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ANTIBACTERIAL MATTE GLASS-CERAMIC COATINGS WITH SATIN TEXTURE FOR CERAMIC TILES

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Abstract. Antibacterial satin glass-ceramic coatings for ceramic tiles have been developed by one-stage firing on the basis of high-calcium zinc aluminum silicate frits, which are modified with heavy metal cations. The antibacterial effect of the developed matte glass-ceramic coatings with a satin texture was established due to the effect of potentiating the antibacterial activity of the combined action of the hardystonite crystalline phase and fillers of zinc and tin oxides.

Keywords: glass-ceramic coatings, ceramic tile, satin texture, antibacterial effect, hardystonite.

1. Introduction

Currently, residential and industrial construction is developing in the world. The demand for building materials, which are manufactured at enterprises that are equipped with modern equipment and use advanced technologies, including the production of ceramic tiles, is growing. The peculiarity of this technology is the production of high-temperature compositions of masses and glass coatings, which are characterized by high operational properties and allow to obtain competitive products of high quality using natural raw materials.

The ceramic tile market will grow from 2020 to 2025 due to population growth, disposable income, rise in renovations, and increase in investments in the residential and commercial sectors.[1]

An important restraining factor of the development of industries, and, as a result, the decline of the world economy is the rapid spread of COVID-19.[2] Reduction of production capacity, cancellation of projects in the commercial and industrial construction sector led to a decrease in demand for ceramic tiles in 2020.

Among global manufacturers, such corporations as Pamesa Ceramica, STN Group (Spain), Ceramica carmelo fior (Brazil),PT Arwana Citramulia (Indonesia) increased the production and export of ceramic tiles in 2020.[3]

The increase in demand for ceramic materials will be most observed for the Asia-Pacific region, especially for construction, with a tendency towards market fragmentation, which will allow domestic manufacturers to enter the global market. On the Ukrainian market, the availability of domestic raw materials, modern production bases and significant scientific and technical potential create favorable conditions for the production of competitive ceramic tiles and porcelain stoneware. According to the results of the first half of 2021, the total percentage of ceramic tile production volume of “Golden Tile” – the Ukrainian leader in the field of production and distribution of ceramic tiles is 27 %, ATEM – 25 %, CERSANIT – 18 %, Interkerama – 15 %, Epicenter K – 11 % , Zeus Ceramica – 4 %. However, the rapid growth of competition in ceramics technology in the conditions of globalization and, as a result, the need to increase competitiveness is achieved thanks to the development of innovative activity and increasing indicators of its economic efficiency.

The conduct of military operations on the territory of Ukraine since February 2022 has led to a significant loss of housing, industrial and administrative stock. The projected need for construction materials will grow rapidly during the reconstruction period, which will contribute to scientific and technical progress and the emergence of new industries.

Expanding the range and introducing materials with special characteristics (decorative properties, easy to clean, antibacterial properties, *etc.*) to the market is an important indicator of the consolidation of domestic ceramic tile manufacturers at the world level.

The spread of the pandemic and the man-made burden on the environment causes considerable concern in society due to the emergence and spread of a variety of infections and diseases.[4] Thus, resistant *enterococci* and *staphylococci* retain the ability to reproduce during the

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day on materials used in health care systems. In order to ensure antimicrobial protection in medical facilities, it is advisable to use antibacterial materials. This will help to reduce the number of intra-hospital infections and reduce the use of disinfectants such as hydrogen peroxide, hypochlorite, *etc.*, which have a short duration of action and are toxic to the environment. Most antimicrobial polymeric materials are capable of inhibiting or killing microbes on their surface, but they have significant drawbacks: low antimicrobial activity, problems with microbial resistance, and difficulty functioning in dynamic environments.[5]

Microbial contamination, adhesion, resistance of microbes to antibiotics, colonization of surfaces are harmful both to human health and to the integrity of structures when affected by mycelial fungi and damaged surfaces. The use of Ag, Zn, Cu, Fe, Au metal ions and nanomaterials is promising for combating pathogenic microorganisms and fungi.[6,7] The antibacterial mechanism of action of metal ions, such as reduction of membrane permeability, inhibition of enzymatic activity, is well known. However, the combination of different metal ions in the structure will lead to synergistic effects, which will allow to increase the microbial action and mitigate the potential side effects, which consist, in particular, in the accumulation of one type of metal in the living organism. One of the effective methods of a comprehensive approach to preventing the spread of pathogenic microorganisms is the use of antimicrobial materials with prolonged action against a wide range of pathogenic microorganisms. The use of environmentally safe ceramic materials will significantly reduce the microbial load in common areas, ensure a high level of quality of life and preserve the environment by eliminating the use of toxic disinfectants during processing.

Therefore, for the realization of a high level of social security of society, it is urgent to develop new innovative approaches to solving the problems of antimicrobial protection of objects of human life by developing innovative competitive ceramic materials with high antibacterial properties.

Analytical Review

Today, the use of ceramic materials,[8] glasses,[9] glass-ceramic coatings on steels[10,11] for antibacterial protection of human life objects is widely known. The development of bactericidal glazes for ceramic tiles takes into account the basic provisions of creating antibacterial glass materials,[12] considering the specifics of their structure. However, taking into account the stricter operating conditions of ceramic tiles and the significant demand in the world market of building materials, it is necessary to develop the physico-chemical provisions of their synthesis and practical application.

Most of the known methods of ensuring the antibacterial activity of glazes for ceramic tiles are based on the modification of their surface with bactericidal agents (Table 1). Argentum ions are traditionally used to ensure antibacterial activity in the production of ceramic materials. A promising method is the deposition of nanoparticles of argentum in the form of ink for screen printing on ceramic tiles (Table 1).[13] It does not require technological changes in the production process of ceramic tiles and provides significant opportunities for ceramic design. The integration of argentum nanoparticles into an organic or inorganic matrix suppresses or minimizes their aggregation, contributing to their stability during application, as well as during subsequent heat treatment. The use of matrices containing argentum nanoparticles minimizes the occupational risk associated with the use and processing of particles of nanometric sizes. However, the use of argentum ions significantly increases the cost of ceramic tiles, is ineffective against a wide range of pathogenic microorganisms and can lead to heavy metal accumulation in the environment.

