**Eurasian Journal of Physics and Functional Materials**

**2026, 10(2), 147-163**

# Determination of the influence of component ratio variation in solid-phase synthesis of lithium-containing ceramics based on lithium aluminate

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DOI: **10.32523/ejpfm.2026100204**
Received: 15.04.2026 - after revision

As is known, synthesis of high-strength, stable lithium-containing ceramics capable of withstanding high mechanical loads during operation is one of the key problems in the field of materials science, the solution of which will determine the potential for using new lithium-containing ceramics for blankets. In the work, using the method of mechanical mixing and subsequent thermal annealing, samples of lithium-containing ceramics based on lithium aluminate were obtained, and the variation of the ratio of the components during mixing made it possible to obtain ceramic samples with different phase ratios, a change in which, according to the data obtained, leads to a change in the strength and mechanical properties of the ceramics. According to X-ray diffraction analysis and Raman spectroscopy data, it was found that variation in the ratio of components in the composition of lithium aluminate due to an increase in the proportion of aluminum oxide leads to the formation of glass phases, as well as transformations of the tetragonal phase $LiAlO_2$ into the cubic $LiAl_5O_8$ with subsequent dominance of this phase in the composition at concentrations of 0.9 M $Al_2O_3$. Moreover, the analysis of optical spectra showed that the change in the phase ratio is accompanied by the formation of oxygen vacancies, the minimum density of which is observed for samples of single-phase ceramics with the tetragonal phase $LiAlO_2$. The evaluation results of the mechanical properties of ceramics showed that the formation of two-phase ceramics containing the tetragonal phase $LiAlO_2$ and the orthorhombic phase $Li_5AlO_4$ leads to higher hardness and crack resistance compared to single-phase $LiAlO_2$ ceramics. At the same time, the formation of two-phase ceramics, including the cubic phase $LiAl_5O_8$, leads to less pronounced changes in resistance to external influences due to the presence of glass-phase inclusions in the structure.

**Keywords:** phase transformations; impurity phases; solid-phase synthesis; strengthening; mechanical properties.

# Introduction

In today's world, increased energy consumption due to the growth of industrial production, urbanization and technological development requires the search for new environmentally friendly and practically inexhaustible sources of energy. In this regard, nuclear and thermonuclear energy is considered one of the most promising and highly effective areas for the development of energy technologies of the future [1,2]. At the same time, the prospects for the development of thermonuclear energy are due to the need to solve problems in the field of increasing energy consumption and reducing dependence on hydrocarbons and fossil fuels [2,3].

At the same time, emphasis in thermonuclear energy is placed on the use of deuterium and tritium synthesis reactions, which are characterized by high energy output, high energy output, as well as the almost complete absence of nuclear waste accumulation in the process of energy generation [4,5]. The high efficiency of tritium nuclear reactions is due to relatively low ignition thresholds compared to other synthesis options, which makes it possible to implement it in conditions that are currently achievable in experimental tokamaks under development. In this case, a significant portion of the energy is transferred by neutrons, which can subsequently be effectively used to heat the blanket and subsequently convert thermal energy into electrical energy. It should also be noted that tritium production can occur directly in the reactor through the interaction of neutrons with lithium-containing blanket materials, which opens up additional possibilities and enhances the potential of fusion energy as a sustainable and long-term energy source [6–8].

One of the key challenges in the development of thermonuclear energy is the search for optimal compositions of ceramic materials used for breeding tritium, the fuel that is the basis for thermonuclear reactions [9,10]. As a rule, lithium-containing ceramics or lithium-enriched ceramics are considered to obtain tritium in the quantity required to sustain thermonuclear reactions. The principle of tritium production using lithium-containing ceramics is based on the nuclear reaction of lithium with neutrons, which results in the formation of nuclear reaction products in the form of tritium and helium, as well as the release of energy [11,12]. Today, the most commonly used types of lithium-containing ceramics are lithium titanate or lithium orthosilicate, the production of which is actively pursued by leading research centers in the field of thermonuclear materials [13–16]. At the same time, despite the great prospects of these types of lithium-containing ceramics and a number of scientific research works [13–18] showing the resistance of these ceramics to destruction processes associated with the accumulation of nuclear reaction products during the production of tritium, work aimed at finding new types of lithium-containing ceramics is of great interest. In this case, interest in such research is driven by the need to expand the range of potential candidate materials, as well as to address a number of issues related to the enhancement of the resistance of ceramics to external influences and degradation processes that occur during operation [19,20]. In this regard, the main aim of this study is to investigate the prospects of obtaining lithium-containing ceramics based on lithium aluminate compounds using the method of mechanical mixing and thermal sintering. The use of these two processes to produce lithium-containing ceramics, as well as the ability to change the phase composition by variation of the ratio of components during mixing, makes it possible to propose one of the simplest and cheapest methods for obtaining lithium-containing ceramics with a controlled phase composition, as well as controlled strength and mechanical properties. The choice of the possibility of the component ratio variation during mixing to obtain lithium-containing ceramic powders is due to the possibility of controlling the phase composition of ceramics by changing the phase formation processes due to supersaturation of the mixture with components over a wide range. In the case of variability in the ratio of components, technological solutions are developed to obtain both single-phase lithium aluminate ceramics and two-phase ceramics in which the strengthening effect is realized due to the presence of mechanical boundaries.

# Materials and methods

The synthesis of lithium-containing ceramics based on lithium aluminate was carried out by mixing lithium carbonate ($Li_2CO_3$) and aluminum oxide ($Al_2O_3$) in different ratios from 0.1 M to 0.9 M, followed by mechanical mixing in a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany). The grinding speed was 200 rpm, grinding was carried out for 30 minutes, followed by removal from the grinding bowl and separation of powders from the grinding media. After grinding, the obtained powders were subjected to thermal annealing in a Nabertherm LE 4/11/R6 muffle furnace (Nabertherm, Lilienthal, Germany) at a temperature of $1000\,^{\circ}\mathrm{C}$ for 5 hours, followed by cooling of the samples in the furnace for 24 hours until complete cooling. The heating rate was $20\,^{\circ}\mathrm{C/min}$. The choice of annealing conditions at $1000\,^{\circ}\mathrm{C}$ was determined by the need to inhibit lithium evaporation and volatilization during high-temperature processing, as well as to prevent the formation of glass phases, the presence of which reduces the ceramics' resistance to mechanical stress. The main synthesis reaction is carried out by a solid-phase interaction reaction at high sintering temperatures:

$$\mathrm{Li_2CO_3 + Al_2O_3 \rightarrow 2\,LiAlO_2 + CO_2 \uparrow} \qquad (1)$$

