This study investigates spodumene glassy materials in the R_2O-RO-RO_2-R_2O_3-Li_2O-CaO-P_2O_5-SiO_2 system.

The task addressed is to obtain lightweight glassy materials with high microhardness and resistance to cracking, while maintaining a low apparent density and moderate energy consumption during manufacture. DTA/DSC, XRD, and optical microscopy were used to examine the structure and phase composition of samples obtained by one- and two-stage heat treatment.

Based on the research results, a series of compositions were developed; the structural characteristics of the glass matrix were determined for them. The resulting data show that the low-temperature two-stage heat treatment (nucleation at 530°C, crystallization at 850…900°C) contributes to the formation of a fine-grained structure, in which β-spodumene predominates (80…85 vol.%). Compared to the single-step process, HV and H increased by 9…20%, K_{1C} by 20…31%, and E by 25%. This effect can be explained by metastable micro liquefaction and early nucleation, leading to the formation of highly dense, fine-grained prismatic β-spodumene grains that inhibit crack propagation.

The choice of oxides and composition of nucleators (TiO_2, ZrO_2) is crucial. The introduction of fluorides and small amounts of rare-earth oxides reduces the melt viscosity and nucleation temperature. The addition of P_2O_5 promotes localized micro liquefaction of the fine-grained morphology of the target phase. These factors reconstruct the glassy phase and contribute to mechanical strengthening, distributing stresses more evenly within the finely dispersed crystalline matrix.

The practical significance of this study is that the obtained spodumene-containing composite materials have both high mechanical properties ($HV = 7.9…9.2$ GPa; $K_{1C} = 1.8…3.4$ MPa·$m^{0.5}$) and a reasonably low apparent density ($\rho = 2370…2450$ kg/m^3) compared to other protective materials. These materials are suitable for the manufacture of lightweight individual bulletproof composite components

Keywords: aluminosilicate glass-ceramic materials, armor element, impact resistance, wave propagation velocity, physical-mechanical properties

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DESIGNING AND DETERMINING THE PHYSICAL-CHEMICAL PROPERTIES OF LITHIUM ALUMINOSILICATE GLASS-CERAMIC MATERIALS FOR ARMOR PROTECTION

Sviatoslav Riabinin
Doctor of Philosophy (PhD)*
Artem Zakharov
PhD*
Mykyta Maistat
Corresponding author
Doctor of Philosophy (PhD)*
E-mail: aichemict777@gmail.com
Stanislav Lihezin
Doctor of Philosophy (PhD)*
*Department of Ceramic Technology, Refractories, Glass, and Enamels
National Technical University "Kharkiv Polytechnic Institute"
Kyrpychova str., 2, Kharkiv, Ukraine, 61002

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1. Introduction

Wars and armed conflicts of the 21st century are characterized by the widespread use of highly effective weapons – from modern small arms to cluster munitions and fragment munitions – resulting in an increasing ballistic threat to military personnel and civilians. Therefore, there is an urgent need to design new high-strength materials and multilayer structures for individual and platform armor protection to balance high ballistic performance, minimal weight, and acceptable manufacturability [1].

As a result, with the continuous evolution of weapons, we need new materials and structures to better balance "quality/protection/durability", improve resistance to multiple impacts, and balance reasonable manufacturability. However, practical application requires the development of formulations and technologies that allow the production of lightweight armor components with higher crack resistance, impact toughness, and resistance to multiple fractures, while reducing energy consumption in production and ensuring the scalability of the technology. Results of such research could help develop better and more effective modules for individual and platform protection.

The conventional scheme "hard ceramic layer + energy-absorbing substrate" (α-Al_2O_3, SiC, B_4C + UHMWPE/aramid) remains the main one as the ceramic can locally damage or deform and penetrate the element, while the substrate can absorb the rest of the energy. However, ceramic materials also have some disadvantages [2, 3]: high density, high cost, easy brittle fracture, and difficult processing (especially pure B_4C/SiC), which limits their tactical characteristics and economic feasibility. The physical and mechanical properties of the basic ceramic materials used for the manufacture of armor protection elements [4–8] are given in Table 1.

In this regard, glassy crystalline materials (GCMs), especially those based on lithium aluminosilicates (Li_2O-Al_2O_3-SiO_2), are of particular interest. GCMs have several important advantages, including controlled crystallization (the ability to

"design" the phase composition, morphology, and crystal size), relatively low density, and lower energy consumption during production compared to conventional engineering ceramics. All of these factors make them promising candidates for application in light armor components and multilayer local protection modules [9, 10].

Table 1

Physical and mechanical properties of ceramic materials for the manufacture of armor protection elements

Composition of ceramics	Apparent density ρ, kg/m^3	Modulus of elasticity E, GPa	Micro-hardness H_V, MPa	Longitudinal speed of sound ν, km/s	Crack resistance K_{1C}, MPa·m$^{1/2}$	Bending Strength σ_{bend}, MPa	Source of information
$A1_2O_3$	3950	407	18	10.4	3.5 ± 0.3	220 ± 20	[4]
B_4C	2400...2520	475	28	12.4	4.0 ± 0.3	350 ±2 0	[5]
SiC	3000	350 ± 20	20	10.5	3.2 ± 0.3	440 ± 20	[6]
TiB_2	4480...4510	550...565	25	11.0...11.3	6.2	270...400	[7]
AlN	3250	380...400	13	11.0	3.6	310...428	[8]

Given the growing threat of ballistics and the limitations of conventional ceramic solutions, research into glassy crystalline systems has become particularly relevant. Of particular interest are glassy spodumene materials, which combine high mechanical properties, moderate density, and low-energy manufacturing processes. Therefore, the design and optimization of glassy spodumene materials for armor protection is an important area of research.

