZrO_3 \rightarrow Li_2ZrO_3$ *type phase transformations in ceramics, depending on the annealing temperature, on the strength and thermophysical parameters of ceramics are obtained. During the studies, it was found that the change in hardness and crack resistance are directly dependent on the phase composition and concentration of impurity phases in the composition of ceramics. It has been determined that the displacement of lithium oxide and zirconium dioxide impurity phases leads to an increase in hardness and an increase in resistance to cracking under single compression. It has been established that at annealing temperatures above 900°C, the change in strength and thermophysical parameters is minimal. At the same time, a change in the phase composition of the* $LiO/ZrO_2/Li_2ZrO_3 \rightarrow Li_2ZrO_3$ *type ceramics leads to an increase in the thermal conductivity coefficient by (15-20)%.*

Keywords: lithium-containing ceramics, phase transformations, hardness, thermal conductivity, nuclear materials

Introduction

In recent years, much attention has been paid to the study of new types of lithium-containing ceramics, as well as their thermophysical and mechanical properties. The interest in these studies is due to the great demand for tritium, which is one of the alternative energy sources, the accumulation of which is required to maintain the efficiency of thermonuclear fusion and the operation of thermonuclear reactors, including TOKAMAK or ITER [1–3]. As is known, traditional methods for producing tritium today cannot meet the demand for it, which requires additional research in ways to obtain it [4,5]. One such way is to reproduce the classical nuclear reaction of the $^6Li + n \rightarrow He + T$ type, which makes it possible to obtain tritium from lithium, with its subsequent accumulation to support thermonuclear fusion. At the same time, as shown in a number of scientific papers [6-10], the tritium production is usually accompanied by the release of helium and other products of nuclear reactions, which leads to the material degradation, as well as a decrease in its resistance to external influences and a deterioration in strength properties.

In this regard, when developing a technology for creating lithium-containing ceramics, much attention should be paid to studying the effect of the phase composition on the strength and thermal properties of ceramics, since these parameters play a very important role in determining the performance of ceramics during their operation [11-15]. As is known, the phase composition of ceramics, as well as the presence of impurities in the composition of ceramics, can have both a positive and a negative effect on the strength properties of ceramics, including the resistance to compression and external pressure. In turn, the presence of impurities can have a significant effect on heat transfer in the material, thereby reducing the efficiency of heat removal from ceramics and the occurrence of overheating [16-18].

Based on the foregoing, the purpose of this work is to study the effect of the phase composition of Li_2ZrO_3 ceramics obtained by solid-phase synthesis and annealed at different annealing temperatures in the range from 600 to 1100°C on the strength and thermophysical parameters of ceramics. This work is part of a cycle of works devoted to the study of the Li_2ZrO_3 ceramic properties and evaluation of the possibility of their use as blanket materials for tritium propagation, which is one of the promising research areas in modern energy [18-20]. Li_2ZrO_3 ceramics were chosen as objects of study, which, as was shown earlier in [18-20], are highly resistant to radiation damage.

Experimental part

Synthesis of Li_2ZrO_3 ceramics was carried out by the method of solid-phase synthesis with further thermal annealing of the resulting mixtures in a muffle furnace (RusUniversal, Russia) at temperatures of 600-1100°C. $LiClO_4 \cdot 3H_2O$ and ZrO_2 powders (Sigma Aldrich Saint Louis, Missouri, USA), whose chemical purity was 99.95 %, were used as initial components. As a result of thermal annealing in the temperature range of 600-1100°C, it was found that with an increase in the annealing temperature, phase transformations of the following type $LiO/ZrO_2/Li_2ZrO_3 \rightarrow LiO/Li_2ZrO_3 \rightarrow Li_2ZrO_3$ are observed [19]. At the same time, at an annealing temperature above 900°C, the structure of ceramics is single-phase Li_2ZrO_3 ceramics with a monoclinic structure type.

Study of strength properties was carried out using the indentation method, which was implemented using a LECO LM 700 microhardness tester (LECO Corporation, USA). A Vickers pyramid was used as an indenter, with an indenter load of 10 N. Determination of resistance to single compression was carried out by testing the compression of samples in a press with a compression rate of 0.1 mm/min. Thermal conductive characteristics were evaluated using formula (1), which makes it possible to determine the value of the thermal conductivity coefficient.

$$\lambda = \frac{q\delta}{t_{c1} - t_{c2}}, \tag{1}$$

where q is the heat flux density, W/m^2; t_{c1} and t_{c2} are sample temperatures on both sides, K; δ is the sample thickness.