Moreover, in the case of exposure to high-temperature heating, the initial stage of synthesis is carried out through the thermal decomposition of lithium carbonate, followed by the formation of lithium oxide and carbon dioxide: $\mathrm{Li_2CO_3 \rightarrow Li_2O + CO_2 \uparrow}$, followed by the interaction between aluminum oxide and lithium oxide $\mathrm{Li_2O + Al_2O_3 \rightarrow 2\,LiAlO_2}$. Thus, the synthesis process occurs simultaneously in two stages in the solid phase during high-temperature annealing. In turn, the use of variations in the weight contribution of the mixed components allows for the initiation of not only the processes of lithium aluminate $LiAlO_2$ formation, but also the formation of various inclusions of other phases, the formation of which occurs in the case of supersaturation of the mixture with either lithium oxide (at high concentrations of the lithium-containing component) or aluminum oxide.

At the same time, it was established a priori that the annealing temperature growth above $1000\,^{\circ}\mathrm{C}$ leads to an increase in the volatility of lithium-containing components, which leads to a violation of the stoichiometry of the components, as well as the formation of impurity inclusions in the form of aluminum oxide or lithium-deficient compounds, which disrupts the phase homogeneity and reduces the resistance of ceramics to external influences.

The proposed method for producing ceramics, which involves mechanochemical milling of the starting components followed by thermal sintering, enables the production of lithium-containing ceramic powders that can be pressed into pellets of any shape and geometry, used as filler materials for tritium breeders, or used as bulk powder. A key difference from known methods for producing lithium-containing ceramics, including hydrothermal or chemical precipitation, is the proposed synthesis method's ability to produce ceramics with controlled phase composition and size effects, which involve controlling grain size by varying the grinding conditions during milling. Furthermore, the ability to subsequently produce powders allows for reduced porosity due to denser packing of the ceramics within the pellets, as well as increased resistance to external influences.

The determination of the morphological features of the synthesized lithium-containing ceramics depending on the variation of the mixing ratio of the components was carried out using the scanning electron microscopy method performed using a Phenom™ ProX scanning electron microscope (Thermo Fisher Scientific, Eindhoven, Netherlands).

The determination of the structural features of the synthesized ceramics depending on the variation in the ratio of components in the composition, as well as the determination of the phase composition, was carried out by measurements and subsequent full-profile analysis of X-ray diffraction patterns. The diffraction patterns were obtained on a D8 Advance ECO powder diffractometer (Bruker, Germany), the survey was carried out in Bragg–Brentano geometry, in the angular range of $2\theta = 20-90^{\circ}$, the survey step was $0.05^{\circ}$, the data collection time at a point was 1 sec. The analysis of structural parameters, including the crystal lattice parameters, the degree of structural ordering, as well as the deviation of parameters from reference values associated with changes in phase composition and deformation processes during phase formation, was carried out using the DiffracEVA v.4.2 software code. To determine the phase composition, the PDF-2 database, the data from which were used to evaluate the phases and changes in their weight ratios depending on the variation in the ratio of components during mixing, was used.

The weight contributions of each phase were determined by determining the areas of diffraction reflections of the studied samples depending on the component ratios, followed by calculating their weights in the diffraction patterns. This method allowed us to estimate the contribution of each phase to the sample composition with an accuracy of approximately 0.1 wt.% and eliminate inconsistencies by using corundum numbers when refining the weight contributions.

Also, to confirm the results of X-ray phase analysis and the kinetics of changes in the phase composition depending on the variation in the ratio of components in the composition, the method of Raman spectroscopy, performed on an Enspectr

M532 Raman microscope (Spectr-M LLC, Chernogolovka, Russia), was used.

The determination of the resistance of ceramics to cracking under variable mechanical load was carried out on a single-column electromechanical testing machine LFM-L 10kH (Walter + Bai AG, Loningen, Switzerland) according to the single-compression method, which includes recording the maximum load at which cracking of ceramic samples occurs. The determination of the magnitude of the load at which cracking occurs was carried out using the extensometry method. The determination of the ceramic surface hardness was performed using the indentation method implemented on a Duroline M1 microhardness tester (Metkon, Bursa, Turkiye). A Vickers pyramid was used as an indenter, the load on the indenter was about 100 N, the number of repetition cycles for each sample was at least 10 to collect statistics and determine the measurement error.

## Results and discussion

One of the most reliable methods to control the ceramic formation processes is the method of X-ray structural analysis, the use of which includes obtaining and subsequent analysis of X-ray diffraction patterns of ceramic samples with the ability to calculate both the structural parameters and the phase composition of the resulting samples when the conditions for their synthesis or variation of the ratio of components in the initial mixed powders change.