2. Literature review and problem statement

In [9], transparent and opaque GSMs for ballistic protection are described. The main focus is on the relationship between microstructure and energy absorption characteristics. Studies have shown that fine-grained prismatic phases can improve the dissipation of impact energy. However, several important issues remain unresolved. In particular, the quantitative relationship between the formulation, phase composition, and dynamic properties of the material needs to be clarified. Also, the issue of reproducibility of ballistic tests between different laboratories remains unresolved. A separate difficulty is the scaling of laboratory regimes to pilot or industrial production. The reason is the multidimensionality of parameters, the high cost, and logistical limitations of ballistic tests and the influence of heat and mass transfer and batch geometry during scaling. A solution is to systematically map the parameter space in the laboratory to determine the kinetics of phase formation and selective bench ballistic tests to validate the most promising formulations. This approach is consistent with the combined DTA/DSC, XRD, and microscopy approach.

Work [10] reports real-time and temperature experiments of crystallization of LAS glass crystals. It demonstrates the influence of heating regimes on the nucleation stage and the growth of Li phases. A direct relationship between nucleation conditions and the grain size of the target phase is shown. However, whether these results can be generalized to industrial batch production with the addition of catalysts and fluoride additives remains an unresolved question. The reason is the differences in heat and mass transfer and batch quality. One possible solution is to combine real-time analysis with a controlled heating process on a pilot scale.

Study [11] demonstrated the controlled deposition of Li_2SiO_2 and related phases in the LAS system and highlighted the role of catalysts in shaping the morphology. The study showed that the right choice of nucleating agents can effectively solve the problem of excessive grain growth. However, the interaction between different catalysts in multioxide formulations remains unresolved. The influence of impurities (such as Mn, Ce, etc.) also needs to be studied. This is mainly due to the complexity of multidimensional experimental environments. One possible solution is to combine experiments with statistical experimental design (DoE).

In [12], the results of the structural evolution study of the P_2O_5-modified LAS framework at short and medium scales are reported. The study showed that P_2O_5 plays an important role in phase separation and local network recombination. This confirms that P_2O_5 can induce micro-dilution, thereby contributing to the formation of fine morphology of the target phase. However, quantitative data on the optimal concentration of P_2O_5 in multicomponent systems (especially in fluorine-containing compounds and rare-earth oxide systems) are still limited. The reason is that it is difficult to explain local structural changes, and it is necessary to combine different methods (NMR, XAS, HT-XRD). To overcome this problem, it is necessary to expand spectroscopic studies to achieve accurate quantitative correlation.

In [13], the kinetics of calcination of spodumene (α-phase) were studied and a detailed kinetic analysis of the thermodynamic transformation was performed. Parameters affecting the stability of α- and β-phases during heating were defined. However, due to the static nature of the calcination study (laboratory conditions), the formation of a fine-grained β-structure could not be explained. This was especially true for the two-stage calcination process in the presence of catalysts and fluorides. To address this issue, studies that combine decomposition/conversion kinetics with actual glass melts and their subsequent processing are needed.

Papers [14, 15] provide valuable data on spodumene GSMs. They give the formulations, manufacturing technology, and mechanical properties, including hardness K_{1C}. The practical implementation of β-spodumene matrices is shown. The problem is that some of the results are published in local journals and contain a limited number of modern analytical methods. Because of this, it is difficult to compare them with the data from current publications. This makes it necessary to re-check key formulations with state-of-the-art methods.

Study [16] establishes protection levels and test protocols for armored systems. It provides criteria (protection levels) to which it is useful to orient the development of materials for individual protection. The limitation is that the standard defines only external requirements. It does not give direct instructions on the phase composition and formulations. Because of this, there is a need to translate the properties of materials into ballistic results. For this purpose, an approach is needed that would establish such a translation "formulation – static properties – expected ballistic behavior".

Work [17] shows that P_2O_5 can induce early phase separation in Li-silicate systems and analyzes in detail the stages of nucleation. The publication provides important experimental evidence for the role of P_2O_5 in controlling morphology. An unresolved problem is the quantitative limit of P_2O_5 in

complex multicomponent formulations; at the same time, it is necessary to study the influence of compatible catalysts (TiO_2, ZrO_2). To solve this, it is necessary to systematically prepare a series of formulations combining P_2O_5 and catalysts, for further optimization of their concentration.

In [18], the effect of Al_2O_3 content on LAS glass crystallization was investigated. The results showed that higher Al_2O_3 content promotes β-phase formation but also increases the melting boiling point. This provides a practical basis for finding a "compromise" between optimal mechanical properties and process performance. One of the outstanding issues is minimizing energy consumption while maintaining a high β-phase content. One possible solution is the introduction of effective fluorides/modifiers or alternative catalysts to lower the boiling point.