Results and discussion

One of the important conditions for the applicability of lithium-containing ceramics as blanket materials for tritium propagation is their mechanical strength and resistance to external mechanical influences that may occur during operation, as well as due to a change in the material volume, which can lead to additional pressure and deformation. As a rule, the strength properties of materials are determined by measuring the hardness indices by indentation methods, and the difference in values may reflect the processes of hardening or softening of materials. At the same time, several factors affect the hardness of the material, including density, phase composition, and dislocation concentration play an important role in these characteristics. The combination of these factors can have a very significant effect on the strength characteristics of ceramics. Figure 1 shows the results of changes in the microhardness of Li_2ZrO_3ceramics depending on the phase composition of the ceramics.

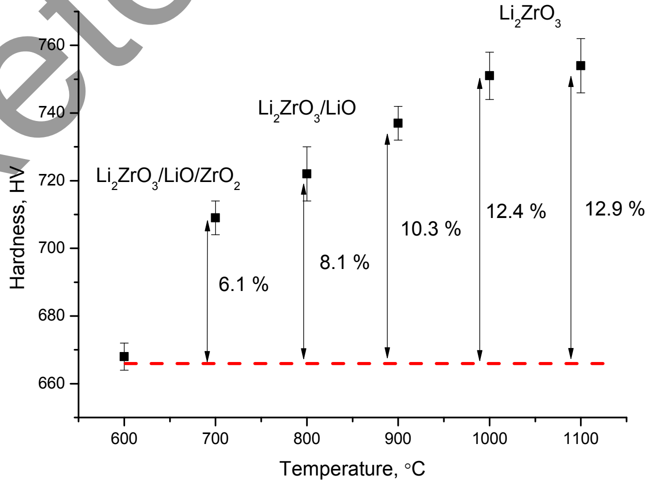

Fig.1. Results of measuring the Li_2ZrO_3 ceramic microhardness depending on the phase composition of ceramics

As can be seen from the presented data, an increase in the annealing temperature, which leads to a change in the phase composition of the ceramics, leads to an increase in the hardness indices, which indicates the effect of strengthening the ceramics associated with a change in the crystal structure of the samples under study. At the same time, in the case of specimens containing LiO and ZrO_2 impurity phases in the composition of ceramics, the hardness values are rather low compared to pure ceramics. The displacement of impurity inclusions from the composition of ceramics, as well as an increase in the structural ordering degree, leads to an increase in the strength and hardness of ceramics. However, it should be noted that the complete displacement of impurity phases from Li_2ZrO_3 ceramics at annealing temperatures of 1000-1100°C does not lead to a significant increase in strength, which may be evidence of the saturation effect of ceramic consolidation, which does not lead to serious hardening and is associated only with a change in the concentration of point structural defects.

Figure 2 shows the results of changes in the resistance of ceramics to cracking under single compression, which characterizes the properties of ceramics to external pressures. As can be seen from the data presented, a change in the phase composition of ceramics leads not only to an increase in hardness, but also to an increase in crack resistance. At the same time, the change in crack resistance has a similar trend with changes in the hardening and hardness of ceramic samples.

However, if the displacement of impurity phases from the ceramic structure leads to the strengthening of ceramics by 10-12 %, in the case of resistance to cracking of these data, the effect of displacement of impurity phases leads to an increase in resistance by 40-60 %. At the same time, an increase in the annealing temperature from 900 to 1100°C does not lead to large changes, which indicates that the main effect in hardening is associated with a change in the phase composition of ceramics, while for single-phase ceramics obtained at temperatures of 1000-1100°C the change in strength characteristics is insignificant.

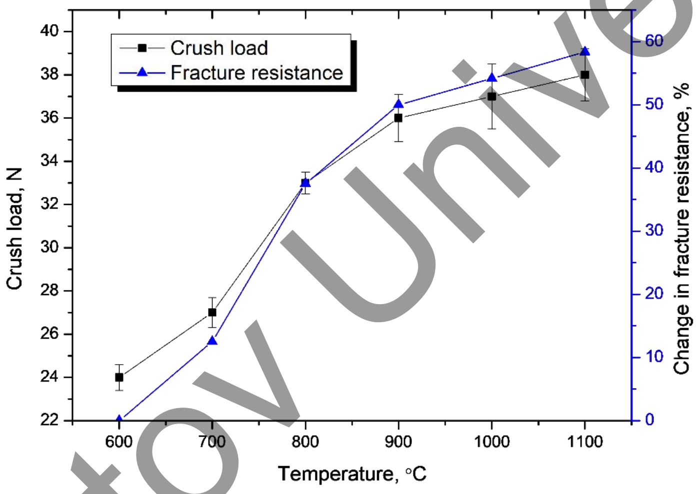

Fig.2. Results of change in the resistance to single compression of ceramics

Figure 3 presents the results of a comparative analysis of changes in the ceramic hardening and consolidation trends associated with a change in density values, which was determined using the X-ray diffraction method by analyzing data on changes in the crystal lattice volume. The general form of changes indicates a significant difference in trends, associated with a difference in changes in the measured values. In the case of changes in the consolidation value, the trend of changes depending on temperature is close to linear, which indicates that the main contribution to consolidation is made by structural ordering caused by a change in the defect structure, as well as partial annihilation of defects as a result of thermal annealing.