Figure 1 shows the results of X-ray diffraction of the studied samples of lithium-containing ceramics with variations in the ratio of components in the composition after mixing and thermal annealing at $1000\,^{\circ}\mathrm{C}$. According to the presented set of X-ray diffraction patterns obtained for samples with different component ratios, it can be concluded that the main phase in the process of mixing and subsequent heat treatment is the tetragonal phase $\gamma$–$LiAlO_2$ (PDF-00-038-1464), the presence of which is confirmed by a set of diffraction reflections corresponding in intensity and position to the card data PDF-00-038-1464 from the PDF-2 database. It should be noted that a change in the ratio of components according to the given X-ray diffraction patterns leads to a change in the structural parameters of this phase, as evidenced by a change in the shape and position of diffraction reflections, which are associated with both the deformation effect of impurity phases, the presence of which is also recorded in the diffraction patterns, and a change in the density of structural defects, in particular, oxygen vacancies, the formation of which in the structure leads to deformation distortion of the crystal structure. At low concentrations of $Al_2O_3$, according to X-ray diffraction data, the ceramics contain inclusions in the form of the orthorhombic phase $Li_5AlO_4$ (PDF-01-070-0432), the presence of which is due to the excess of lithium in the ceramics. With a weight contribution of $Al_2O_3$ equal to 0.5 M, according to the X-ray phase analysis data, the composition of the ceramics is represented by the dominant phase $\gamma$–$LiAlO_2$ with small impurities in the form of inclusions of the $Li_5AlO_4$ phase, and in the case of an $Al_2O_3$ concentration equal to 0.6 M, the phase composition of the ceramics is represented by a single phase $\gamma$–$LiAlO_2$ without any impurities in the composition. In this case, the formation of the $Li_5AlO_4$ phase in the ceramics indicates an excess of lithium in the ceramics, which, with a lack of aluminum oxide, leads to the stabilization of inclusions in the form of a lithium-enriched phase $Li_5AlO_4$, the formation of which is a competitive phase formation process due to the presence of local areas with excess lithium in the structure. The main mechanism of formation of the $\gamma$–$LiAlO_2$ phase is associated with the diffusion interaction of the $Li_2O$ (formed as a result of the thermal decomposition reaction $Li_2CO_3 \rightarrow Li_2O + CO_2 \uparrow$) and $Al_2O_3$ oxides, while in the case of a deficiency of aluminum oxide and an excess of lithium-containing components in the composition, the phase formation process shifts to the region of formation of stable lithium-excess compounds of the $Li_5AlO_4$ type, the proportion of which is significant at low concentrations of $Al_2O_3$ (0.1–0.25 M). With an increase in the proportion of $Al_2O_3$ in the composition of ceramics, the phase formation processes are leveled out due to an increase in the concentration of the $\gamma$–$LiAlO_2$ phase and its stabilization. The optimal ratio of components for obtaining single-phase $\gamma$–$LiAlO_2$ ceramics is 0.4 $Li_2CO_3$ and 0.6 $Al_2O_3$, at which full completion of diffusion processes and the formation of a thermodynamically stable state, in which a balance is maintained between the diffusion rate and the chemical reactivity of the components, with minimization of the free energy of the system, are observed.

At $Al_2O_3$ concentrations of 0.75–0.9 M, the observed changes in the diffraction patterns are associated with the formation of an aluminum-enriched phase $LiAl_5O_8$ (PDF-01-071-1736) with a cubic type of crystal structure, the dominance of which is observed for samples with an $Al_2O_3$ concentration of 0.9 M. Moreover, the change in the shape of the reflections for this phase, caused by their broadening and clearly expressed asymmetry, indicates an increase in the concentration of defects in the structure, caused by changes in the phase composition due to the formation of the cubic phase $LiAl_5O_8$, the formation of which leads to an increase in microdeformation inclusions in the composition of ceramics. The mechanism of formation of the $LiAl_5O_8$ phase is associated with an excess of $Al_2O_3$, in which part of the lithium is included in the structure of the aluminum-enriched matrix, forming more complex oxide compounds, followed by a redistribution of cations in the crystal lattice with the formation of a new cubic phase in the composition. It should also be noted that the formation of an aluminum-enriched phase in the structure of ceramics is also accompanied by the appearance of glass phases, the presence of which causes a decrease in the degree of structural ordering, as well as a broadening of diffraction reflections. The presence of glass phases in the composition of ceramics was recorded due to changes in the intensity of the background signal in the diffraction patterns and the broadening of diffraction reflections, indicating the formation of amorphous inclusions or areas of disorder. The presence of glass phases in the composition of lithium-containing ceramics at aluminum oxide concentrations of 0.25–0.9 M was confirmed by the results of changes in the degree of structural ordering ($S_{\text{cryst}}$), according to which, at the given ratio of components, a decrease in $S_{\text{cryst}}$ from 94% to 86–88% is observed (see data given in Table 1). According to the analysis, the phase distribution within the ceramics is uniform throughout the entire volume. This is due to the synthesis method, in which mechanical action on the powders leads to intensive mixing of the components within the composition, followed by a uniform distribution of the components within each other. This, during sintering, leads to the formation of phases distributed equally throughout the sample. During sintering, this ensures the formation of phases without pronounced localization of individual components or the formation of regions of concentration heterogeneity. Thus, a statistically uniform phase distribution is observed throughout the sample, as confirmed by the results of structural and microscopic analysis.

This structural morphology has a positive effect on the properties of the ceramic material, as the absence of pronounced phase segregation promotes a more uniform distribution of internal stresses, increased structural stability, and improved performance characteristics. Furthermore, a uniform phase distribution can contribute to increased mechanical strength, thermal stability, and the material's resistance to localized defects that arise during operation.

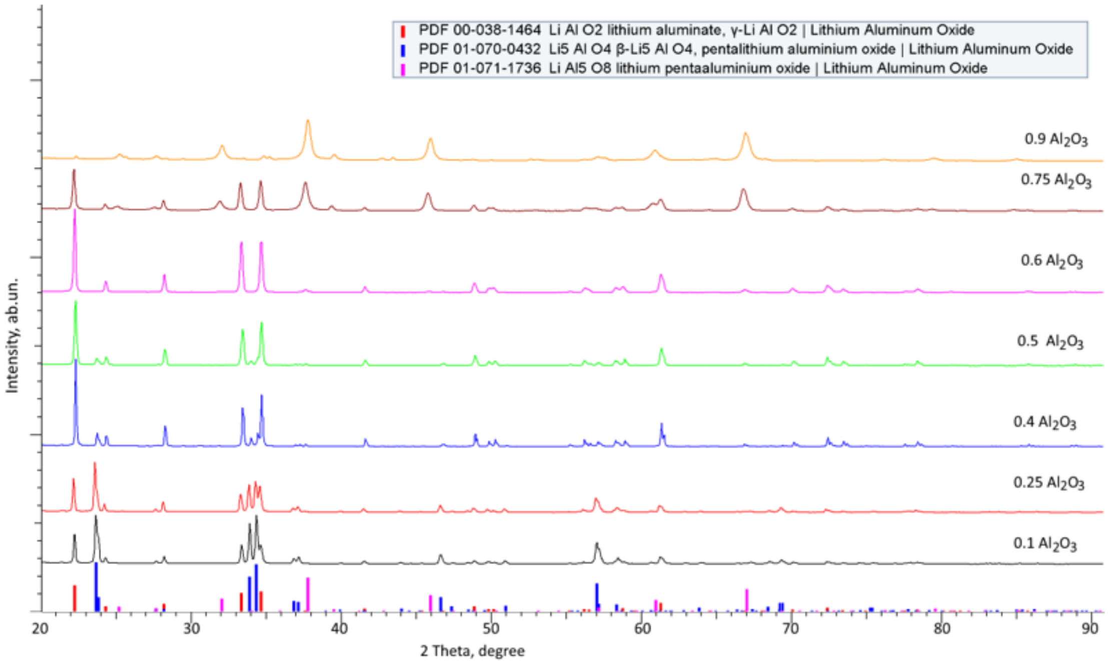


Figure 1. Results of X-ray diffraction analysis of studied lithium-containing ceramics with variation of the ratio of components in the composition.