A glazed ceramic surface covered with a layer of biocidal antimicrobial molecular barrier (BAMB) exhibits significant antibacterial properties. This development is an example of a stable non-migrating antibacterial coating on the glazed surface of ceramic tiles (Table 1).[14] However, the use of ammonium compounds in the structure of such a coating can cause a negative impact on human health, in particular, increase the risk of malformation of the human fetus.[15]

The most widely used antibacterial glazes for ceramic tiles with TiO_2 additive. Inhibition of bacteria *S. aureus*, *E. coli* on the surface of ceramic tiles is similar to the action of amoxicillin. The highest inhibition of the growth of the pathogenic organism *S. aureus* with a diameter of the growth retardation zone of 7.7 mm on a dense medium by the diffusion method is observed for a ceramic glaze with a content of 5 wt. % TiO_2 (Table 1).[16] It was established that TiO_2 powder in the modification of nano-sized anatase provides a higher antibacterial effect compared to micro-sized anatase. However, the addition of anatase to the glaze significantly increases its viscosity, and a significant amount of anatase in the composition of the coating can change not only its color during heat treatment,[17] but also reduce antibacterial activity due to the crystallization of TiO_2 in the modification of rutile at firing temperatures above 1073 K . Therefore, the use of titanium oxide as a bactericidal agent is also limited by the need to ensure its photocatalytic activity in the form of anatase at sufficiently high glaze firing temperatures.

A high ability to inhibit pathogenic organisms on the surface of glazes can be achieved by simultaneously introducing argentum cations and metal ions of variable valency into their composition. Ensuring a synergistic effect when introducing heavy metal cations with compounds Ag_2CO_3 and Bi_2O_3, CuO, SnO_2, ZnO, TiO_2 makes it possible to intensify the antimicrobial effect of glazes (Table 1).[18] The effect of potentiation of the antiviral ability against coronaviruses with the simultaneous introduction of silver/copper into the structure of zeolites was confirmed by the authors.[19] Studies have shown a 2.06 log10 reduction in TCID 50 (Median Tissue Culture Infectious Dose) after 4 hours and a 5.13 log10 reduction in TCID 50 within 24 hours.

Prolonged action of antibacterial glass coatings can be ensured by the directed crystallization in their composition of crystalline phases, which are characterized by the potentiation effect. As an example there can be developed glass-ceramic coatings with a zinc titanate content of about 50 vol. %, which are characterized by a high biocidal effect in relation to a wide range of microorganisms in harsh operating conditions (colony-forming units (CFU) 10^8-10^9 cells/mL).[20]

Antibacterial glaze, which was developed by combining two glazes with different Zn^{2+} content are known. The surface crystallization of feldspar allows to provide a positive charge with current values up to 1.5 V, which accumulates at the interface between the glaze and the bacteria, and provokes the death of bacteria. This is explained by the fact that the electrical potential present at the interface significantly exceeds the potential for bacterial membrane disintegration. Due to the volume crystallization of feldspar, the bactericidal properties of the glaze are preserved for a long time (Table 1).[21] However, the provision of the piezoelectric effect can be realized only when significant loads are applied.

Ensuring antibacterial and self-cleaning ability can be realized by depositing on the surface of ceramic tiles at a temperature of 823-923 K in a hydrogen-oxygen flame nano-sized titanium oxide, which is modified with particles of argentum. The obtained coatings are characterized by the presence of titanium oxide particles with a size of 50-200 nm and argentum particles of 1-3 nm. Glass coating is characterized by a defined surface relief, wetting ability, photocatalytic and antibacterial properties (Table 1).[22]

Antimicrobial floor tiles are known, which are characterized by high hydrophobicity due to the introduction of titanium oxide and antibacterial fillers in the amount of 5 to 20 wt. %, [23] or titanium oxide modified with niobium oxide (Table 1).[24] The ceramic tile surface and hydrophobicity can also be provided by forming a micropatterned surface relief containing nanocrystalline ZnO or acrylic/zinc oxide.[25] The spread of bacteria on tiles with zinc glaze is inhibited by more than 99 %. However, the effectiveness of the application of antimicrobial coatings on the surface of glazes is limited by their low mechanical strength and inability to have a prolonged effect over a long period of time.

Table 1. Ways of providing an antibacterial effect to the glass coating for ceramic tiles

№	Antibacterial material	Type of bactericidal agent, concentration	Bactericidal effect, standard (method)	Developers, country
1	Ceramic paint for screen printing	Colloidal silver - 3.0 wt. % Kaolin with the addition of silver ions 0.3 wt. %	99.99 % 99.00 %, JIS Z 2801	J. F. Noguera Spain[13]
2	Biocidal antimicrobial molecular barrier	BAMB $[(CH_3O)_3Si(CH_2)_3N(CH_3)_2(CH_2)_{17}CH_3]Cl$ solution of 0.5 wt. %, density 1 g/L	96 –99.66 % ASTM E2180-07	Selçuk Özcan, Turkey[14]
3	Ceramic filler	TiO_2 1.0 – 5.0 wt. %	6–7.7 mm diffusion method (Kirby-Baeur)	E. Maryani, Indonesia[16]
4	Ceramic filler	Ag_2CO_3 2– 4 wt. % + 2–4 wt. % and Bi_2O_3, CuO, SnO_2, ZnO, TiO_2	Bactericidal effect, JIS Z2801:2000	Alvin Lamar Campbell, JR., USA[18]
5	Bactericidal glaze	Volume crystallization of feldspar (30-40 vol. %), modified with zinc cations on the glaze surface	Bactericidal effect, 90.00 %	Julian Jimenez Reinosa, Spain[22]
6	Bactericidal film on the glaze surface	film from TiO_2 nanoparticles modified with argentum	High photocatalytic capacity 90.00 %	Jyrki Mäkelä Mikko Aromaa, Finland[22]
7	Bactericidal film on the glaze surface	film from TiO_2 nanoparticles modified with niobium oxide	High self-cleaning ability ISO 10678 and JIS R1703-2	Andre L. da Silva, Brazil[24]

Therefore, the introduction of antibacterial glazes for ceramic tiles can ensure the protection of objects of human life in the environment by inhibiting the spread and development of pathogenic microorganisms and associated viruses.[26] However, increasing the competitiveness of innovative high-quality products in the ceramic industry affects the high added value due to the introduction of new stages in the production process and the significant cost of antibacterial additives. Another problem is that the antibacterial effect, which is provided by the formation of a coating on the surface of the glaze, is short-lived, due to the constant chemical and mechanical impact during the operation and processing of ceramic tiles. Also, an important aspect of ensuring environmentally sustainable production of antibacterial ceramic tiles is the regulation of the impact of heavy metals on the environment.[25] Giving the ceramic coating a satin texture will allow not only to provide high aesthetic and decorative characteristics, but also to increase their antibacterial activity due to their wetting ability. Therefore, the development of an innovative approach to the creation of antibacterial ceramic tiles with high operational properties, manufacturability and justified cost is an important scientific and technical task, the solution of which is aimed at this work.

