**Conclusion.** The data on the structure and phase formation of ceramic materials with close to zero thermal expansion, synthesized based on the $Li_2O$ – $Al_2O_3$ – $SiO_2$ 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.

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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 recommended for use in health facilities, clinics, pools, food processing facilities to fight different bacterial strains, with significant resistance toantibiotics, antiseptics and disinfectants [1]. Even though leading foreign manufacturers produce antibacterial glazed ceramic tiles substantial research was not conducted in this area in Belarus.

International experience shows that a large number of chemicalsis applied to obtainan tibacterial building materials. These substances can be divided into two groups. The first group comprises organic compounds like phenols, chloroform, cresols, neutral soaps, detergents, ethers, hydrogen ions, alcohols, toluenes [2]. However, organic antimicrobial compounds cannot be added in glazes for porcelain tiles due to high firing temperature of 1170–1200 °C. Treating the tiles surface by different organic disinfectants is inefficiency too, because it cannot provide reliablelong-term antibacterial protection of a surfaceduring the life cycle of ceramic tiles.

The second group includes the following inorganic materials: potassium permanganate, hydrogen peroxide, heavy metal ions ($Ag^{+}$, $Hg^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Au^{3+}$, $Ni^{2+}$, $Zn^{2+}$ and etc.), titanium dioxide and others [3–4]. Taking into account the above, copper oxide was used in glaze compositions as abiocidal agent.

As is known, copper and some of its alloys are characterized by pronounced biological activity. Antibacterial properties of copper compounds are used in the manufacture of medicine equipment, in food industry and animal husbandry [5, 6], and to provide antifungaland antimicrobial properties of sanitary ceramics, ceramic tiles [7].

The aim of this work was to study the formation of the glaze coatings for ceramic porcelain tiles with the required physico-mechanical properties and aesthetic characteristics, as well as reliable antibacterial protection.

**Experimental.** The glaze slip was prepared by combined wet grinding of the components of the glaze batch in a ball mill (Speedy, Italy) to 0.1–0.3 % residue in a No. 0056 sieve with material : milling body : water ratio 1 : 1.5 : 0.5. Sodium tripolyphosphate in the amount of 0.25 over 100 % was used as the deflocculant. The suspension obtained with moisture content 30–40 % was deposited on ceramic porcelain tiles predried to moisture content no more than 0.5 % and coated with engobe. The tiles glazed with the experimental glaze compositions were fired in an FMS-2500 gas-flame furnace (Sacmi, Italy) at temperature (1200±5) °C for (50±2) min under the extant conditions at Keramin JSC (Minsk, Republic of Belarus). The temperature rise rate, holding time at maximum temperature and total firing time corresponded to the production parameters.

Physical-chemical properties of glaze samples after synthesis were tested for conformity with the requirements of technical standards documents.

The research included a determination of the luster using a FB-2 photoelectronic brightness meter (Russia) and uviol glassas the reference. The linear thermal expansion coefficient (CLTE) of the synthesized glazes was measured with a DIL 402 PC (Netzsch, Germany) electronic dilatometer in the temperature interval 20–400 °C and the microhardness with a Wolpert Wilson Instruments (Germany) apparatus. X-ray phase analysis was performed with a D8 ADVANCE (Bruker, Germany) setup. A JSM-5610 LV scanning electron microscope with an EXS JED-2201 JEOL chemical analysis system (Japan) was used to investigate the microstructure of the glaze coatings.

The antimicrobial activity tests of the glaze coatings were conducted in the laboratory of microbiology of RUE “Scientific and Practical Center of Hygiene”(Minsk, Republic of Belarus). The laboratory is accredited in the field of determination of antibacterial activity on ceramic surfaces, including tiles in accordance with ISO 22196: 2011.

**Results and discussion.** Raw composition for producing metallized glazesincluded 13–30 % fritin addition to feldspar, copper (II) oxide, dolomite, quartz, alumina, kaolin and refractory clay. The glazes of the series 1, 3 contained frit 2–154, which is used for production of transparent coatings for porcelain stoneware. The frit 2–154 includes (in %): $SiO_2$ – 46.89; (CaO + MgO) – 39.87; $B_2O_3$ – 6.45; $Al_2O_3$ – 3.46; $ZrO_2$ – 2.10; ($Na_2O$ + $K_2O$) – 1.23. For obtaining the glazes of the series 1, 4 OR frit [8] was used. Normally OR frit is part of opacified wear-resistant glazes, since it provides uniform bulk crystallization of anorthite during firing. It must be noted, for a variety of color range of coatingsiron (III) oxide was added into the glaze composition. Chemically pure iron (III) oxide and basalt were used in the glazes of the series 3 and 4 respectively. The oxide compositions of the experimental glazes are given in Table 1.