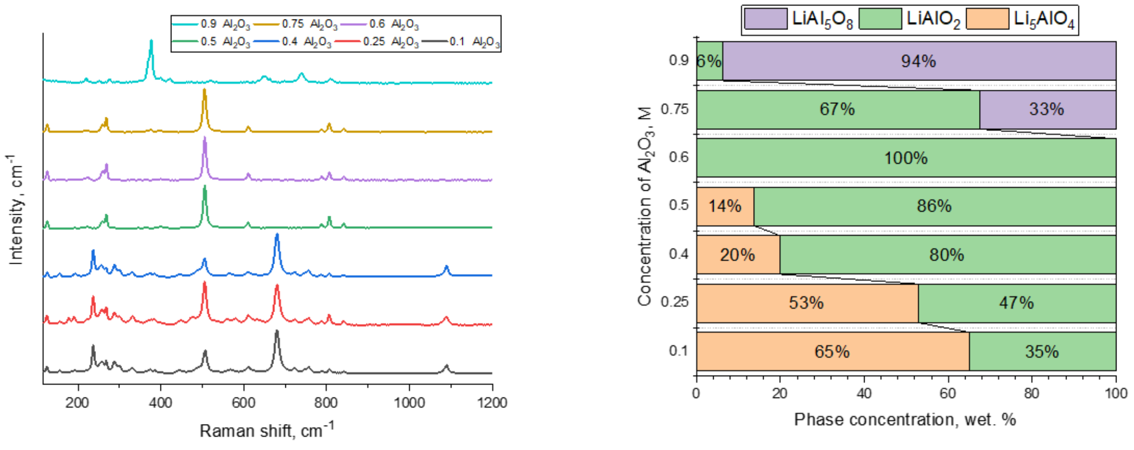
Table 1 shows the results of the assessment of changes in the crystal lattice parameters of each of the established phases of the samples studied depending on the variation in the ratio of components in the composition. According to the presented data on the structural parameters, a change in the ratio of components in the composition of the obtained ceramics has a significant effect on the structural parameters of the main phase $\gamma$–$LiAlO_2$, which is manifested in a deviation from the reference values of the crystal lattice parameters of this phase in the form of changes in the lattice volume, the reduction of which is due to structural ordering. It should be noted that in the case of single-phase ceramics, the values of the structural parameters are minimal, which indicates structural self-organization, as well as the absence of the influence of impurity phases that have a deformation effect on the crystalline structure. In turn, the presence of impurity phases, established using the X-ray phase analysis method, leads to the formation of point and vacancy defects in the structure, the change in the density of which causes the occurrence of non-stoichiometry in oxygen and lithium, which occurs as a result of partial evaporation of lithium during thermal sintering, which in turn leads to the formation of local distortions of the crystal structure of the main phase $\gamma$–LiAlO$_2$. Moreover, the change in the ratio of components during mixing, as well as variations in the weight contributions of the phases, according to the assessment, leads to the stabilization of the crystalline structure of $\gamma$–LiAlO$_2$ and an increase in the degree of structural ordering.

Table 1.
Data on the structural parameters of the studied ceramics.

| Phase | Crystal structure parameters | | | | | | |
|---|---|---|---|---|---|---|---|
| | Concentration of Al$_2$O$_3$ in the composition of the initial mixture of components, M | | | | | | |
| | 0.1 | 0.25 | 0.4 | 0.5 | 0.6 | 0.75 | 0.1 |
| $\gamma$– Tetragonal, P4212(90) | LiAlO$_2$,<br>$a$=5.1705 Å,<br>$c$=6.2777 Å,<br>$V$=167.83 Å$^3$ | $a$=5.1653 Å,<br>$c$=6.2826 Å,<br>$V$=167.62 Å$^3$ | $a$=5.1653 Å,<br>$c$=6.2651 Å,<br>$V$=167.16 Å$^3$ | $a$=5.1629 Å,<br>$c$=6.2639 Å,<br>$V$=166.93 Å$^3$ | $a$=5.1571 Å,<br>$c$=6.2715 Å,<br>$V$=166.79 Å$^3$ | $a$=5.1745 Å,<br>$c$=6.2852 Å,<br>$V$=168.29 Å$^3$ | $a$=5.1827 Å,<br>$c$=6.2951 Å,<br>$V$=169.09 Å$^3$ |
| Li$_5$AlO$_4$, Orthorhombic, Pnmn(59) | $a$=6.4379 Å,<br>$b$=5.3205 Å,<br>$c$=4.6163 Å,<br>$V$=187.84 Å$^3$ | $a$=6.4513 Å,<br>$b$=5.3206 Å,<br>$c$=4.6255 Å,<br>$V$=183.61 Å$^3$ | $a$=6.4098 Å,<br>$b$=5.2931 Å,<br>$c$=4.6145 Å,<br>$V$=186.13 Å$^3$ | $a$=6.4123 Å,<br>$b$=5.2919 Å,<br>$c$=4.6163 Å,<br>$V$=186.25 Å$^3$ | – | – | – |
| LiAl$_5$O$_8$, Cubic, P4332 (212) | – | – | – | – | – | $a$=7.9251 Å,<br>$V$=497.75 Å$^3$ | $a$=7.8904 Å,<br>$V$=491.25 Å$^3$ |
| Degree of structural ordering, % | 91.7±1.2 | 92.8±1.5 | 92.5±1.3 | 92.8±1.5 | 93.9±1.3 | 88.2±1.6 | 86.6±1.3 |
| $\gamma$–LiAlO$_2$ (PDF-00-038-1464) – $a$=5.1715 Å, $c$=6.2840 Å, $V$=168.06 Å$^3$,<br>Li$_5$AlO$_4$ (PDF-01-070-0432) – $a$=6.4200 Å, $b$=6.3020 Å, $c$=4.6200 Å, $V$=186.92 Å$^3$,<br>LiAl$_5$O$_8$ (PDF-01-071-1736), $a$=7.9080 Å, $V$=4.94.54 Å$^3$ | | | | | | | |

