

LITHIUM-ALUMINOSILICATE CERAMIC MATERIALS WITH CLOSE TO ZERO THERMAL EXPANSION

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The article submits the outcomes of studies of the ceramic materials derived by slip casting method, based on the lithium aluminum silicate system, which includes, %¹: 2.5–12.5 Li₂O; 12.5–47.5 Al₂O₃; 50.0–80.0 SiO₂. Refractory clay «Keramic-Vesco», Proslanovsk kaolin, lithium carbonate, quartz sand and technical alumina were used as raw components. Specimen firing was executed under the temperature of (1100–1250)±10 °C with 1 hour exposure [1].

Ceramic materials with the following set of properties under the optimum firing temperature of 1200 °C were produced based on the studied mass compositions: shrinkage – 2.5–6.2 %, water absorption – 9.7–25.9 %, apparent density – 1480–2090 kg/m³, open porosity – 18–42 %, mechanical compressive strength – 36–65 MPa, thermal linear expansion coefficient (TLEC) – (minus 0.72– plus 4.21)·10⁻⁶ K⁻¹.

Outcomes of the study of the synthesized material thermal expansion in relation to the mass chemical composition and the burning temperature conditions enabled to establish the oxide ratio at which the thermal linear expansion coefficient values close to zero are reached. The specimens formed under the burning temperature of 1200 °C, with 7.5 and 10.0 % Li₂O content under the ratio of SiO₂/Al₂O₃ in the range of 1.2–2.4 and 1.6–2.0, respectively, are characterized with the lowest TLEC indicators. This is due to the maximum crystallization of lithium aluminum silicates which are characterized with the low thermal expansion. Heat resistance of the specimens related to the specified composition area pursuant to GOST 473.5–81 makes more than 100 thermal cycles (350–20) °C. When Li₂O content amounts to 12.5 %, the ceramic specimen TLEC values increase to 1.04·10⁻⁶ K⁻¹

¹ Hereinafter, the mass content is given.

under the burning temperature of 1200 °C, which is associated with the vitreous phase formation. Specimens with 2.5 % lithium oxide content which amount is not enough to form lithium aluminum silicates in significant volumes are characterized with the maximum TLEC parameters, and the excess of silicon and aluminum oxides is forwarded to crystalline phase formation with higher thermal expansion.

X-ray diffraction study established that the synthesized specimen crystalline component is represented with solid solutions of β -spodumene and β -eucryptite type, as well as the mullite, and lithium metasilicate (Fig. 1). Silicon oxide is present in α -quartz and β -cristobalite forms, alumina retains α -corundum original structure. When the specimen burning temperature increases from 1100 to 1200 °C, the ceramics qualitative composition does not undergo significant changes, but the crystalline phase quantitative content is changed which is confirmed by a change in the intensity of the relevant X-ray reflexes.

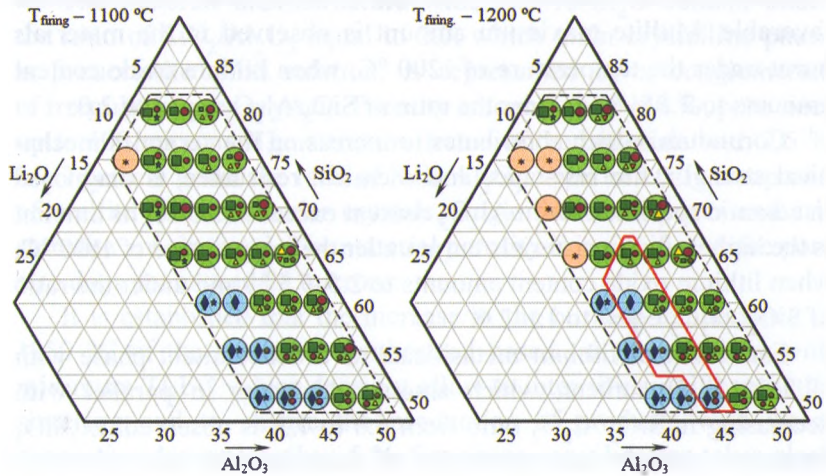


Fig. 1. Phase composition of synthesized ceramic materials: ■ – β -spodumene solid solutions; ◆ – β -eucryptite solid solutions; ▲ – mullite; ★ – lithium metasilicate; ⬠ – corundum; ▼ – cristobalite; ● – α -quartz; * – burned out; large icon – the main phase; small – concomitant; — — — area of compositions with maximum crystallization of lithium aluminosilicates