2. Experimental

2.1 Research Methodology

The aim of the work is the development of antibacterial satin glass-ceramic coatings for ceramic tiles by one-stage firing.

The presence of the crystalline phase was established using X-ray phase ("DRON-3" diffractometer) and petrographic (NU-2E polarizing microscope) and raster electron microscopy (electron microscope) methods of analysis.

Microbiological studies were carried out in a certified microbiological laboratory of the Research Institute "Ukrainian Research Institute of Environmental Problems" (certificate of compliance of the measurement system with the requirements of DSTU ISO 100122005 dated 07.19.2021).

The antibacterial and fungicidal properties of coatings on ceramic tiles were determined by quantitative (counting) methods adapted for the study of glass materials and taking into account their structure. The quantitative method is based on the control of the growth level of biotest microorganisms, which are inoculated into liquid nutrient media, in the presence of test samples and without them.

To determine the antibacterial properties of the samples, 0.1 mL of *Escherichia coli* biotest inoculum was added to a test tube with a medium of meat-peptone broth (MPB) in the amount of 6 mL. The *E. coli* O157:H7 strain was used. From each test tube with the medium into which the corresponding biotest was inoculated, 0.1 mL was taken and cultured on meat-peptone agar (MPA). For the inoculum of the biotest in the amount of 0.1 mL, inoculation was also done on MPA. The optical density of the initial inoculum of each biotest was determined on a FEK-M photocolorimeter at $\lambda = 490$ nm and sensitivity = 3. The initial concentration (C_{init}) for *E. coli* was chosen taking into account the use of ceramic tiles in public places with a moderate and high level of epidemiological threat and was 10^3–10^7 cells/cm^3. To determine the biocidal effect, the samples were placed in test tubes with the appropriate nutrient medium, into which the suspension of biotests was previously inoculated. The test tubes were hermetically closed and set for incubation at room temperature with periodic shaking. The exposure time for *E. coli* was 24 hours in the intensive growth phase. After incubation of the samples, the optical density of the contents of the tubes with control and experimental samples was measured alongside with the method of comparison with the standard solution.

To prepare the inoculum of *Aspergillus niger*, the fungus cultures were grown in test tubes on shoals of agarized selective medium of Czapek-Dox at a temperature of 299 ± 2 K. To reveal the fungicidal properties of the material in relation to vegetative cells, fungal cultures were grown for 72 hours until the exponential phase of growth. To detect the fungicidal properties of coatings in relation to spores, fungal cultures aged 14 days from the day of sowing, in the form of mature sporulation, were used. After passing the specified term, using a bacterial loop, the biomass of the fungus was transferred to distilled water and a suspension of fungi with 10^3-10^7 column-forming organisms in 1 mL was obtained by means of serial dilutions.

The experiment was carried out in a triplicate. Statistical processing of the results was carried out on a computer using the package of programs for statistical processing

"STATISTICA" and "Origin". The processing of the data of the second experiment was carried out according to the Student's method.

The properties of the developed antibacterial glazes were determined in accordance with EN ISO 10545 in a certified incoming inspection laboratory of PJSC "KhPZ" (certificate No. 2011516 to 17025: 2017).

2.2. Development of Frit Compositions and Glaze Coating for Ceramic Tiles

Obtaining a glaze coating simultaneously with antibacterial properties and a matte satin texture without a significant change in the technological process and an increase in cost will be carried out due to the potentiation effect by:

– using zinc-containing frit as a glass matrix and antibacterial fillers that act as biocidal agents – nano- and micro-sized compounds of oligodynamic components;

– provision of a programmed structure of the glass coating by directed crystallization, which will determine a certain given orientation of metal cations and their uniform continuous placement in the near-surface layer of the coating with a roughness of Ra=1–3 μm.

For the development of frit, the $Na_2O - K_2O - CaO - ZnO - MgO - BaO - Al_2O_3 - SiO_2$ system was chosen, in which the area was limited in the following concentration ranges, wt. %: Na_2O 3.4÷5.0; K_2O 3.0÷5.0; MgO 0.1÷0.4; CaO 12.0÷14.0; ZnO 9.5÷10.3; BaO 10.0÷11.1; Al_2O_3 11.0÷12.5; SiO_2 46.8÷48.8.

The choice of high-calcium zinc aluminum silicate frits was based on the need to ensure a short interval of formation of a glass-ceramic coating during one-stage firing at a temperature of 1423 K and their ability to form areas of immiscibility and crystallization of crystalline phases that contain cations of bactericidal metals. A significant content of CaO can lead to vitrification of the frit and surface crystallization of the coating. The introduction of zinc oxide will also reduce the temperature of melt formation, increase its reactivity and promote the crystallization of aluminates and silicates that strengthen the coating. The simultaneous introduction of calcium and zinc oxides will significantly increase the chemical resistance of the glaze coating.

The introduction into the frit composition of barium oxide, which is a flux and contributes to the devitrification of the frit (above 3.0 mol. %), will allow the formation of a low-temperature phase and solid solutions based on a monoclinic celsian. This is due to the fact that, unlike high-temperature phases (hexagonal), for which modification transitions are inherent, low-temperature forms contribute to the increase in the material strength.[15] At the same time, in order to reduce the temperature of the appearance of the first crystalline phase, a necessary condition is to ensure the value of the ratio R_2O+RO/SiO_2=0.5-0.7, which determines the structural state of the silicon-oxygen framework.

For the purpose of crystallization of zinc-containing and barium-containing crystalline phases of hardystonite and celsian, which will simultaneously contribute to the strengthening of the antibacterial effect and provide high aesthetic and decorative characteristics (satin texture, whiteness).

The crystallization of hardystonite is determined by the initial content of calcium and zinc oxides and is realized at a temperature of 1700 K with an optimal content of 15.2 wt. % with the content of CaO=10.4 wt. % and ZnO=10.4 wt. % and SiO_2. The possibility of obtaining alkali-free coatings in relation to low-temperature high-speed firing is realized with the optimal ratio of phase-forming oxides CaO/ZnO=1.4–2.0.[16] Taking into account the following provisions, the ratio of CaO/ZnO=1.2–1.4 and $BaO/Al_2O_3 \approx 0.8–0.9$ was chosen for the crystallization of hardystonite and solid solutions based on the monoclinic celsian (Table 2).