Figure 2a shows the results of Raman spectroscopy of the studied ceramics depending on the variation in the ratio of components in the composition of the ceramics, which reflect the change in structural features caused by phase formation processes occurring as a result of thermal sintering. At concentrations of 0.1–0.4 M Al$_2$O$_3$, peaks appear at 156, 193, 237, 287, 298, 330, 445, 492, 506, 680, 723 and 755 cm$^{-1}$, which may be associated with the formation of lithium-rich phases [21,22]. There are also some modes that can be attributed to $\gamma$-LiAlO$_2$, the change in the weight contribution of which is observed depending on the ratio of components in the composition. With an increase in the concentration of Al$_2$O$_3$ to 0.5–0.7 M, the changes in the Raman spectra are associated only with the amplification of signals characteristic of the $\gamma$-LiAlO$_2$ phase, characterized by a set of peaks at 125, 259, 268, 506, 610, 788, 807 and 841 cm$^{-1}$ [23]. In this case, two regions can be distinguished in the spectra: low-frequency up to 500 cm$^{-1}$, characterizing vibrations of Li–O or Al–O, and high-frequency (above 500 cm$^{-1}$), which is characterized by the description of vibrations of Al–O bonds. It should also be noted that the presence of a peak at 125 cm$^{-1}$ in the spectra may be due to vibrations in tetrahedra of the LiO$_4$-AlO$_4$ type, peaks at 259 and 268 cm$^{-1}$ with stretching vibrations of Li–O–Al, peaks at 506 and 611 cm$^{-1}$ with bending vibrations of Al–O, and at 788 and 807 cm$^{-1}$ with stretching vibrations of Al–O [24]. It should also be noted that when the ceramics contain 0.9 $Al_2O_3$, peaks are observed in the spectra, the presence of which may be associated with the formation of $\alpha$-$Al_2O_3$ in a highly disordered form or in the form of glass phases, the presence of which is recorded using the X-ray phase analysis method in the form of changes in the shape of reflections of the aluminum-enriched phase and an increase in background radiation.

Based on the obtained X-ray diffraction patterns, using the method of evaluation of the weight contributions of the established phases, an assessment was made of the change in the phase composition of the synthesized ceramics depending on the variation in the ratio of components in the composition of the ceramics. The assessment results of the weight contributions depending on the variation of the concentration of components in the composition are shown in the form of a diagram in Figure 2b. As can be seen from the data presented in the diagram, based on the results of the analysis of X-ray diffraction patterns of the studied samples, it can be concluded that by variation of the ratio of components in the composition of ceramics, it is possible to obtain two-phase ceramics, which are a solid solution of two phases: $\gamma$–$LiAlO_2$ and lithium-enriched phase $Li_5AlO_4$, at low concentrations of aluminum oxide from 0.1 to 0.4 M. When the content of the $Al_2O_3$ component is equal to 0.6 M, single-phase ceramics with a tetragonal phase $\gamma$–$LiAlO_2$ are obtained. At $Al_2O_3$ concentrations from 0.75 M, the composition of the ceramics is represented by a mixture of two phases: $\gamma$–$LiAlO_2$ and aluminum-enriched phase $LiAl_5O_8$, the formation of which is accompanied by the formation of glassy or amorphous inclusions in the composition, the presence of which may be due to inclusions in the form of amorphous or highly disordered aluminum oxide, the presence of which in the composition is confirmed by Raman spectroscopy data.



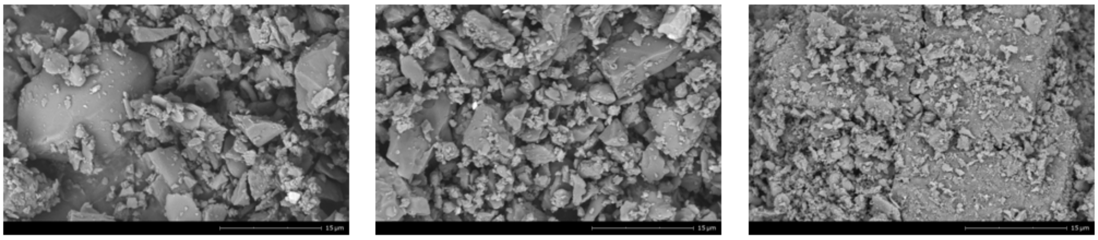
a) b)

Figure 2. a) Results of Raman spectroscopy of the studied ceramics depending on the variation of the ratio of components in the composition; b) Results of the assessment of the weight contributions of the established phases in the composition of ceramics.

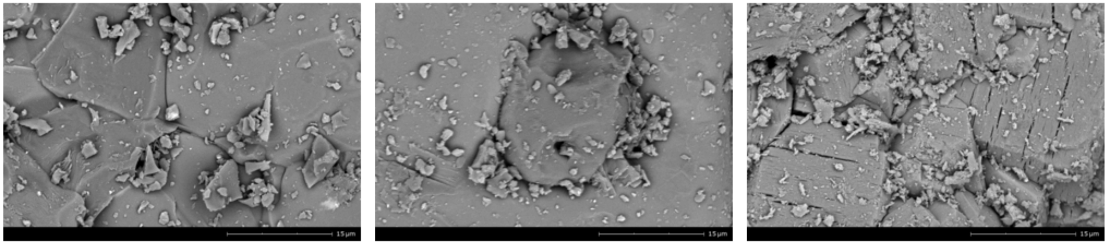
Figure 3 shows the results of changes in the morphological features of the synthesized lithium-containing ceramics depending on the variation in the ratio of components in the composition. For ceramic samples with a low $Al_2O_3$