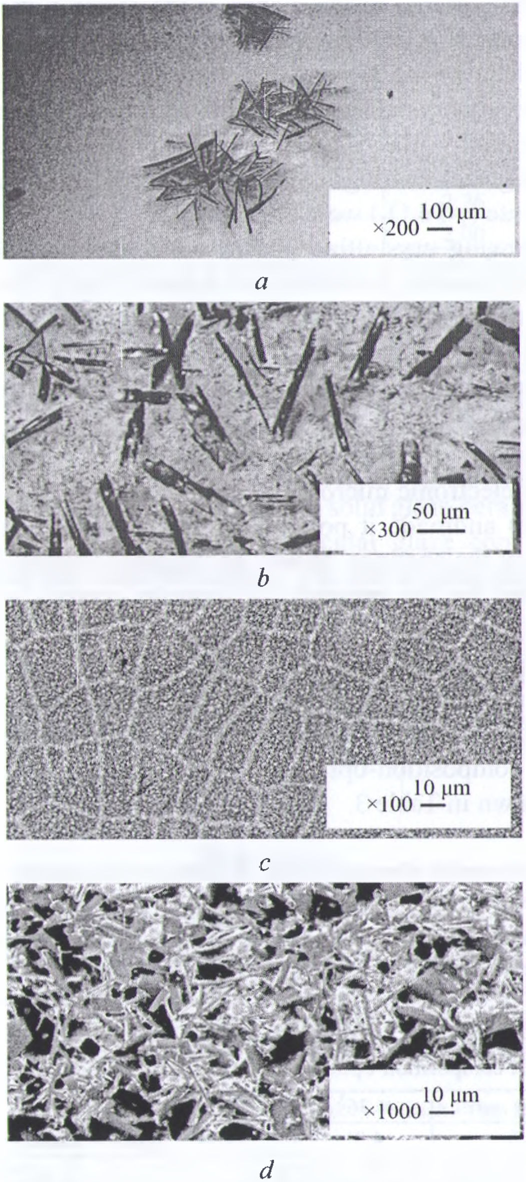
*Table 1.* **The oxide compositions of the experimental glazes**

| Oxide | Oxide ratios of the glazes of the series, % | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $SiO_2$ | 37–44 | 38–44 | 35–41 | 37–42 |
| $Al_2O_3$ | 15–17 | 21–23 | 13–15 | 19–22 |
| $(CaO+MgO)$ | 15–23 | 11–13 | 17–23 | 14–18 |
| $(Na_2O+K_2O)$ | 5–6 | 6–8 | 5–6 | 2–4 |
| $CuO$ | 11–22 | 12–22 | 10–19 | 8–15 |
| $B_2O_3$ | 1–2 | 1–2 | 1–2 | 1–2 |
| $Fe_2O_3$ | – | – | 5–7 | 5–8 |

A visual assessment of the coatings showed thathigh-quality black and dark grey glazes having a metallic shinewere obtained in the studied systems ofraw materials. The study of physical-chemical properties founded that, synthesized glaze coatings conformed to requirements of technical standards documents, as well as had high decorative effect (Table 2). In addition, all glaze coatings were chemically stable.

*Table 2.* **Physical-chemical properties and decorative-aesthetic characteristics of the glazes**

| Description | The glazes of the series | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Color | Black | Dark grey | Dark grey | Dark grey |
| Surface texture | Semi-matte, lustrous | Matte | Matte, semi-matte, lustrous | Matte, semi-matte |
| Luster, % | 45–100 | 16–31 | 5–100 | 34–43 |
| Microhardness, MPa | 3900–6100 | 5100–6800 | 5800–7800 | 5400–7100 |
| CLTE, $\alpha \cdot 10^{-7}$, Ê$^{-1}$ | 84.9–89.5 | 67.9–74.6 | 58.7–72.1 | 59.0–73.1 |
| Heat resistance, °C | 100–200 | 150–200 | 125–150 | 125–150 |
| Class of surface abrasion resistance | 1 | 2 | 1–2 | 2 |



Electronic photographs of a composition-optimized glaze coatings of the series 1 (*a*), 2 (*b*), 3 (*c*) and 4 (*d*)

The XRD patterns of the glazes of the series 1 showed tenorite ($CuO$) and anortite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). However, the presence of the amorphous halo in the X-ray diffraction patterns, along with broad and low intensity crystalline peaks indicated that the coatings contained predominantly glassy phase. Glassy phase was also predominantly in the glazes coatings of the series 3, small amounts of tenorite and maghemite ($\gamma$-$Fe_2O_3$) were also detected.