To obtain frits, which under the conditions of high-speed heat treatment will allow obtaining glass-ceramic coatings characterized by the formation of a finely dispersed structure with the presence of uniformly distributed crystalline phases, it is necessary to ensure the total content of modifying oxides in the melt composition for the formation of structurally formed sybotaxic groups, which are the nuclei of the crystalline phase and the creation of favorable conditions for nucleation during cooling and growth of crystals during rapid heat treatment. All designed glazes are characterized by the high crystallization ability, as evidenced by the values of structural factors:[16] crystallinity coefficient $K_{cr} \geq 3.5$, transparency coefficient $K_{tr} \geq 2.1$. All developed compositions are within the values of the specified components with the highest value of K_{cr} for M 8.

The structural factors which characterize the structural strength of the glass $f_{Si} \geq 0.32$ and $\Psi_{Al} > 1$ will allow creating conditions for the formation of $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedra in the glass structure, which will contribute to the high chemical resistance in contact with aggressive environments.

In this system, frit compositions of the M series were synthesized as the basis for obtaining a glass-ceramic coating for ceramic tiles. M series frits were synthesized in corundum crucibles under the same conditions in an electric furnace at 1733-1743 K with heaters and gradual cooling for 12 h. The frit structure after melting is amorphous.

Table2. Structural factors and characteristic ratios for the chemical composition of the developed frits

Structural factors and characteristic ratios	Frit marking							
	M 8	M 7	M 6	M 5	M 4	M 3	M 2	M 1
Coefficient of silicon-oxygen framework bonding f_{Si}	0.32	0.32	0.33	0.32	0.32	0.32	0.32	0.32
Structural state of aluminum Ψ_{Al}	3.46	3.28	3.25	3.08	3.41	3.29	3.49	3.71
Crystallinity coefficient K_{cr}	45.3	42.3	43.5	41.9	39.3	38.7	41.7	42.0
Transparency coefficient K_{tr}	2.40	2.38	2.36	2.35	2.42	2.39	2.40	2.47
CaO/ZnO	1.4	1.2	1.22	1.14	1.39	1.22	1.25	1.26
BaO/Al_2O_3	0.925	0.857	0.857	0.857	0.832	0.858	0.850	0.900

To study the crystallization ability, high-speed heat treatment of experimental frit samples was carried out at a temperature (T) of 1413 K for 10 min. The indicated mode corresponds to the mode of one-stage firing of ceramic tiles for monocottura.

The following composition of the glaze was chosen to obtain a satin glaze coating marked MR2, wt. %: M 8 frit – 68; "Prima" Andriivska clay – 2; AK Prime brand kaolin – 11.0; ZPN 01627MB zircon –12; D 120 dolomite – 7; zinc whites 1–3 or tin oxide 1–3; sodium tripolyphosphate 0.03; KMC CARBOCEL, ST/25-PT 0.10–0.12.

The properties of glaze slip and coating: residue on sieve No. 0045 – 0.5–2.0 %; density – 1.93–1.92 g/cm^3, fluidity 70–90 sec; TCLE of glaze ($5.25 \cdot 10^{-6}$) degree – 1.

MR2 glass-ceramic coating was obtained by a one-stage firing regime at a temperature of 1423 K under the conditions of PJSC "KhPZ".

3. Results and Discussion

3.1 Study of the Crystallization Ability and Structure of the Developed Frits

According to X-ray phase and petrographic analyses, after heat treatment, the experimental frits contain 20-40 vol. % of hardystonite crystalline phase ($2CaO \cdot ZnO \cdot 2SiO_2$) and 5-10 vol. % of barium orthoclase ($BaAl_2Si_2O_8$). The size of the hardystonite crystal phase for M 1 and M 2 frits is more than 3–5 µm in the volume of the material, which can be explained by a decrease in the frits viscosity during the formation of crystallization nuclei due to the significant content of alkaline oxides (7.5 wt. %) in the frits composition. This can negatively affect the strength of coatings based on them. For M 3, M 4, M 5, M 6, and M 7 frits, the 20–30 vol. % hardystonite content is insufficient for the formation of a volume crystallized structure of the coating, which can lead to the decrease in the antibacterial activity of the coatings.

The presence of hardystonite (40 vol. %) and barium orthoclase (5 vol. %) with a size of about 1 µm in the composition of the M 8 experimental frit after heat treatment at 1423 K (Fig. 1) allows us to assume the possibility of creating a strengthened sitallized coating on its basis.

For a detailed study of the M 8 frit structure formation, according to the data of the gradient-thermal analysis, the following characteristic temperatures of heat treatment for 10 minutes were chosen: glass softening at a temperature of T=1123 K; opalescence at T=1173 K (stage of nuclei formation); opacification at T=1273 K (growth of crystalline phase); volume crystallization T=1423 K (stage of formation of the sitallized structure).

Thermal treatment of M 8 frit at T=1123 K contributed to the appearance of a high concentration of fluctuations, which are observed as densely packed spherical inhomogeneities 20–50 nm in size (Fig. 2 a I), which form chains (Fig. 2 a II). This process is characteristic of the phase separation of glass with the formation of a two-frame structure when the relative of each of the phases approaches 50 vol. %. This differentiation of the structure is characteristic of liquation according to the spinodal mechanism and manifests itself in the fusion of spherical nanoinhomogeneities of about 100 nm into separate, interpenetrating phases of 0.3 µm in size (Fig. 2 a III). The continuous growth of the phase is a characteristic feature of the metastable liquation as a phase transition.

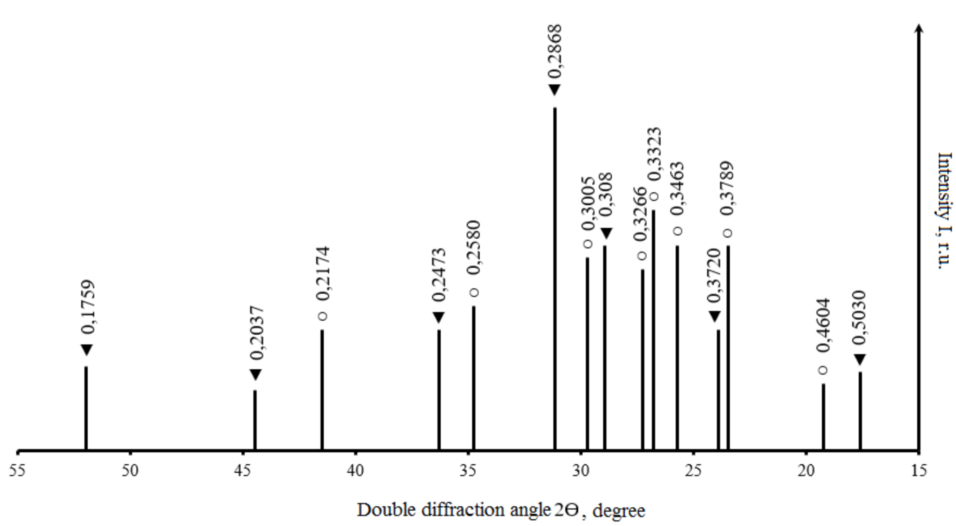

Fig. 1. Line diffraction pattern of M 8 frit after heat treatment at 1423 K:
▼$Ca_2ZnSi_2O_7$; ○ $BaAl_2Si_2O_8$