content, the morphological features of the ceramics are presented in the form of a mixture of large and fine fractions, which indicates incomplete solid-phase reactions, as well as the presence of uncalcined and unreacted inclusions. Moreover, the high degree of agglomeration and the developed surface of the particles indicate the presence of lithium-enriched phases in the composition, as well as increased structural defects. With an increase in the $Al_2O_3$ content to 0.4 M, the particle structure becomes more uniform, while the pronounced agglomeration of large particles with fine inclusions in the composition remains, and the particles themselves acquire clearer outlines, indicating the progression of phase formation and an increase in the content of the $\gamma$–$LiAlO_2$ phase, and the structure itself is still characterized by the presence of intergranular voids and a non-uniform distribution of particle sizes. In the case of samples with a concentration of 0.5–0.6 M $Al_2O_3$, according to SEM images, there is a compaction and structural ordering of the microstructure of ceramics, caused by the coarsening of grains with well-formed edges, which indicates an intensification of phase formation processes, which is accompanied by the coarsening of grains, and the concentration of fine inclusions decreases. For samples with a single-phase structure obtained at a concentration of 0.6 M $Al_2O_3$, the formation of a compact structure with well-formed grains, densely packed into a single structure, is observed. With an increase in the concentration of aluminum oxide to 0.75 M and above, the structure of the ceramics becomes non-uniform, which is due to the formation of an aluminum-enriched phase, the presence of which in the composition leads to the formation of microcracks associated with the formation of local stresses. In this case, the dominance of aluminum-enriched phase $LiAl_5O_8$ in the composition of ceramics, at a concentration of 0.9 M $Al_2O_3$, the morphology of ceramics is characterized by looseness, with clearly expressed inclusions of irregularly shaped agglomerates and micropores, the presence of which indicates the formation of a glass-phase component in the structure. The obtained results of the morphological and structural features of lithium-containing ceramics were summarized in a diagram of the ceramic formation processes, shown in Figure 3.

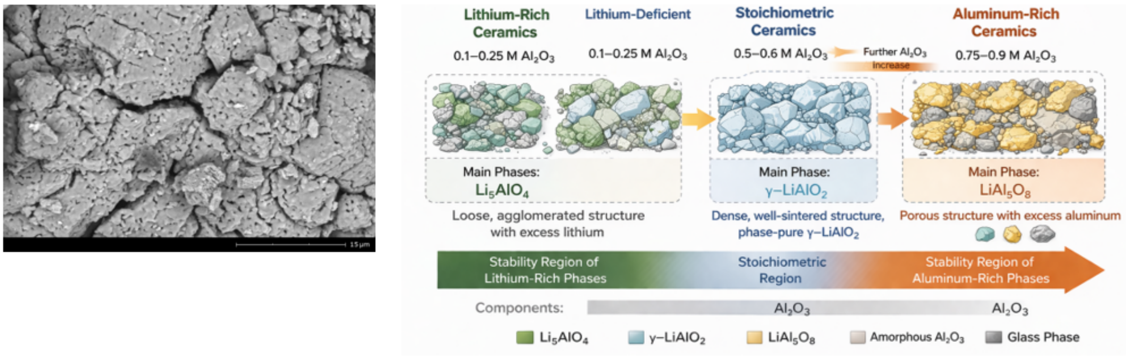
Figure 4 shows the optical absorption spectra of lithium-containing ceramics depending on the variation in the ratio of components in the composition, changes in which, according to X-ray phase analysis data, lead to variations in the phase composition of the ceramics. According to the data obtained, the formation of intense absorption bands characteristic of electronic transitions in oxide ceramics is observed in the optical spectra in the short-wavelength region of the spectrum. Moreover, the highest intensity of the bands is observed for samples with a low content of aluminum oxide, which are characterized by the formation of two-phase ceramics, including the $\gamma$-$LiAlO_2$ phase and the lithium-enriched $Li_5AlO_4$ phase. Comparing the results of changes in the phase ratio shown in Figure 2b with the results of changes in the intensities of the absorption bands characteristic of electronic transitions, one can conclude that there is a direct relationship between the intensity of the absorption bands and the content of the $Li_5AlO_4$ phase in the composition, a decrease in which, due to the structural ordering of $\gamma$–$LiAlO_2$ with an increase in the concentration of $Al_2O_3$ in the composition, leads to a decrease in the absorption bands, and, as a consequence,



0.1 $Al_2O_3$ 0.25 $Al_2O_3$ 0.4 $Al_2O_3$



0.5 $Al_2O_3$ 0.6 $Al_2O_3$ 0.75 $Al_2O_3$



0.9 $Al_2O_3$ Scheme of ceramic production

Figure 3. Results of evaluation of morphological features of synthesized lithium-containing ceramics.

a decrease in the density of localized states in the band gap and a decrease in defects. The observed smoothing of spectral features for samples containing 0.4–0.6 M $Al_2O_3$ in the composition is due to a change in structural ordering and, as a consequence, a decrease in the density of defective inclusions in the composition of ceramics. Moreover, the analysis of the obtained spectral dependences showed that in the case of single-phase lithium-containing ceramics, the reduction of absorption bands in the near UV region indicates a minimal content of structural defects, and the results themselves are a direct confirmation of the data on the degree of structural ordering obtained from the analysis of X-ray diffraction patterns. An increase in the concentration of aluminum oxide to 0.75–0.9 M leads to an increase in the intensity of absorption bands in the region of 250–350 nm, which are associated with the formation of an aluminum-enriched phase $LiAl_5O_8$ phase, as well as structural defects associated with the presence of glass-phase inclusions and amorphous-like aluminum oxide in the form of residual forms that did not react during the sintering process. The observed increase in absorption is due to an increase in the concentration of structural defects, microdeformations and interphase boundaries, which create additional localized energy levels in the band gap. Also, in the case of samples containing the $LiAl_5O_8$ phase, a shift in the fundamental absorption edge to the long-wavelength region is observed, which indicates a decrease in the band gap width due to an increase in the defect fraction and the presence of glass phases, the formation of which is associated with an excess of aluminum oxide, which leads to an increase in background absorption due to disordering of the crystalline structure.

Based on the absorption spectra, one can conclude that there is a qualitative change in the concentration of defect states associated with oxygen vacancies. The most pronounced absorption in the region of the fundamental absorption edge and the enhancement of the defect tail are observed for samples with a low $Al_2O_3$ content, as well as for aluminum-rich compositions, which indicates an increased concentration of oxygen vacancies. The minimum defectiveness is characteristic of samples with a composition of 0.5–0.6 M $Al_2O_3$, which is consistent with the formation of a predominantly single-phase $\gamma$-$LiAlO_2$ structure.