The following crystalline phases were identified in the glazes of the series 2: tenorite, anorthite and cuprite ($Cu_2O$). The phase composition of the coatings of series 4 were represented by anorthite, cuprite, and tenorite. In contrast tothe glaze sof the series 1 and 3 there was almost no the amorphous halo on the XRD patterns of the glazes of the series 2 and 4.

The data obtained in the investigation of the structure of glazes by means of electronic microscopy correlated with X-ray phase analysis (Figure) andmade it possible to establish, that dark grey and black colors of the coatings, as well as the glossy metallic appearance were provided by the presence of tenorite crystals with different habits and sizes.

Furthermore, antibacterial activity tests of glaze coatings by using were carried out with the test strain *Escherichia coli* ATCC 8739 and *Staphylococcus aureus* ATCC 6538. The antimicrobial properties of a composition-optimized glaze coatings of the series 1, 2 and 3 are shown in Table 3.

*Table 3.* **Test results of measurement of antibacterial activity on samples of glazed porcelain tiles in accordance with ISO 22196:2011**

| Test organism | Control sample | | Sample | The value of antibacterial activity |
|---|---|---|---|---|
| | at "0 h" contact time | at "0 h" contact time | at "0 h" contact time | |
| A composition-optimized glaze coating of the series 1 | | | | |
| *Staphylococcus aureus* | $4.36^{2}$ | 3.70 | 0.81 | 2.89 |
| *Escherichia coli* | 4.31 | 3.64 | 1.09 | 2.56 |
| A composition-optimized glaze coating of the series 2 | | | | |
| *Staphylococcus aureus* | 4.19 | 2.74 | 2.10 | 0.64 |

*End of table*

| Test organism | Control sample | | Sample | The value of antibacterial activity |
|---|---|---|---|---|
| | at “0 h” contact time | at “0 h” contact time | at “0 h” contact time | |
| A composition-optimized glaze coating of the series 3 | | | | |
| *Staphylococcus aureus* | 4.28 | 4.26 | 2.26 | 2.00 |
| *Escherichia coli* | 4.41 | 4.17 | 2.00 | 2.17 |
| [2]The number of viable bacteria was arithmetic means of three replicates, lg(CFU/ml) | | | | |

Lustrous glazes had a higher antimicrobial activity owing to the peculiarities of their structure. The major phase present after firingin the glazes of the series 1 and 3 was the vitreous phase as detailed above. It contained single crystals of tenorite and anorthite. Consequently, the diffusion and mobility of $Cu^{2+}$ ions in it were higher than in the glazes of the series 3, which had a solid glass-ceramic structure.

**Conclusions.** In our research biocidal glaze compositions for porcelain floor tiles were developed. The use of ceramic tiles decorated with elaborated compositions of glaze compositions will provide reliable antibacterial protection against strains of *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* ATCC 8739. The tests performed under production plant conditions at Keramin JSC (Minsk, Republic of Belarus) showed that the newly developed coatings can be used in industrial manufacturing.

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# LARGE DIAMETER SILICON CARBIDE (SiC) SINGLE CRYSTALS

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**Abstract.** Single crystal Silicon carbide (SiC) is suitable for high-temperature, high-power and aggressive environment (nuclear radiation / chemical) applications. In single crystal form, it has unique combination of physical and electronic properties such as wide band gap, high thermal conductivity, high mechanical hardness, high electric breakdown, high radiation resistance and high saturation drift velocity, which are collectively superior to those of conventional semiconductor materials such as Si and GaAs. The Johnson's figure of merit for SiC is about 100 times higher than that of GaAs or Si [1–2]. Theoretical appraisals have indicated that SiC power MOSFET's and diode rectifiers would operate over higher voltage and temperature ranges, have superior switching characteristics, and yet have die sizes are nearly 20 times smaller than correspondingly rated silicon-based