The increase in the intensity of the phase separation process at T=1173 K for M 8 frit is expressed in the growth of nano- and micro-inhomogeneities in its structure and the formation of nucleators and is explained by the presence of areas of immobility of the zinc silicate and calcium silicate glass framework. The emergence of secondary delamination against the background of spherical formations (Fig. 2 b I) in the structure of the experimental frit is a stage of heterogeneous nucleation of crystal centers, which is associated with the formation of stabilized clusters – heterophase fluctuations that form a self-organizing nanostructure. The formation of the dissipative structure is realized by the appearance of distinct spherical inhomogeneities (Fig. 2 b II), which unite and grow (Fig. 2 c III).

When the temperature rises to 1273 K, the fusion of spherical inhomogeneities (Fig. 2 in I) into columnar β-$CaSiO_3$ crystals (Fig. 2 in II) is observed, which, according to the reaction β-$CaSiO_3$+ ZnO=$Ca_2ZnSi_2O_7$, turn into hardystonite. When the temperature is further increased to 1423 K, clearly defined short-columnar hardystonite crystals up to 1 μm in size are observed, which are placed at an angle to each other (Fig. 2 I). This circumstance allows us to assert the reinforcement of the glass matrix with hardystonite crystals and the possibility of obtaining a strengthened sitallized coating on the basis of M 8 frit. The difficulty of detecting barium orthoclase in the frit structure is related to the similarity of its short-prismatic habit to the habit of hardystonite and its small content in the glass structure.

It is the provision of a finely dispersed volume crystallized structure of the glass material with the simultaneous content of crystalline phases, which are characterized by the presence of zinc and barium cations, that will ensure a significant strength of the coating and create an additional opportunity to implement the effect of potentiation of cations in order to inhibit the growth of pathogenic microorganisms.

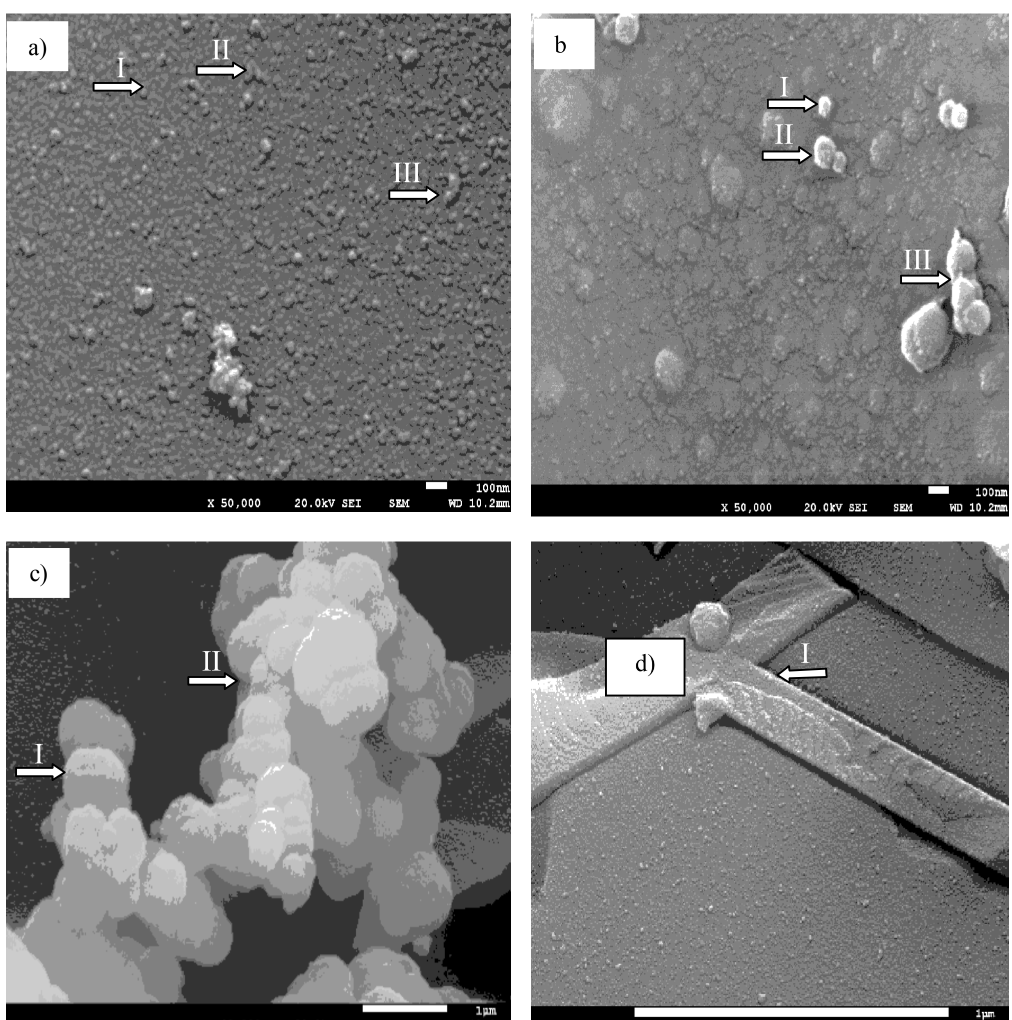

Fig. 2. Photomicrographs of the M 8 frit structure during heat treatment
a – T=1123 K; b – T=1173 K; c –T=1273 K; d – T=1423 K

3.2 Research of the Relationship between Texture and Operational Properties of the Developed Glass-Ceramic

The study of the texture of the obtained coating made it possible to establish that the roughness index $Ra = 3 \mu m$ for the developed coating causes the formation of its satin matte surface to create a decorative effect and increase the antibacterial ability due to the surface crystallization of zinc- and barium-containing crystalline phases.

In order to strengthen the antibacterial properties, ZnO, SnO_2 were added to the composition of the slip. The effectiveness of the application of the developed coating, which is characterized by the presence of a zinc-containing crystalline phase and ZnO, SnO_2 fillers, is explained by the selective toxicity of these fillers with respect to microorganisms and minimal impact on humans.