Formation of β -eucryptite solid solutions in the area with the Li_2O content of 7.5 % and of 10.0–12.5 % under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ oxides – 1.2 and 1.3–2.2, respectively, is established. β -spodumene solid solutions are crystallized in the rest studied area. Material heat treatment under the temperature of 1200 °C triggers more active crystallization of the specified lithium aluminum silicate phases.

Mullite and α -quartz are the basic crystalline phases when lithium oxide content amounts to 2.5 %. Reduction of SiO_2 content from 80 to 50 % triggers the decrease in α -quartz amount. Moreover, when SiO_2 content amounts to 6–8 % and under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the range of 1.3–2.2, β -cristobalite formation that adversely affects the ceramics thermal stability is observed.

Mullite formation in the specimen with 2.5–7.5 % Li_2O content is the general regularity in the cross section of the system under study. Mullite represents refractory high-density crystalline phase, it is characterized by significant mechanical strength and thermal resistance, which makes its presence in the synthesized materials favorable. Mullite maximum amount is observed in the materials burnt under the temperature of 1200 °C, when lithium oxide content amounts to 2.5 % and under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 2.0.

Corundum, which contributes to increasing the ceramics mechanical strength, fire resistance and chemical resistance, is diagnosed in ceramic specimen when Al_2O_3 content exceeds 32.5 %. Its amount is the highest in the materials burnt under the temperature of 1100 °C, when lithium oxide content amounts to 2.5–7.5 % and under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 1.1–2.0.

Formation of lithium metasilicate as a concomitant phase with 12.5 % Li_2O content, which amount decreases in parallel with decreasing in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 6.0 to 1.3, is observed. Li_2SiO_3 formation leads to sharp narrowing of mass sintering interval which results in specimen burnout. Calculation of the space unit parameters of the formed solid solutions was executed based on X-ray diffraction data. It is established that the chemical structure diagram of formed β -spodumene solid solutions corresponds to the following composition: $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3(4.0-5.4)\text{SiO}_2$; β -eucryptite solid solutions are

characterized by low SiO_2 content. Reduction of silicon oxide amount in mass chemical composition results in formation of β -spodumene and β -eucryptite solid solutions with a lower SiO_2 content.

The specimen micro-structure study enabled to establish the features of the sintering processes and to monitor the change in the crystalline formation morphology. It is established that the crystals take the form of a tetragonal dipyramids with the facet size up to 8 microns during formation of β -spodumene solid solutions from sufficiently mobile melt, which is typical for the materials burnt under the temperature of 1200 °C, with 7.5 % Li_2O content under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 6.3. Specimen porosity amounts to 30–35 %, pore size-up to 110 microns. Crystals of β -spodumene solid solution with 7.5 % Li_2O content and under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, amounting to 1.9, lose crystallographic distinct outlines and are represented in the form of grains without a clear facet. Inclusions of fibrous habitus are observed which is typical for mullite. The material structure gets bunched-up, there significant number of small-size pores.

The material microstructure with 10.0 % Li_2O content under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 2.0, which main crystalline phase is β -eucryptite solid solution, is represented by a conglomerate of irregular shaped crystals. Porosity amounts to 30–40 %, pore size-up to 100 microns. The structure frame of the materials with 2.5 % Li_2O content under the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 2.0, is composed of mullite fibrous-acicular crystals, single facets of quartz and cristobalite are observed. The material porosity is insignificant, the pore size does not exceed 25 microns.