Based on our review of published data, technically sound performance benchmarks for GSMs used in personal protective equipment were established:

– apparent density $\rho = 2350...2800$ kg/m^3;

– coefficient of linear thermal expansion $\alpha \approx (20...30) \times \times 10^{-7}$ K^{-1};

– modulus of elasticity $E = 250...350$ GPa;

– Vickers microhardness $H_V = 10...12$ GPa;

– crack resistance $K_{1C} = 8...12$ MPa·m$^{0.5}$;

– impact strength $KCU = 5...6$ kJ·m^{-2}.

These recommendations emphasize the need to adjust both composition and microstructure to achieve the target performance parameters.

This review confirms that the target microstructure is small prismatic grains of β-spodumene within the glassy phase. This is a feasible strategy that combines low density and high impact strength. The literature also indicates that the combined approach of "composition modification + catalyst/fluoride + two-stage heat treatment" is effective.

Meanwhile, the following key questions remain unresolved:

1. Quantitative limitations of additives. Currently, there is no systematic data on the optimal concentrations of P_2O, fluorides, and nucleating agents in multicomponent formulations that would achieve stable microphase formation and the desired β-phase ratio. This is due to the multidimensionality of the parameters and high experimental costs. One possible solution is to use a combined approach (experimental design + temperature/real-time studies + high-temperature X-ray diffraction) with subsequent pilot scale expansion.

2. Scalability of the process. Laboratory experiments using small samples should be verified in pilot or full-scale tests (heat and mass transfer, batch quality, product shape). The solution is to conduct pilot tests to switch control modes and monitor phase formation kinetics.

3. Comprehensive dynamic validation. Direct comparison of materials to STANAG/NIJ standards is difficult because of the lack of ballistic and high-velocity test data in the related literature. This is due to high costs, organizational and safety constraints. The solution is a validation plan that progresses in stages from static mechanical testing to limited bench-fire testing and then to large-scale ballistic testing.

Therefore, the concept of a finely dispersed β-spodumene matrix is relevant and promising. For practical application, systematic studies are needed that combine composition optimization (P_2O, fluorides, rare earth oxides), seed processing and crystallization at intermediate temperatures, as well as comprehensive testing of the final static and dynamic properties according to ballistic test criteria.

3. The aim and objectives of the study

The aim of this study is to investigate the influence of formulation and process parameters on the microstructure, physical and mechanical properties of Li-Al-Si-O glassy crystalline materials. This may contribute to improving the stability of armor protection by increasing the energy density and resistance to cracking of the hard layer while simultaneously reducing its mass, thereby laying the foundation for validation and application in the design of personal armor protection systems (PAPSs).

To achieve this aim, the following objectives were accomplished:

– to determine the comprehensive physical and mechanical properties (H_V, H, K_{1C}, E, ρ) of the obtained GSM and evaluate its suitability as an impact-resistant material;

– to compare and analyze the effect of one-stage and two-stage heat treatment on the mechanical properties of the material and the content of the β-phase;

– to establish a relationship between the formulation and process parameters, the phase composition determined from the data, and the obtained mechanical properties.

4. The study materials and methods

Our study focuses on spodumene glassy materials in the R_2O-RO-RO_2-R_2O_3-Li_2O-CaO-P_2O_5-SiO_2 system.

This study hypothesizes that precise control over the material formulation could be achieved by changing the matrix composition and introducing modifiers (nucleating agents, fluorides, and P_2O_5). This allows for the targeted formation of fine-dispersed microstructures based on β-spodumene. Such a structure is expected to improve the microhardness and crack resistance of the material while maintaining a low apparent density. And this, combined with a two-stage low-temperature heat treatment (nucleation-crystallization), further contributes to the formation of a homogeneous and fine-dispersed microstructure of β-spodumene.

Assumptions adopted:

– the charge is considered chemically homogeneous after mixing and melting;

– laboratory regimes reproduce the main thermodynamic stages of nucleation and growth relevant for scaling;

– the effect of devaporization of volatile components is considered to be controlled provided that mass losses during melting are fixed.

The accepted simplifications are as follows:

– analysis is performed for the average composition of the charge; local chemical gradients are not modeled;

– thermomechanical gradients in massive products are taken into account indirectly and are subject to evaluation during scaling;

– nucleation/growth kinetics are represented by effective parameters derived from DTA/DSC.

The design of model compositions for obtaining impact-resistant spodumene-containing GSMs was carried out using predictive calculations of a complex of structure-sensitive coefficients. These coefficients are used as criteria that determine the structural features and crystallinity of glasses [19, 20]. These include crystallinity coefficient (K_{cr}), transparency coefficient (K_t), cohesion coefficient of the silicon-oxygen framework of the glass (f_{Si}), and the coefficient of the coordination state of B and Al atoms in their simultaneous presence (ψ_B).

To prepare the charge, natural mineral raw materials (Novoselivskyi sand, zircon), technical products (alumina, calcium carbonate, boric acid, strontium carbonate, disubstituted ammonium phosphate), and chemically pure oxides (ZnO, TiO_2, CeO_2, MgO) were used.

Glass melting was carried out in corundum crucibles in a laboratory silite electric furnace at temperatures of 1250...1450°C for 6 h with subsequent pouring onto a metal plate. GSM was obtained using ceramic technology. Glass grinding was carried out in a laboratory ball mill until it completely passed through sieve No. 0063.