The antibacterial activity of ZnO, SnO_2 is realized by the following mechanisms:

- oxidation and decomposition of organic components of bacteria by photocatalytic means under the action of ultraviolet radiation;
- irreversible inhibition of enzymatic activity by binding the functional group of the enzyme molecule;
- denaturation of proteins due to the formation of mercaptides, albuminates, violation of the permeability of cell membranes and connection with DNA of cells by the catalytic oxidation;
- the formation of active oxygen due to the contact of cations with water, which oxidizes and destroys the DNA of microorganisms.

Determination of the antibacterial activity of the original MR2Z coating and developed coatings containing zinc and tin oxides 1 wt. % marked with MR2Z and MR2S, respectively, made it possible to establish their significant inhibitory capacity against *Escherichia coli* in the active phase of growth at a concentration of 10^7 cells/mL (Table 3) in the exponential growth phase of *Escherichia coli* for 1 day. A decrease in the concentration of *Escherichia coli* affects the decrease in the antibacterial effect, which is associated with a decrease in the density of bacteria. In general, the developed coatings show a high antibacterial capacity against Escherichia coli, especially with the content of zinc oxide as a filler.

The fungicidal effect of the MR2Z and MR2S developed coatings is lower than the antibacterial effect, which is due to the ability of *Aspergillus niger* to biosorb heavy metals.[27] In general, the coatings have a prolonged fungistatic effect during a long period of exposure in the exponential growth phase of *Aspergillus niger* for 7 and 14 days with a significant concentration of the microorganism 10^7–10^8 cells/mL. This allows us to conclude that the developed coatings have protective properties against the corrosive action of mycelial fungi.

The high antibacterial and fungistatic effects of the developed coatings are realized due to the effect of potentiation of the inhibitory ability with the simultaneous content of the crystalline phase of hardystonite and the filler of zinc and tin oxides. The content of these compounds also significantly increases the chemical resistance of the coating, which allows the use of heavy metal cations in the structure of the glass-ceramic coating, excluding negative impact on the environment.

Table 3. Change in the concentration of *Escherichia coli*, cells/mL, in contact with the developed coatings and their antibacterial effect after 24 hours of exposure

Experimental coatings and cell culture concentration ($K_{cultures}$) after 24 hours of exposure	Initial concentration of *Escherichia coli*, cells/mL				
	$1.0 \cdot 10^7$	$3.0 \cdot 10^6$	$1.5 \cdot 10^5$	$5.0 \cdot 10^4$	$2.0 \cdot 10^3$
	Change in the concentration of *Escherichia coli*, cells/mL, upon contact with the coatings				
$K_{cultures}$ after interacting with MR2 initial coating	$5 \cdot 10^9$	$11 \cdot 10^8$	$1.2 \cdot 10^7$	$9.1 \cdot 10^5$	$8.9 \cdot 10^5$
$K_{cultures}$ after interacting with MR2Z coating with ZnO content	$1.10 \cdot 10^9$	$5.83 \cdot 10^8$	$0.8 \cdot 10^7$	$6.9 \cdot 10^5$	$7.25 \cdot 10^5$
$K_{cultures}$ after interacting with MR2S coating with SnO_2 content	$3.04 \cdot 10^9$	$9.6 \cdot 10^8$	$1.1 \cdot 10^7$	$8.30 \cdot 10^5$	$8.6 \cdot 10^5$
	Change in the concentration of *Escherichia coli* after 24 hours of exposure				
Escherichia coli cell culture concentration	$11.9 \cdot 10^9$	$13.6 \cdot 10^8$	$1.4 \cdot 10^7$	$9.4 \cdot 10^5$	$9.1 \cdot 10^5$
Experimental coatings	Antibacterial effect, %				
MR2 initial coating	58	20	14.3	3.2	2.2
MR2Z coating with ZnO content	90.8	57	43	26.6	10.3
MR2S coating with SnO_2 content	75.0	29.5	22	11.7	5.5

Table 4. Change in the concentration of *Aspergillus niger*, cells/mL, in contact with the developed coatings and their fungicidal effect

Experimental coatings and cell culture concentration $K_{cultures}$ after 24 hours of exposure	Initial concentration of *Aspergillus niger*, cells/mL			
	Duration of exposure, days			
	7 days		14 days	
	$1.0\cdot10^{7}$	$1.0\cdot10^{6}$	$2.0\cdot10^{7}$	$2.05\cdot10^{6}$
	Change in the concentration of *Aspergillus niger*, cells/mL, upon contact with the coatings			
MR2 initial coating	$2.75\cdot10^{7}$	$1.64\cdot10^{6}$	$6.30\cdot10^{7}$	$5.68\cdot10^{6}$
$K_{cultures}$ after interacting with MR2Z coating with ZnO content	$1.25\cdot10^{7}$	$1.15\cdot10^{6}$	$3.50\cdot10^{7}$	$2.50\cdot10^{6}$
$K_{cultures}$ after interacting with MR2S coating with SnO_2 content	$1.80\cdot10^{7}$	$1.60\cdot10^{6}$	$3.80\cdot10^{7}$	$2.90\cdot10^{6}$
Cell culture concentration of *Aspergillus niger*	$3.50\cdot10^{8}$	$2.20\cdot10^{7}$	$6.80\cdot10^{7}$	$5.30\cdot10^{7}$
Experimental coatings	Fungicidal effect, %			
MR2 initial coating	12.7	13.4	10.79	19.6
MR2Z coating with ZnO content	28	19.1	19.42	21.2
MR2S coating with SnO_2 content	19.5	13.75	17.9	21.27

Table 5. Operational properties of the developed MR2 glass-ceramic coating according to EN ISO 10545

Parameters	Values of parameters according to EN ISO 10545	The actual value of the parameters
Water absorption, %	Eb ≤ 10 %	15.5 %
Bending strength limit, N/mm² Destructive load, N	Not less than 15.0 At least 200	29.4 843
Thermal stability, K	Heating and cooling in the temperature range from 423 K to 293 K, at least 10 cycles	10 cycles
Cracking resistance	Exposure at a temperature of 433 K and a pressure of 500 kPa for 2 hours for at least one cycle without changes to the front surface	More than two cycles
Chemical resistance	Acids of low concentration Acids of strong concentration Household chemicals	Class GLA, Class GHA Class GA
Stain resistance	Minimum class 3	Class 3

The study of the operational properties of the developed glass-ceramic coating for ceramic tiles made it possible to establish their compliance with EN ISO 10545, which determines its competitiveness in the production of European-level ceramic tiles for walls (Table 5).