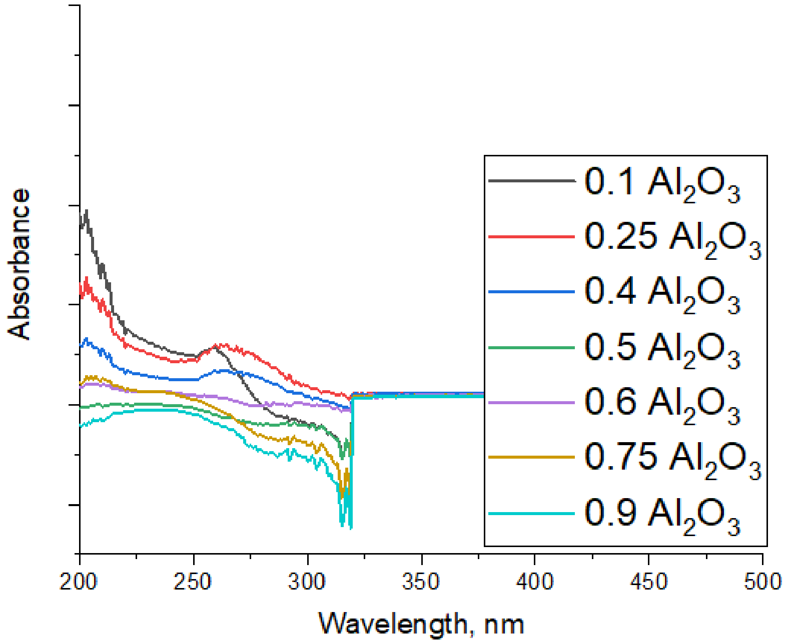
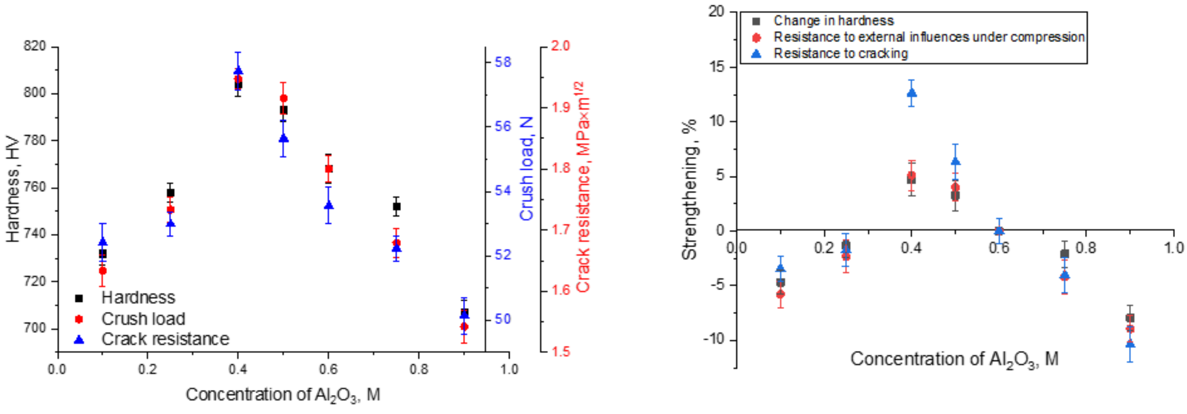


Figure 4. Results of optical absorption spectra of the studied ceramics with variations in the ratio of components in the composition.

One of the key and important factors determining the potential applicability of ceramics as structural or functional materials is their mechanical properties, which determine the stability and resistance of ceramics to external influences during their operation. It is well known that the mechanical properties of ceramics are directly related to changes in microstructural features, phase composition and defect concentration. Moreover, unlike metals, ceramics are more brittle under mechanical influences, which makes monitoring their strength properties one of the most important technological processes in their manufacture. Moreover, the phase composition features play a major role in determination of the mechanical characteristics of ceramics, including the boundary effects they create and interphase boundaries, which can play a dual role: in one case, they act as barriers to restrain destabilization under external loads, and in the other, they serve as activation centers for the propagation of microcracks due to structural heterogeneities or amorphous inclusions.

Figure 5a shows the results of the assessment of hardness, the value of the critical load under single compression and crack resistance of the studied ceramics depending on the variation in the ratio of components in the composition. The general trend of changes observed on the graph indicates a direct correlation between phase changes associated with the processes of formation of lithium- or aluminum-enriched inclusions in the structure and changes in the mechanical properties of ceramics. Moreover, the observed trend has a clearly expressed nonlinear dependence on the composition of the ceramics, caused not only by variations in the phase composition, but also by morphological features, the results of which are shown in Figure 3. According to the data obtained, an increase in the content of the $\gamma$–LiAlO$_2$ phase in the composition of ceramics leads to an increase in mechanical properties and an increase in resistance to cracking under external loads. Moreover, in the case of single-phase $\gamma$–LiAlO$_2$ ceramics, the values of mechanical characteristics are somewhat lower than in the case where the ceramics contain inclusions in the form of a lithium-enriched phase $Li_5AlO_4$, the weight contribution of which is no more than 14–20 wt.%. In this case, the dispersion strengthening mechanism, in which finely dispersed inclusions of the secondary phase are uniformly distributed in the $\gamma$–LiAlO$_2$ matrix and prevent the propagation of cracks, is implemented. Such inclusions act as restraining barriers, causing a deviation in the trajectory of crack propagation, their branching and partial inhibition of growth, which in turn leads to an increase in the fracture energy and, as a consequence, an increase in the crack resistance of ceramics. It should also be noted that with a low content of $Li_5AlO_4$ inclusions, the formed grain boundaries lead to the restraint of external mechanical influences due to differences in the crystal lattices, which create local microdeformations that prevent the propagation of cracks, increasing stability due to internal stresses.