Heat treatment of the samples was carried out in a SNOL muffle electric furnace. The selection of heat treatment modes was carried out on the basis of DTA/DSC analysis, the results of which are reported in [21]. The devised scientific provisions are given in [14, 15, 21–23]. To adopt practical modes, the following were taken into account: the position and intensity of the exothermic peaks of DTA/DSC, the temperature intervals with the highest probability of nucleation and crystal growth, as well as the technical limitations of laboratory furnaces. As a result of the analysis, two applied modes were selected for experimental verification:

– one-stage annealing at a temperature of 450...950°C with a holding time of 6 h;

– two-stage cycle: nucleation at a temperature of 530°C with a holding time of 4 h, and crystallization at a temperature of 850...900°C with a holding time of 4 h.

To ensure high particle packing density, the size of the fractions and their ratio were selected taking into account data from [22], namely with a fraction size of 63...125 μm ≈ 70 vol. %, 63...25 μm – 15 vol. %, less than 25 μm – 15 vol. %. Pressing of the samples was performed on a laboratory hydraulic press in three stages (1st stage – 7.36 MPa, 2nd stage – 11.78 MPa, 3rd stage – 14.71 MPa). The molded samples were subjected to heat treatment under a two-stage regime: stage I – Tmax = 780°C; τ = 5.0 h; stage II – Tmax = 1050°C, τ = 0.5 h.

The phase composition of GSM samples was investigated by X-ray diffraction using a DRON-3M diffractometer. X-ray diffraction allows for qualitative and quantitative determination of the phase composition based on the position and intensity of diffraction peaks. The DRON-3M is a laboratory powder diffractometer operating under the θ-2θ scanning mode and was chosen for X-ray analysis because it offers sufficient resolution and stability of the measurement geometry. This ensures reliable phase identification and phase content estimation, usually with an accuracy of a few percentage points. The choice of scanning mode and measurement parameters fully takes into account the characteristics of both ceramic and glassy samples, which allows for accurate data collection for subsequent quantitative analysis.

Petrographic studies were performed using a NU-2E optical polarizing microscope. Petrography is used to visually assess crystal morphology, grain size, and the difference between crystalline and glassy phases using transmitted and polarized light. The NU-2E microscope is equipped with observation capabilities under light, dark, and polarized modes, allowing for phase-contrast observations and basic morphological measurements.

Flexural strength was measured according to the standard method ISO 23146:2012 [24], which involves the preparation of controlled specimens and the application of a four-point bending load to the rupture of the specimen with simultaneous recording of the load and deformation. These results were used to evaluate the flexural strength.

Impact toughness (KCU) was measured according to the standard method EN 1288-1:2000 [25]. This method measures the energy absorbed by the specimen during impact under standard conditions and is used to assess the susceptibility of a material to impact loading. The tests were performed on an impact test bench equipped with a standardized indenter and a fracture energy recording system.

Vickers microhardness was measured using a PMT-3 microhardness tester, conducting 10 indentation tests under a load of 200 g. This diamond indentation method allows for the assessment of local hardness and its distribution in the material. The PMT-3 optically measures the indentation diagonal and allows for precise load application.

Knupp hardness was measured using a TMV-1000 hardness tester in accordance with ASTM C730-98 (2021) [26]. The TMV-1000 is an electromechanical hardness tester with a calibrated load and a digital display.

The crack resistance index (K_{1C}) was calculated using the semi-empirical dependence by Niihara [27] based on the average value of H_V obtained from the results of 5 measurements on TMV-1000 at a load of 49 N. The Niihara method allows us to estimate the crack resistance based on microhardness and the correlation formula.

The elastic modulus of model glasses was determined by the method of the dependence of the deflection arrow of the thread pulled from the melt on the applied load. The method involves measuring the vertical deflection of the glass thread under calibrated loads using sensitive deflection sensors; from the obtained dependence, the elastic modulus is determined under the condition of elastic behavior of the material.

The Li_2O-Al_2O_3-SiO_2 system was chosen as the basis for designing spodumene GSMs (Fig. 1). There are 3 ternary compounds in the system: petalite $Li_2O{\cdot}Al_2O_3{\cdot}8SiO_2$, spodumene $Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ and eucryptite $Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$, which have low-temperature (α) and high-temperature (β) forms.

Petalite melts at 1370°C without decomposition and is characterized by a TCL = $3.0 \cdot 10^{-7}$, deg^{-1} at temperatures up to 1200°C. Spodumene melts congruently at 1423°C, at temperatures up to 1200°C it is characterized by a TCL = $9.0 \cdot 10^{-7}$, deg^{-1}.

Instead, low-temperature α-eucryptite at a temperature of 972 ± 10°C transforms into β-eucryptite, which is characterized by a large anisotropy of thermal expansion: from $-176 \cdot 10^{-7}$ deg^{-1} ($\parallel c$ axis) to $+82.1 \cdot 10^{-7}$ deg^{-1} ($\perp c$ axis).

The presence of low-temperature eutectics (at 980°C between spodumene, lithium disilicate, and SiO_2, as well as at 985°C between lithium disilicate, lithium metasilicate, and spodumene) indicates the possibility of synthesizing GSM under energy-saving heat treatment conditions.

The probability of low-temperature crystallization of metastable crystalline phases capable of recrystallization with the formation of a volumetric fine-crystalline structure of GSMs, the target phase of which is thermodynamically stable β-spodumene, was investigated. It is this microstructure and single-crystal phase composition, represented by β-$LiAlSi_2O_6$, that should provide the necessary functional properties of impact-resistant GSMs.