4. Conclusions

The main provisions for the synthesis of frits for the production of antibacterial glass-ceramic coatings for ceramic tiles in the conditions of one-stage firing were established. Frits were developed in the system, which are characterized by the ratio CaO/ZnO=1.2–1.4, BaO/Al_2O_3=0.832–0.925 and the values of structural factors f_{Si} = 0.31–0.33; Ψ_{Al} = 3.08–3.7; 1 K_{cr} = 38.7–45.3; K_{tr} = 2.35–2.47, for the synthesis of antibacterial glass-ceramic coatings with a satin structure.

The mechanism of the structure formation of the glass-ceramic coating during heat treatment was established: the glass phase separation with the formation of a two-frame structure by the spinodal mechanism (T=1123 K); the formation of a dissipative structure with the presence of heterophase fluctuations – nucleators (T=1173 K); crystallization of β-$CaSiO_3$ (T=1273 K); sitallization of glass with the presence of $Ca_2ZnSi_2O_7$ and $BaAl_2Si_2O_8$ crystals (1423 K). It was established that the volume and surface crystallization for the glass-ceramic coating, which is determined by the ratio of CaO/ZnO=1.4 and BaO/Al_2O_3=0.925 and Ra = 3 μm, allows ensuring high operational properties of ceramic tiles according to EN ISO 10545 and its satin texture. The presence of hardystonite with a size of about 1 μm after heat treatment at 1423 K in the M 8 experimental frit suggests the possibility of creating a strengthened sitallized coating on its basis.

Scientific novelty of the work is that the mechanism of the structure formation of the glass-ceramic coating during heat treatment was experimentally determined: the glass phase separation with the formation of a two-frame structure by the spinodal mechanism (T=1123 K); the formation of a dissipative structure with the presence of heterophase fluctuations – nucleators (T=1173 K); crystallization of β-$CaSiO_3$ (T=1273 K); sitallization of glass with the presence of $Ca_2ZnSi_2O_7$ and $BaAl_2Si_2O_8$ crystals (1423 K).

It was established that providing the ratio of CaO/ZnO=1.4 and BaO/Al2O3=0.925 in the composition of frits leads to the volume and surface crystallization with a hardystonite content of 40 vol. % and celsian of 5 vol. % with a size of about 1 μm after heat treatment at 1423 K. This allows to ensure high operational properties of ceramic tiles according to EN ISO 10545 and its sitallized satin texture.

It has been established that the high antibacterial effect of 75-90 % and the fungistatic effect of 10-28 % with the simultaneous satin texture of Ra= 3 μm of glass-ceramic coatings for ceramic tiles, which are operated in areas of high risk of infection with pathogenic microorganisms and initial concentration of *Escherichia coli* and *Aspergillus niger* up to 10^7 cells/mL, provided by the introduction of biologically active fillers of tin or zinc oxides in the amount of 3 wt. % to the composition of the sitallized coating based on hardystonite and barium orthoclase due to the potentiation effect.

The practical significance of the obtained results for the technology of glass-ceramic coatings for ceramic tiles lies in the development of new compositions of glazes based on high-calcium zinc aluminum silicate frits, which are modified with barium, zinc and tin oxides. This opens up prospects for a comprehensive solution to the problem of the production of biocidal ceramic materials with high antibacterial and fungistatic properties for the protection of medical institutions and public places in conditions of variable microbial load. Reducing the use of heavy metal ions as biocides in ceramic tile technology meets the urgent requirements of environmental safety.

The introduction of the developed antibacterial matte glass-ceramic coatings with satin texture for ceramic tiles at PJSC "KhPZ" will significantly increase the competitiveness of domestic products on the European market.

References

[1] Ceramic Tiles Market by Type (Porcelain, Glazed, Unglazed), Application (Floor, Internal Wall, External Wall, Others), End-Use Sector (Residential & Non-residential), & Region - Global Forecast to 2025. https://www.marketsandmarkets.com/Market-Reports/ceramic-tiles-market-228236779.html (accessed 2022-11-08).

[2] Vitenu-Sackey, P.A.; Barfi, R. The Impact of Covid-19 Pandemic on the Global Economy: Emphasis on Poverty Alleviation and Economic Growth. *The Economics and Finance Letters* **2021**, *8*, 32-43. https://doi.org/10.18488/journal.29.2021.81.32.43

[3] Indian Council of Ceramic Tiles and Sanitary Ware. http://www.icctas.com/pdf/magazine_2021.pdf (accessed 2022-11-08)

[4] *Antimicrobial Materials for Biomedical Applications*. Series 5; Domb, A.J.; Kunduru, K.R.; Farah, S., Eds.; London: Royal Society of Chemistry, 2019.

[5]. Luo, H.; Yin, X.-Q.; Tan, P.-F.; Gu, Z.-P.; Liu, Z.-M.; Tan, L. Polymeric Antibacterial Materials: Design, Platforms and Applications, *J. Mater. Chem. B* **2021**, *9*, 2802-2815. https://doi.org/10.1039/D1TB00109D

[6] Zhang, E.; Zhao, X.; Hu, J.; Wang, R.; Fu, S; Qin, G. Antibacterial Metals and Alloys for Potential Biomedical Implants. *Bioact. Mater.* **2021**, *6*, 2569-2612. https://doi.org/10.1016/j.bioactmat.2021.01.030

[7] Godoy-Gallardo, M.; Eckhard, U.; Delgado, L.M.; de Roo Puente, Y.J.D.; Hoyos-Nogués, M.; Gil, F.J.; Perez, R.A. Antibacterial Approaches in Tissue Engineering Using Metal Ions and Nanoparticles: From Mechanisms to Applications. *Bioact. Mater.* **2021**, *6*, 4470-4490. https://doi.org/10.1016/j.bioactmat.2021.04.033

[8] Ceramic Products Market in Japan. Tableware, Wall & Floor Tiles, Bio-ceramics. Challenges and Opportunities for European Companies. https://www.eu-japan.eu/sites/default/files/ publications/docs/ceramicproductsmarket_spupapaza_min15-2.pdf (accessed 2022-11-09).

[9] Development of Sol-gel Antibacterial and Antiviral Coating for Glass NEWS RELEASE. https://www.nsg.com/-/media/nsgcom/downloads/en/2021/17mar2021sol-gelcoatingforglass_e01.pdf (accessed 2022-11-09).