In the case of hardening of ceramics, the trend of changes in this value is non-linear and has a pronounced dependence on the phase composition of ceramics, which is reflected in the following facts. The presence of impurity phases in ceramics obtained at an annealing temperature of 600°C leads to the fact that the values of hardness and stability are quite small, which indicates a low resistance to external influences. Displacement of impurity phases with an increase in the annealing temperature leads to a sharp increase in strength and hardness, which is reflected in a change in the trend. However, complete displacement of impurity phases at annealing temperatures of 1000-1100°C, accompanied by structure ordering, does not lead to significant changes in strength characteristics.

One of the factors that make it possible to explain this nature of changes in strength properties, in addition to the phase composition and its changes depending on the annealing temperature, is changes in the dislocation density of ceramics due to changes in the grain size. Figure 4 shows the results of changes in the dislocation density of ceramics depending on the annealing temperature.

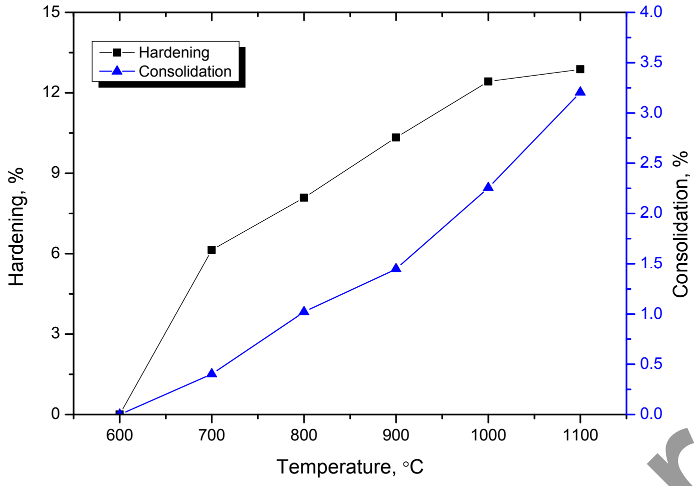

Fig.3. Results of a comparative analysis of changes in the ceramic hardening and consolidation trends

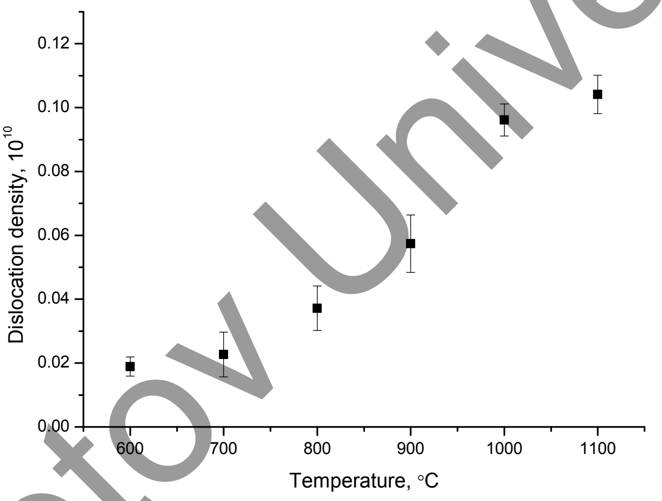

Fig.4. Results of changes in the density of ceramics depending on the annealing temperature

As can be seen from the data presented, the change in dislocation density has a similar trend to changes in strength characteristics and a pronounced nature associated with changes in the phase composition of ceramics. At the same time, the displacement of impurity phases leads to a decrease in the grain size, which in turn leads to an increase in the dislocation density, the changes of which have an inverse quadratic dependence on the grain size. In the case typical for ceramics obtained at a temperature of 1000-1100°C, for which no changes in size were observed, the dislocation density values are also practically unchanged. Thus, we can conclude that the hardening of ceramics is related to the dislocation density, as well as the phase composition of ceramics. As is known, at certain values of the dislocation density, the effects of hardening of materials are observed, as well as an increase in the resistance to destruction under external influences, which is an important factor for materials subjected to mechanical stress, as well as deformation processes.

An important factor determining applicability of ceramics as breeder materials in combination with the mechanical and strength properties of ceramics is their thermophysical characteristics, which characterize the ability to remove heat from the system. At the same time, it is necessary that the materials retain their heat-conducting characteristics over a wide temperature range. Figure 5 shows the results of changes in the thermal conductivity coefficient depending on the heating temperature in the range from 400 to 800°C.