Basic lithium aluminosilicate glasses were modified by introducing ZnO, SrO, MgO, CaO oxides to reduce the viscosity of the melt during glass melting, increase strength and microhardness, and also regulate the thermal expansion of the glass phase. Oxides B_2O_3, K_2O, Na_2O were introduced to reduce the density of the glasses, as well as reduce the melting and heat treatment temperatures. In addition, titani-

um and zirconium dioxides ($\Sigma TiO_2 + ZrO_2 \leq 8.0$ wt. %) and manganese, tin, and cerium oxides $MnO_2 \leq 4.0$; $CeO_2 \leq 0.5$ were introduced into the glass composition as crystallization catalysts. In particular, the introduction of CeO_2 should promote nucleation at lower temperatures, which will make it possible to reduce the temperature and duration of holding in the second stage while maintaining the phase composition and high degree of crystallization of sital.

To form a fine-crystalline structure by the liquefaction mechanism, P_2O_5 was also introduced into the composition of the initial glasses in an amount of 2.0–3.0 wt. %, which would make it possible to reduce the stresses that arise when the impact energy is absorbed by the protective element [8]. As is known, finely dispersed metastable liquefaction of glass (the so-called "micro liquefaction") occurs under conditions of increased melt viscosity. This causes slow growth of crystals that form in areas of the phase concentrated inside the drops, which contributes to the formation of a fine-dispersed crystalline structure of GSM.

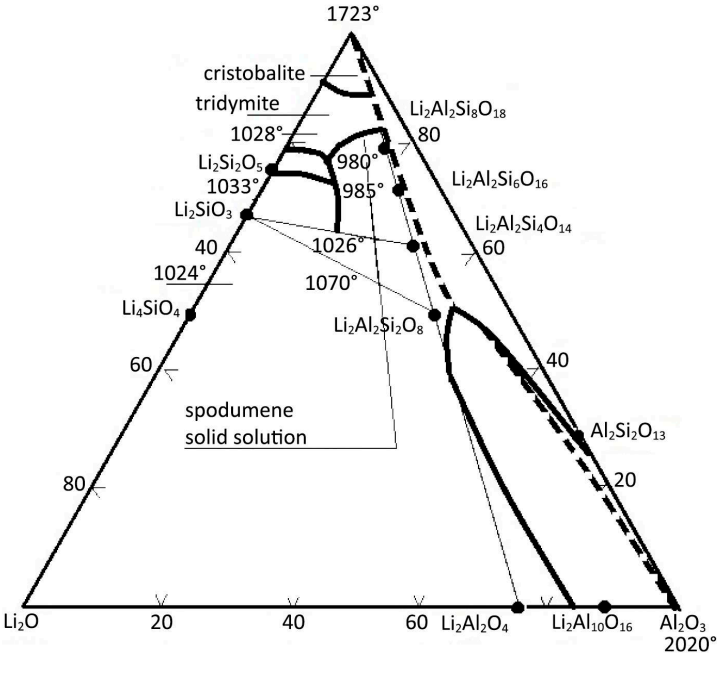

Fig. 1. Li_2O-Al_2O_3-SiO_2 system state diagram [28]

Therefore, the content of oxides in the composition of model glasses was limited by the following concentrations of components, wt. %: Σ (Na_2O, K_2O, Li_2O) – 6.0...13.5; LiF – 0.0...6.5; Σ (CaO, MgO, ZnO) – 0.0...9.5; CaF_2 – 0.0...15.0; Σ (Al_2O_3, B_2O_3) – 10.0...39.0; Σ (TiO_2, ZrO_2) – 0.0...8.0; P_2O_5 – 0.0...3.09; SiO_2 – 37.3...65.8; MnO_2 – 0.0...2.49; CeO_2 – 0.0...0.51. The chemical composition of the model glasses is given in Table 2.

An important stage in the design of GSMs with a microcrystalline structure and a given phase composition is a predictive analysis of the structural features and crystallization ability of selected model glasses. In this case, the design of GSM compositions was based on theoretical ideas about the structure of glass melts. Special attention was paid to their structural strength. Signs of the presence of polymerized silica-oxygen anions and cybotaxic groups were also taken into account. They correspond in stoichiometry to the composition of the target compounds (silicates, aluminosilicates, etc.).

Table 2

Chemical composition of model glasses for the synthesis of spodumene GSMs

Model glass components	Content, wt. %									
	SP-1	SP-2	SP-3	SP-4	SP-5	SP-6	SP-7	SP-8	SP-9	SP-10
SiO_2	64.00	65.80	37.30	39.90	60.00	60.00	55.00	60.30	59.70	61.86
Li_2O	6.00	11.00	0.00	0.00	10.00	10.00	7.00	10.05	7.96	7.22
LiF	0.00	0.00	5.20	6.50	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	10.00	10.50	31.60	33.83	12.80	11.00	11.00	15.07	19.90	18.56
B_2O_3	0.00	0.00	7.40	0.00	1.20	5.00	8.00	2.01	1.49	1.55
Na_2O+K_2O	0.00	2.20	9.80	10.47	3.50	3.50	3.50	0.00	0.00	0.00
CaO+MgO+ZnO	0.00	0.50	8.70	9.30	6.50	6.00	9.50	7.04	4.98	4.12
CaF_2	15.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.01	2.49	0.00
TiO_2+ZrO_2	5.00	8.00	0.00	0.00	3.00	2.00	3.00	0.00	0.00	3.09
SnO_2	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
CeO_2	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.50	0.49	0.51
P_2O_5	0.00	2.00	0.00	0.00	2.00	2.00	3.00	3.02	2.99	3.09