It is established that the increase in the burning temperature to 1250 °C of the materials synthesized based on compositions with minimum TLEC values does not allow to intensify significantly the sintering and to ensure the production of products with water absorption degree less than 5 %. Specimen consolidation takes place due to small pore disappearance, but significant amount of voids with the size up to 30–60 microns remains, herewith the porosity amounts to 20–25 %. Temperature of the specimen heat treatment up to 1250 °C contributes to the gradual development of the phase formation processes. The amount of β -spodumene, β -eucryptite and mullite solid

solutions increase with a simultaneous decrease in corundum and α -quartz content, which is stipulated by more active interaction of silicon and aluminum oxides. This results in a change in the parameters of the formed solid solution space unit with an increase in the space unit volume, which is associated with a decrease in SiO_2 amount in its structure, and affects the synthesized material thermal expansion. Therefore, sharp decline to negative values (minus $(2.72\text{--}3.02)\cdot 10^{-6} \text{ K}^{-1}$ in TLEC indicators of ceramic materials based on β -eucryptite solid solutions is observed, which is typical for solid solutions, which are close in composition to the stoichiometric β -eucryptite.

On the contrary, a slight increase in TLEC from $(0.26\text{--}0.42)\cdot 10^{-6}$ to $(0.53\text{--}0.69)\cdot 10^{-6} \text{ K}^{-1}$ is observed in the specimens containing β -spodumene solid solutions as the main crystalline phase.

Comparative analysis of the synthesized material quality using the Harrington's generalized desirability function enabled to choose as the optimal one the compositions of the 21 and 31 masses for further modification aiming at activating the sintering processes. These compositions are characterized by the following properties at burning temperature of $1200 \text{ }^\circ\text{C}$: shrinkage 4.3–5.5 %, water absorption 18.7–22.4 %, apparent density 1524–1563 kg/m^3 , open porosity 29–35 %, TLEC $(0.26\text{--}0.39)\cdot 10^{-6} \text{ K}^{-1}$, mechanical compressive strength 50–55 MPa. The established range of compositions is limited to the content of oxides, %: 7.5 Li_2O ; 32.5–42.5 Al_2O_3 ; 50.0–65.0 SiO_2 .

Production of densely sintered ceramic materials with improved mechanical properties is intended based on β -spodumene (21 composition) and β -eucryptite (31 composition) matrix with additive application at maintaining TLEC values close to zero.

The paper also has studied the effect of the chalk of Vaukavysk, dolomite of the Ruba deposit, magnetite of the Satka, datolite concentrate, calcium borate, colemanite and apatite concentrate of the Oleniy Ruchey deposit additives which are introduced in the amount of 1–7 % on the sintering process of the elaborated materials related to the 21 and 31 compositions.

It is established that apatite concentrate and colemanite additives in the amount of 5 % decrease the temperature of liquid phase formation most actively due to low-melting eutectics, which is evidenced

by the shift of the temperature interval in the Differential Scanning Calorimetry curves corresponding to the specified process to the lower-temperature area by 30–45 °C [2]. At the same time they intensify the sintering process, which enables to reduce water absorption to 3.3–4.0 % under the specimen burning temperature of 1200 °C, to increase the mechanical strength under compression to 65–74 MPa, herewith TLEC indicators range from minus $0.66 \cdot 10^{-6}$ to plus $1.23 \cdot 10^{-6} \text{ K}^{-1}$ (Fig. 2). When certain additives are introduced in the amounts exceeding 5 % the specimens burnt under the temperature of 1200 °C demonstrate the burnout signs.

X-ray diffraction study of the materials modified with colemanite and apatite concentrate demonstrated that the basic crystalline phase that provides high temperature resistance to the specimen is represented by β -spodumene (21 composition) or β -eucryptite (31 composition)