[10] Savvova, O.V. Biocide Apatite Glass-Ceramic Materials for Bone Endoprosthetics. *Chem. Chem. Technol.* **2013**, *7*, 109-112. https://doi.org/10.23939/chcht07.01.109

[11] Savvova, O.V.; Bragina, L.L. Use of Titanium Dioxide for the Development of Antibacterial Glass Enamel Coatings. *Glass Ceram.* **2010**, *67*, 184-186. https://doi.org/10.1007/s10717-010-9258-8

[12] Karasu, B.; Yüksel, G.; Uysal, N. The Recent Developments in Ceramic Glazes. *Seramik* [Online], **2020**, *58*, 116-128. https://www.researchgate.net/publication/344172770_The_Recent_Developments_in_Ceramic_Glazes (accessed 2022-11-16).

[13] Noguera, J.F.; Moreno, A.; Gozalbo, A.; Orts, M.J. Development of Ceramic Glaze Compositions with Bactericidal and Fungicidal Properties. *Qualicer'10 Castellon (Spain)* [Online] **2010.** https://www.qualicer.org/recopilatorio/ponencias/pdfs/2010189.pdf (accessed 2022-11-16).

[14] Özcan, S.; Çaliş Açikbaş, N.; Açikbaş, G. Formation of antibacterial effect on ceramic tile surfaces. *Anadolu University Journal of Science and Technology A- Applied Sciences and Engineering* [Online] **2017,** 18, 122-130. https://doi.org/10.18038/aubtda.300424

[15] Hrubec, T.C.; Melin, V.E.; Shea, C.S.; Ferguson, E.E.; Garofola, C.; Repine, C.M.; Chapman, T.W.; Patel, H.R.; Razvi, R.M.; Sugrue, J.E. et al. Ambient and Dosed Exposure to Quaternary Ammonium Disinfectants Causes Neural Tube Defects in Rodents. *Birth Defects Research* [Online] **2017**, *109*, 1166–1178. https://doi.org/10.1002/bdr2.1064 (accessed 2022-11-16).

[16] Maryani, E, Nurjanah, N. S, Hadisantoso, E.P.; Wijayanti, R.B. The Effect of TiO_2 Additives on the Antibacterial Properties (Escherichia coli and Staphylococcus aureus) of Glaze on Ceramic

Tiles. *IOP Conference Series: Materials Science and Engineering* **2020**, *980*, 012011. https://doi.org/10.1088/1757-899X/980/1/012011
[17] Hasmaliza, M.; Foo, H.S.; Mohd, K. Anatase as Antibacterial Material in Ceramic Tiles. *Procedia Chem*. **2016**, *19*, 828-834. https://doi.org/10.1016/j.proche.2016.03.109
[18] Campbell, A.L. Ceramic glaze having antimicrobal property. US20090104459A1, 23 April 2009.
[19] Kumar, G.D.; Mishra, A; Dunn, L.; Townsend, A.; Oguadinma, I.C.; Bright, K.R.; Gerba, C.P. Biocides and Novel Antimicrobial Agents for the Mitigation of Coronaviruses. *Front. Microbiol.* **2020**, *11*, A.1351. https://doi.org/10.3389/fmicb.2020.01351
[20] Savvova, O.V.; Bragina, L. L.; Babich, E.V. Study of the Biocidal Properties of $R_2O–RO–TiO_2–P_2O_5–R_2O_3–SiO_2$ Glass Ceramic Coatings. *Glass Ceram.* **2012**, *69*, 20–24. https://doi.org/10.1007/s10717-012-9407-3
[21] Reinosa, J.J.; Rojo, M.M.; del Campo, A.; Martín-González, M.; Fernández J.F. Highly Efficient Antimicrobial Ceramics Based on Electrically Charged Interfaces. *ACS Appl. Mater. Interfaces* **2019**, *11*, 39254–39262. https://doi.org/10.1021/acsami.9b10690
[22] Mäkelä, J.; Aromaa, M. UNCOAT – Enhanced Functionality of Selfcleaning and Antibacterial Surface Coatings. [Online] **2009**, 06120. http://www.diva-portal.se/smash/get/diva2:707171/FULLTEXT01.pdf (accessed 2022-11-18)
[23] Tapkire, G.V. Influence of Antimicrobial & Super Hydrophobic on Flooring Tiles. *Int. res. j. eng. tech*. **2018**, *05*, 1453-1456.
[24] da Silva, A.L.; Dondi, M.; Hotza, D. Self-Cleaning Ceramic Tiles Coated with Nb_2O_5 Doped-TiO_2 Nanoparticles. *Ceram. Int.* **2017**, *43*, 11986-11991. https://doi.org/10.1016/j.ceramint.2017.06.049
[25] Khorshidi, Z.G.; Jallab, M.; Moghbelli E.; Goudarzi, A.; Ghaffari, M. Photocatalytic Analysis of a Hydrophilic Acrylic Coating/Zinc Oxide Nanocomposite on Glass Substrate. *POLYM-PLAST TECH MAT* **2021,** *60*, 1220-1232. https://doi.org/10.1080/25740881.2021.1888986
[26] Savvova, O.V.; Shevetovsky, V.V.; Pokroeva, Ya.O.; Zinchenko, I.V.; Babich, O.V.; Voronov, H.K. Development of Antibacterial Glazing for Ceramic Tiles. *Voprosy khimii i khimicheskoi tekhnologii* **2022**, *3*, 60-66. https://doi.org/10.32434/0321-4095-2022-142-3-60-66
[27] Kapoor, A.; Viraraghavan, T. Heavy Metal Biosorption Sites in *Aspergillus niger*. *Bioresour. Technol.* 1997, *61*, 221-227. https://doi.org/10.1016/S0960-8524(97)00055-2

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АНТИБАКТЕРІАЛЬНІ МАТОВІ СКЛОКРИСТАЛІЧНІ ПОКРИТТЯ З ШОВКОВОЮ ТЕКСТУРОЮ ДЛЯ КЕРАМІЧНОЇ ПЛИТКИ

Анотація. *Розроблено антибактеріальні сатинові склокристалічні покриття для керамічної плитки за одностадійним випалом на основі висококальцієвих цинкалюмосилікатних фрит, які модифіковано катіонами важких металів. Встановлено антибактеріальний ефект розроблених матових склокристалічних покриттів з шовковою текстурою завдяки ефекту потенціонування антибактеріальної активності сумісної дії кристалічної фази гардистоніту та наповнювачів оксидів цинку й олова.*

Ключові слова: *склокристалічні покриття, керамічна плитка, шовкова текстура, антибактеріальний ефект, гардистоніт.*