It was previously established [19] that to obtain GSMs, it is necessary that the structure coefficients meet the following requirements:

1) $K_{cr} \geq 3.5$ indicates that the total content of oxide modifiers in the melt is sufficient for the formation of structurally formed cybotaxic groups, which are the nuclei of the future crystalline phase;

2) $K_t \geq 2.1$ indicates favorable conditions for nucleation during cooling and subsequent crystal growth during subsequent heat treatment;

3) $f_{Si} = 0.20...0.35$: high structural strength, which is an important factor in obtaining impact-resistant glass-crystalline materials;

4) $\Psi_B \leq 0.333$ indicates the presence of [BO_3] and [AlO_4] groups in the melt, which indicates the tendency of glasses to liquation separation due to depolymerization of silicon of the oxygen framework of the glass in the presence of three coordinated boron.

Calculation of these indicators showed that the designed glass compositions are characterized by a high tendency to crystallization (Table 3).

Table 3

Results for SP series glasses

Glass ID	Structure-sensitive coefficients				
	K_t	K_{cr}	Ψ_B	Ψ_{Al}	f_{Si}
SP-1	2.66	16.88	–	5.1	0.29
SP-2	2.32	16.95	–	2.67	0.35
SP-3	1.92	2.40	0.031	0.51	0.22
SP-4	2.00	3.70	–	0.51	0.25
SP-5	2.68	9.84	27.69	4.23	0.28
SP-6	2.62	6.67	6.94	4.96	0.27
SP-7	2.44	4.48	3.68	4.09	0.26
SP-8	2.64	7.08	14.4	4.07	0.27
SP-9	2.42	6.57	11.14	2.38	0.28
SP-10	2.53	8.5	5.5	1.7	0.20

Analysis of the results of predicting the structure of model glasses [19] revealed that all experimental compositions are likely to have a sufficiently high structural strength ($f_{Si} = 0.25...0.35$), which is important for obtaining impact-resistant GSMs. The lowest f_{Si} index is for compositions SP-3, SP-4. For most glasses, the values of their structure-sensitive coefficients correspond to the above criteria: $K_t = 2.32...2.68$; $K_{cr} = 3.70...16.95$, which indicates the possibility of obtaining GSMs based on them. The exception is the composition SP-3, which does not correspond to any of the specified criteria, and the value $0 < \Psi_B < 0.333$ indicates a three-coordinated state B, which may indicate a reduced structural strength of glasses.

5. Results of material studies for spodumene glass-crystalline materials

5. 1. Determining the physical and mechanical properties of resulting glass-crystalline materials

For all obtained samples, a set of physical and mechanical parameters was measured, characterizing their suitability as impact-resistant materials: Knupp hardness (H), Vickers microhardness (H_V), crack resistance (K_{1C}), elastic modulus (E), and apparent density (ρ).

The results of our studies are given in Table 4.

Table 4

Physical-mechanical properties of resulting GSMs

Sample ID	Knupp hardness H, GPa	Vickers microhardness H_V, GPa	Crack resistance K_{1C}, MPa·m^{0,5}	Elastic modulus E, GP	Apparent density ρ, kg/m^3
SP-1	5.840	5.750	2.4	75.6	2390
SP-2	5.900	5.780	2.5	76.0	2400
SP-3	5.700	5.670	2.3	74.4	2430
SP-4	5.780	5.750	2.3	75.0	2450
SP-5	5.360	5.300	1.8	73.5	2370
SP-6	5.450	5.350	1.8	72.4	2370
SP-7	5.500	5.400	1.9	74.0	2375
SP-8	5.550	5.520	2.0	74.2	2380
SP-9	5.600	5.500	2.0	75.0	2385
SP-10	5.650	5.700	2.4	77.0	2410

Values for SP series:
– $H \approx 5.36...5.90$ GPa;
– $H_V \approx 5.30...5.78$ GPa;
– $K_{1C} \approx 1.8...2.5$ MPa·m^{0,5};
– $E \approx 72.4...77$ GPa;
– $\rho \approx 2370...2450$ kg/m^3.

5. 2. Comparative analysis of the impact of one-stage and two-stage heat treatment

To determine the feasibility of two-stage heat treatment of GSMs, a comparative analysis of the mechanical properties of samples obtained using both one-stage and two-stage heat treatment was carried out (Table 5).

Table 5

Comparative characteristics of mechanical properties of samples of glass-crystalline materials obtained under different heat treatment conditions

Sample ID	Knupp hardness H, MPa	Vickers microhardness H_V, MPa	Crack resistance K_{1C}, MPa·m$^{0.5}$	Elastic modulus E, GP
Samples obtained by single-stage heat treatment				
SP-2	6950	6900	2.5	78.0
SP-6	7350	7240	2.2	76.0
SP-9	7890	7740	2.6	80.0
SP-10	–	–	–	–
Samples obtained by two-stage heat treatment				
SP-2	8330	8280	3.0	80.0
SP-6	8590	7900	2.4	85.0
SP-9	9084	8667	3.4	100.0
SP-10	9630	9200	3.5	320.0

As can be seen from Table 5, samples after two-stage heat treatment demonstrate higher H, H_V, K_{1C} and E values compared to the corresponding samples after one-stage heat treatment.