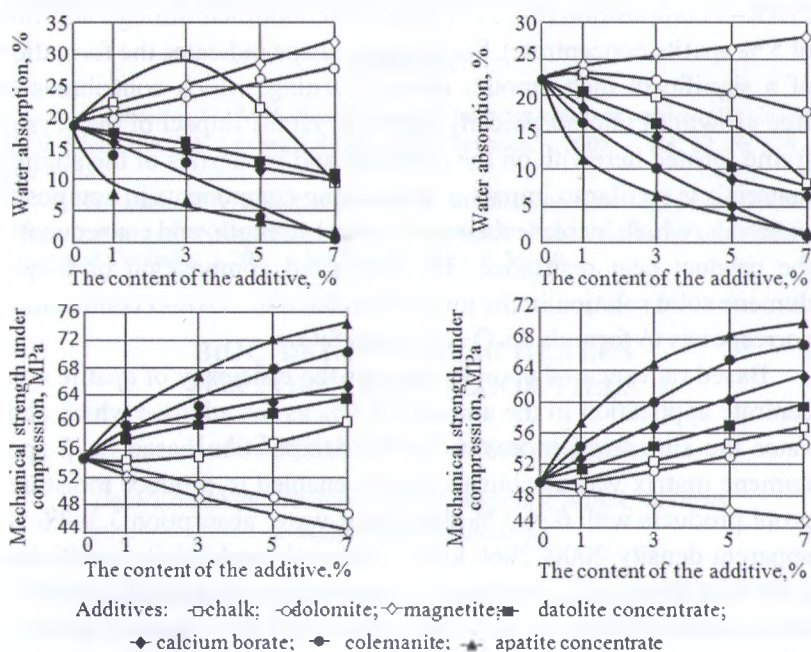


Fig. 2. Dependence of the physicochemical properties of the samples of compositions 21 (a) and 31 (b) on the content of the additive ($T_{\text{firing}} = 1200 \text{ }^\circ\text{C}$)

solid solutions, the number of which increases with an increase in the burning temperature from 1100 to 1200 °C. α -quartz, mullite and corundum are present as the concomitant phases. It was established that the introduction of 5 % of both colemanite and apatite concentrate resulted in the presence of pseudowollastonite, which amount is the maximum one in apatite-containing specimens under the synthesis temperature of 1200 °C. It was established that the addition of 5 % apatite concentrate most actively results in a decrease in the amount of α -quartz and it is not identified under the specimen firing temperature of 1200 °C.

Electron microscopic study has established that the apatite concentrate addition provides crystallization of the forming eutectic melt during cooling. Well-developed crystals of acicular habitus pseudowollastonite are observed in the structure of the material with 21AK-5 composition (the 21 composition, modified through addition of 5 % apatite concentrate). Such crystal shape indicates the formation of a significant melt amount during burning, which contributes to free growth of idiomorphically shaped crystals. Impact of the crystal frame formed herewith on the structure and properties of the studied materials is similar to impact of reinforcing components in composite materials, which increase their mechanical strength, and consequently the product heat resistance. The estimated composition of β -spodumene solid solution in the materials related to 21AK-5 composition corresponds to formula $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6.8 \text{SiO}_2$.

Based on executed complex studies the efficiency of apatite concentrate application in the amount of 5 % as the additive which activates the sintering process in the 21 composition based on β -spodumene matrix was established which enabled to produce moisture-proof products with 6–6.3 % shrinkage; water absorption 3.3–3.6 %, apparent density 2000–2060 kg/m³, thermal conductivity coefficient 0.78–0.79 Watt/(m·K), mechanical compressive strength 72–74 MPa, close to zero TCLE – minus $(0,03-0,04) \cdot 10^{-6} \text{K}^{-1}$. Thermal stability of samples is more than 100 thermal cycles (350–20) °C; chemical resistance – 99.6–99.8 % (to 10 % soda ash solutions) under the firing temperature of 1200 °C.

Conclusion. The data on the structure and phase formation of ceramic materials with close to zero thermal expansion, synthesized based on the $\text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system by slip casting, and the specified the selection of low-expansion crystalline phase have been expanded. The effect of additives intensifying the process of sintering ceramic materials by introducing chalk, dolomite, magnesite, dolomite concentrate, calcium borate, colemanite, apatite concentrate, magnesium orthophosphate, cryolite, etc. for 1.0–7.0 % was investigated. The possibility of the intensification of the process of sintering lithium-aluminosilicate materials by the introducing apatite concentrate, consist in crystallization along with β -spodumenic solid solutions pseudovollastonite needle habit performing reinforcing the role and is conditional on receipt of ceramics with considerable density and durability while ensuring high thermal properties have been established and experimentally confirmed.

Reference

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BIOCIDAL METALLIC GLAZES FOR PORCELAIN FLOOR TILES

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Introduction. Recently, much attention has been paid to development and use of antibacterial materials in various industries and in the home. The urgency of obtaining of antibacterial glaze coatings for floor tiles relates to the lack of efficiency of the known ways to prevent the reproduction of pathogenic bacteria. Such material is recom-