As can be seen from the data presented, a change in the phase composition leads to a sharp increase in the thermal conductivity of ceramics, which is due to a decrease in deformation contributions and cavities that prevent heat transfer. At the same time, it should be noted that the thermal conductivity of ceramics is maintained over the entire measured temperature range, which indicates the stability of heat transfer. It should also be noted that the structural ordering observed for samples annealed at a temperature of 1000-1100°C does not lead to a significant change in the thermal conductivity, which, as in the case of strength properties, indicates that the change in thermophysical parameters is more related to the phase composition of ceramics, as well as impurity inclusions in the form of LiO and ZrO_2 phases, the displacement and phase transformation of which at annealing temperatures above 800°C leads to an increase in thermal conductivity by 15-20 %. Figure 6 shows results of the dependence of ceramics porosity change and average thermal conductivity value. The porosity value was determined by evaluating changes in the ceramic density depending on the annealing temperature.

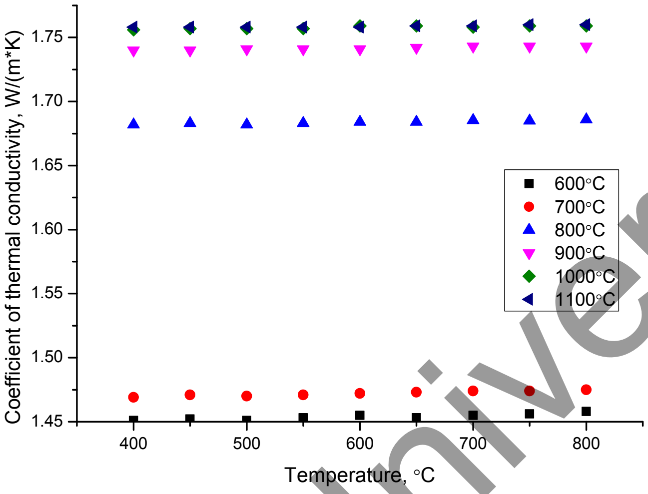

Fig.5. Results of change in the thermal conductivity coefficient

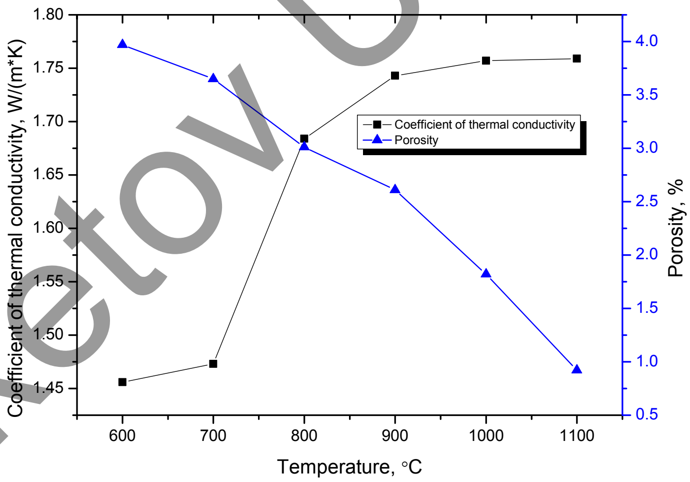

Fig.6. Dependence of the change in the thermal conductivity coefficient and porosity of ceramics

The general trend of changes in the thermal conductivity has a strongly pronounced dependence on the phase composition, as mentioned above. Thus, in the presence of impurity inclusions in the structure, the thermal conductivity is significantly small, which, in addition to the influence of the presence of impurity phases, can also be due to structural distortions that occur during the formation of a complex crystal structure. At the same time, the displacement of impurity inclusions leads to an increase in thermal conductivity, as well as a significant change in porosity, in view of its decrease due to structural ordering. However, the complete displacement of impurity phases from the structure of ceramics does not lead to a significant change in thermal conductivity, the change in which in the annealing temperature range of 900-1100°C does not exceed 1.0-1.5%. At the same time, structural ordering has a significant effect on the ceramic porosity, and a decrease in its value by more than 2.5-3 times compared with the same value for ceramics annealed at a temperature of 600-700°C.

Conclusion

Thus, it can be concluded from the experimental work carried out that the structural ordering and phase transformations associated with the displacement of impurity inclusions in Li_2ZrO_3 ceramics have a significant effect on the strength and thermophysical parameters of ceramics. At the same time, the greatest contribution to changes in the strength and thermophysical properties of ceramics is made by phase transformations associated with the formation of an ordered Li_2ZrO_3 phase in the structure of ceramics. In the case of complete formation of the Li_2ZrO_3 phase and further structural ordering, not at high annealing temperatures above 1000°C, does not lead to significant changes in the thermophysical and strength properties. In the case of the complete formation of the Li_2ZrO_3 phase and further structural ordering at high annealing temperatures above 1000°C, it does not lead to significant changes in the thermophysical and strength properties.

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