5. 3. Establishing the relationship between the formulation and technological parameters and the phase composition

The recommended technological parameters for obtaining spodumene GSMs and information on the content of crystalline new formations according to the results of X-ray phase analysis are given in Table 6.

Table 6

Formulation-technological parameters and phase composition of resulting GSMs

Sample ID	Phase-forming components, wt. %			Crystallization catalysts	Temperature, °C		Crystalline phases present according to X-ray diffraction results	
	Li_2O (LiF_2*)	Al_2O_3	SiO_2		Glass boiling	GSM heat treatment	After boiling	After heat treatment
SP-1	11.0	10.5	65.8	ZnO, ZrO_2, P_2O_5	1400	1 stage – 530; 2 stage – 900	Li_2SiO_3	β-$LiAlSi_2O_6$
SP-2	6.0	10.0	64.0	TiO_2, ZrO_2, CaF_2	1400			β-$LiAlSi_2O_6$
SP-3	5.2*	31.6	37.3	–	1550	1 stage – 530; 2 stage – 850	–	CaF_2
SP-4	5.65*	34.15	40.25	–	1600			$NaAlSiO_4$, CaF_2
SP-5	10.0	12.8	60.0	TiO_2, ZrO_2, SnO_2, P_2O_5	1450	1 stage – 530; 2 stage – 850		β-$LiAlSi_2O_6$
SP-6	10.0	11.0	60.0	TiO_2, ZrO_2, P_2O_5	1450			β-$LiAlSi_2O_6$
SP-7	7.0	11.0	55.0	TiO_2, ZrO_2, P_2O_5	1400			β-$LiAlSi_2O_6$
SP-8	10.0	15.0	60.0	ZnO, P_2O_5, CeO_2, MnO_2	1400	1 stage – 530; 2 stage – 850		$Li_{0,6}Al_{0,6}Si_{2,4}O_6$, Li_2MgSiO_4
SP-9	8.0	20.0	60.0	MnO_2, P_2O_5, CeO_2	1400			β-$LiAlSi_2O_6$ (80 wt. %)
SP-10	7.0	18.0	60.0	MnO_2, P_2O_5, CeO_2	1400			β-$LiAlSi_2O_6$ (85 wt. %)

According to Table 6, for the SP series, different $Li_2O/Al_2O_3/SiO_2$ ratios and catalysts (TiO_2, ZrO_2, ZnO, MnO_2, P_2O, etc.) were used as phase-forming components. After heat treatment under a low-temperature two-stage mode, the presence of β-$LiAlSi_2O_6$ as one of the main crystalline phases was recorded in samples SP-1, SP-2, SP-5–SP-7, SP-9–SP-10.

6. Discussion of the results of investigating the possibility of using spodumene glass-crystal materials for individual body armor

Our experimental data allow for a comprehensive assessment of the suitability of the designed model glasses as matrices for the synthesis of impact-resistant GSMs for individual body armor elements. The results (Tables 4–6) show that the material has a relatively low apparent density (2370...2450 kg/m^3) and excellent mechanical properties, which makes it a promising candidate for the manufacture of lightweight armor elements [9, 14].

These results can be explained as follows:

1. Low-temperature two-stage heat treatment (nucleation temperature = 500...550°C, crystal growth temperature = 850...900°C) gives high-density nuclei at the nucleation stage and ensures controlled growth of β-spodumene at the crystallization stage [10, 11], which is confirmed by X-ray diffraction and microstructure analysis (Table 6).

2. In the first stage, an intermediate lithium silicate phase (e.g., Li_2SiO_3) is formed, which forms a network of nuclei in the glassy phase and reduces the local strain concentration under the influence of impact stress [14].

3. In the second stage, the mesophase transforms into β-spodumene, forming elongated columnar crystals, which inhibits crack propagation and increases the fracture energy [11, 17].

4. The addition of nucleating agents (TiO_2, ZrO_2) can increase the nucleation density, and fluoride and P_2O_5 can cause localized micro-dilution and promote fine crystallization [10, 17]. This is due to the increase in H_V, K_{1C} and E in the SP-1–SP-10 series (Tables 4–6).

Unlike conventional coarse-grained spodumene, which usually forms a massive, dense, and crack-resistant β-phase, controlled compounding and two-stage low-temperature heat treatment yield a well-dispersed β-spodumene matrix with a low apparent density (2370...2450 kg/m^3) and an excellent balance of hardness and crack resistance. Experimental data confirm this finding and are comparable to recent studies in the field of ballistic glass crystals and ceramics [4, 9].

The resulting formulation and process demonstrate that by precisely controlling the charge composition and two-stage low-temperature treatment, it is possible to simultaneously improve microhardness and crack resistance (K_{1C}) without significantly increasing density. This solves the key problem of obtaining lightweight materials with high mechanical strength for individual armor protection elements [10, 14].

The designed GSM is suitable as a hard ceramic layer in the multilayer structure of individual body armor (vest inserts, modular panels, helmet components), as well as a lightweight protective element for drones and mobile shields.