In the case where the aluminum-rich phase $LiAl_5O_8$ begins to dominate in the composition of ceramics, the observed decrease in mechanical properties is associated with several destabilizing factors. First of all, the formation of this phase is accompanied by the emergence of a significant number of interphase boundaries with reduced strength and the presence of microcracks in the composition, on which stresses are concentrated. In addition, the difference in the structural features and lattice parameters of the $\gamma$–LiAlO$_2$ and $LiAl_5O_8$ phases leads to the accumulation of microdeformations and residual stresses that contribute to the initiation of microcracks. Also, the presence of amorphous inclusions and glass phases in the composition of ceramics with an excess of $Al_2O_3$ leads to a weakening of intergranular adhesion, which leads to a decrease in strength and crack resistance, as well as facilitation of the mechanisms of crack propagation along intergranular boundaries. In turn, the increase in porosity (see the data presented in Figure 3) and structural heterogeneity with the dominance of the $LiAl_5O_8$ phase in the composition enhances the effect of stress concentration, which leads to a decrease in resistance to external loads, which is clearly manifested in the results of changes in the critical loads that ceramics can withstand under single compression. In this case, during the formation of two-phase ceramics in which aluminum-enriched phase $LiAl_5O_8$ dominates, the strengthening mechanisms are suppressed by the softening mechanisms caused by the increase in defects and phase heterogeneity of the composition.



a) b)

Figure 5. a) Results of the assessment of changes in the mechanical properties of the studied ceramics depending on the variation of components in the composition; b) Results of the assessment of changes in the strengthening factors of ceramics depending on the ratio of components in the composition.

Figure 5b shows the assessment results of the strengthening factors of the studied ceramics depending on the variation in the ratio of components in the composition. In this case, single-phase ceramics $\gamma$–$LiAlO_2$, obtained by mixing of 0.4 M $Li_2CO_3$ and 0.6 M $Al_2O_3$, was chosen as a comparison sample. The choice of this ratio for comparison of strengthening factors is due to the possibility of identification of the role of phase changes associated with the formation of lithium- or aluminum-enriched phases in the structure, the appearance of which in the composition leads to the emergence of interphase boundaries, the presence of which can act as barriers that increase resistance to external mechanical loads. According to the presented results of the assessment of strengthening factors, in the case of two-phase ceramics containing a low concentration of lithium-enriched phase $Li_5AlO_4$ in the composition (no more than 20 wt.%), the increase in strength characteristics relative to single-phase ceramics is about 5–10%, while the dominance of aluminum-enriched phase $LiAl_5O_8$ in the composition leads to destabilization of mechanical properties and their softening by more than 3–10% relative to single-phase ceramics. Analysis of the results obtained showed that the maximum contribution of strengthening factors is realized in a narrow range of compositions (about 0.4–0.5 M $Al_2O_3$), where the optimal balance between phase composition and microstructure is achieved. Deviation from this composition, either towards excess lithium or aluminum, leads to a decrease in the efficiency of strengthening mechanisms and a transition to the dominance of softening processes.

The strengthening effect associated with size factors was taken into account when analyzing the strength properties of the studied ceramics. It should be noted that the mechanochemical synthesis method promotes the formation of a finely dispersed and fairly uniform microstructure, which directly impacts the mechanical properties of the material. A reduction in grain size and a more uniform distribution of phases within the sample lead to increased resistance to crack propagation and prevent stress localization.

Furthermore, changes in phase composition were accompanied by variations in crystallite size and phase morphology, which also impacted the strength properties. In particular, samples with a finer and more uniform structure demonstrated increased strength, which may be due to the Hall–Petch strengthening mechanism, in which a reduction in grain size increases resistance to deformation and fracture.

The data obtained revealed that the lack of a clear correlation between strength and phase ratio indicates that the system under study employs a combined strengthening mechanism, in which strength properties are determined by the combined effects of phase composition, structural dispersion, grain size, and phase distribution within the ceramic. To more accurately separate the contributions of phase and size factors, additional quantitative analysis of microstructural parameters is necessary, including an assessment of the average grain size, interphase boundary density, and the degree of structural defects.

# Conclusion

The results of the analysis of phase transformations with variations in the ratio of the $Li_2CO_3$ and $Al_2O_3$ components in the composition of lithium-containing ceramics based on lithium aluminate showed that in the case of an excess of $Li_2CO_3$ in the composition, the formation of two-phase ceramics consisting of a stable tetragonal $\gamma$–$LiAlO_2$ and orthorhombic $Li_5AlO_4$ phases occurs. The ratio of components 0.6 M $Li_2CO_3$ and 0.4 M $Al_2O_3$ is optimal for obtaining single-phase $LiAlO_2$ ceramics. In the case of the dominance of aluminum oxide in the mixture, the phase composition of the ceramics is represented by a mixture of two phases $\gamma$–$LiAlO_2$ and a cubic $LiAl_5O_8$ phase, the formation of which is also accompanied by the formation of inclusions in the form of glass phases, the presence of which is confirmed by a change in the degree of crystallinity and broadening of the diffraction reflections of the main phases.

The obtained results of optical absorption spectra showed a direct correlation between changes in the concentration of defective inclusions and changes in the phase composition of ceramics, caused by variations in the ratio of components in the composition. In the case of lithium-enriched phases in the composition of ceramics, the observed intense absorption bands are due to the high concentration of oxygen vacancies, while for aluminum-enriched ceramics, the change in the optical absorption bands is primarily due to the presence of glass phases and a defect fraction associated with an increase in structural disorder in the ceramics.

According to the assessment of the mechanical properties of ceramics, it was found that in the case of single-phase $\gamma$–$LiAlO_2$ ceramics, the values of hardness, resistance to external loads and crack resistance are significantly higher than in the case of two-phase ceramics in which lithium- or aluminum-enriched phases predominate. Moreover, the highest values of mechanical properties of ceramics are achieved for ceramics containing inclusions in the form of a lithium-enriched phase $Li_5AlO_4$, the weight contribution of which does not exceed

14–20 wt.%. In the case where the aluminum-enriched phase $LiAl_5O_8$ dominates in the composition of ceramics, the observed decrease in mechanical properties is associated with the destabilization of the structure due to the formation of amorphous inclusions, as well as glass phases, the presence of which enhances the effect of microdeformations.

Thus, it has been established that the key factor in controlling the properties of lithium-containing ceramics is the control of the $Li_2CO_3/Al_2O_3$ ratio, which determines the mechanisms of phase formation, the level of defects and the microstructure of the material. Optimal characteristics are achieved by forming predominantly single-phase $\gamma$–$LiAlO_2$ with a controlled content of secondary phases, which makes these ceramics promising for use in conditions of high temperatures and radiation loads, including as materials for blankets of thermonuclear reactors.

## Acknowledgement

This research was funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (No. AP23489285).

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