The implementation process must comply with controlled formulations (introduction of nucleating agents and fluorides according to dosage) and recommended thermal cycling; when integrated into silicate-polymer composites, it is necessary to ensure module compatibility and interlayer adhesion; formulations with an increased Al_2O_3 content require further optimization due to increased preparation temperatures and energy consumption.

The proportion of armor components is expected to decrease while maintaining or improving penetration efficiency; fracture toughness and crack propagation resistance are improved (due to the fine β-microstructure); the risk of secondary fracture during penetration is reduced; and product competitiveness is expected to improve due to optimized formulation and production control.

The results of our study confirm the feasibility of the "targeted formulation control + low-temperature two-stage heat treatment" method to obtain fine β-spodumene GSMs with improved mechanical properties and average density. At the same time, the study also points out key technical obstacles (temperature and production process) that need to be overcome in the process of large-scale production and industrial application.

The following are the main limitations of this study that must be taken into account when interpreting, reproducing, and applying the results in practice:

– the increased Al_2O_3 content requires higher batch cooking temperatures (up to 1550...1600°C), which increases the complexity of industrial production and energy consumption;

– the crystallization process is very sensitive to the concentration of catalysts and impurities, during large-scale production strict control of the composition is required;

– for multilayer silicate-polymer composites, an elastic modulus of GSM ≤ 100 GPa is recommended, otherwise the risk of localized stress concentration and delamination increases.

Our study has the following limitations:

– some formulations have high energy consumption and technical costs;

– strict control of process parameters, which complicates large-scale production.

Future research should focus on the following:

– optimization of the glass and raw material melting regime and lowering the melting temperature (testing alternative fluorides and modifiers);

– modeling the phase formation kinetics of the Li_2O-Al_2O_3-SiO_2 system and predicting the β-phase fraction and processing time;

– studying the adhesion and mechanical compatibility of GSM with polymer and metal substrates, as well as conducting ballistic tests according to STANAG/NIJ standards;

– development of alternative nucleating agents/catalysts that can lower the boiling point while maintaining mechanical properties.

7. Conclusions

1. We have measured the physical and mechanical properties of the spodumene GSM: hardness H = 5.36...5.90 GPa, Vickers hardness HV = 5.3...5.8 GPa, crack resistance K_{1C} = 1.8...2.4 MPa m$^{0.5}$, apparent density ρ = 2370...2450 kg/m^3, elastic modulus (E) = 72...77 GPa. The combination of high microhardness and moderate density leads to high specific strength, which makes it suitable for lightweight armor components. Unlike conventional high-density silicate materials, the resulting spodumene GSM retains excellent mechanical properties even at low mass. This property is explained by the finely dispersed β-phase matrix (presence of small columnar grains and a

glassy matrix), which improves local stiffness and prevents crack propagation.

2. Two-stage heat treatment significantly improves the mechanical properties of the material. Knupp hardness (H) and Vickers microhardness (H_V) increase by 9...20%, crack resistance (K_{1C}) increases by 20...31%, and elastic modulus (E) by approximately 25%. At the same time, increased hardness and crack resistance make the material stiffer and more resistant to crack propagation. Unlike simple heat treatment (which leads to grain coarsening and increased density), two-stage heat treatment avoids these negative effects and achieves higher mechanical properties. This is explained by the fact that it forms a finely dispersed β-phase structure with a smaller average grain size. Uniformly distributed small grains prevent crack propagation/bending at phase boundaries, concentrate stresses, and lengthen the crack propagation path, thereby increasing the K_{1C} and H_V values.

3. By introducing nucleating agents (TiO_2, ZrO_2), fluorides (CaF_2), and a small amount of rare earth oxides, as well as using a two-stage heat treatment (nucleation temperature 530°C, crystallization temperature 850...900°C), the target phase composition was formed. The following results were obtained under laboratory conditions: β-spodumene content 80...85 vol. %, $H = 8.3...9.6$ GPa, $H_V = 7.9...9.2$ GPa, $K_{1C} = 2.4...3.5$ MPa·m$^{0.5}$, $E = 80$ GPa, $\rho = 2370–2450$ kg/m^3. A high content of fine-grained β-phase was obtained at the appropriate temperature without a significant increase in apparent density. Unlike single-stage high-temperature processes, the proposed formulation combined with a two-stage cycle allowed us to achieve better mechanical properties without the formation of coarse grains or excessive increase in density. Metastable micro fluidization combined with strong early nucleation led to the formation of high-density fine-grained nuclei. In the second stage, their growth is limited due to mutual inhibition and a decrease in the viscosity of the material, which leads to the formation of a finely dispersed structure with high H_V and K_{1C} values. An increase in the Al_2O_3 content significantly increases the melting point and sensitivity to catalyst dosage, which complicates large-scale production; therefore, pilot/industrial production requires strict control over the formulation and process.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors acknowledge that the ChatGPT tool (OpenAI, model GPT-4o) was used during manuscript preparation. This tool was used exclusively for language editing (grammar, spelling, punctuation). No significant sections of the manuscript (Introduction, Materials and Methods, Results, Discussion, Conclusions) were generated or modified using AI. All AI-generated edits were reviewed and approved by the authors. The use of AI did not influence the conclusions of this study.

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