Research article

# Processes of foaming and formation of the structure of porous glass ceramics from siliceous rocks

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**Abstract.** Porous glass-ceramic materials are used in the construction and repair of industrial and civil facilities. They are produced from rocks and industrial waste. The article establishes the influence of the chemical and mineralogical composition of the charge for the production of porous glass ceramics from siliceous (zeolite-containing) rocks and corrective additives ($Mg(OH)_2$, $MgCO_3$, $Al_2O_3$) on the processes occurring during its heating. The charge was obtained by joint grinding in a planetary ball mill of siliceous rocks, soda ash and corrective additives. The influence of the charge composition on the processes occurring during its heating has been established by methods of thermal analysis (TA), X-ray phase analysis (XRD), etc. Calcite in the composition of siliceous rocks has a significant effect on the foaming process of the charge. The temperature range of foaming is reduced, and the intensity increases. The additives used have a greater influence on the crystallization process of glass ceramics. As a result, anorthoclase, wollastonite, wollastonite-combeite and diopside glass ceramics were developed. Samples of porous glass ceramics have an apparent density from 154.6 kg/m$^3$ to 298.4 kg/m$^3$, compressive strength from 0.84 MPa to 3.31 MPa, bending strength from 0.57 MPa to 1.52 MPa, maximum operating temperature from 840 °C to 870 °C. According to many physico-mechanical and thermophysical properties, the materials obtained are superior to foam glass and other analogues. They can be used as a thermal insulation material in civil and industrial construction.

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## 1. Introduction

Glass-ceramic materials are widely used in many sectors of the national economy. Porous glass-ceramic materials are widely used in the construction industry. They do not burn, have relatively high strength at low density, conduct heat poorly, do not break down when used in chemically aggressive environments and at high temperatures, and also have many other unique properties. Due to their properties, such materials are used for the construction of walls in buildings [1], they insulate facades, ceilings, basements [2, 3], are used as sound insulation materials [4]. Porous glass ceramics are used as thermal insulation of industrial furnaces [5], as well as objects that are operated in chemical aggressive environments [6] and many others.

Construction glass-ceramic materials are obtained both from natural rocks and from industrial waste. Metallurgical slags and ash are mainly used as industrial waste [2, 7, 8], glass production waste is often

used [4, 9]. Siliceous, carbonate, clay and other rocks are used as natural rocks in the production of porous glass-ceramic construction materials [10–13].

According to the literature data, the porous structure of glass-ceramic materials can be obtained in several ways [13–15]. The most widespread method is powder foaming, when the charge is ground together with gas-forming additives. Then it is poured into molds or onto a conveyor belt and fired in an oven. At a certain temperature, the charge begins to soften, and the gas-forming additive releases gas, which foams the charge. Various carbonates [14, 16], manganese oxide together with carbon [4, 17] and many others are used as gas-forming additives. The choice of a gas-forming additive depends on the temperature at which the charge begins to soften. It is very important that the charge is as homogeneous as possible in composition. As a result, preference for obtaining porous glass-ceramic materials is given to raw materials of amorphous composition (slag, ash, glass) [2, 4, 7–9]. As a consequence, it is possible to obtain glass ceramics with a uniform porous structure from natural rocks by powder foaming using a two-stage technology. At the first stage, it is necessary to cook the glass, and then the cooled glass is ground with gas-forming additives and reheated. This technology has found wide application in the production of foam glass. This material, like porous glass ceramics, has a number of unique properties. However, due to the two-stage production process, its cost is significantly higher than glass ceramics [18].

Reducing the cost of production of foam glass, as well as the development of compositions and technologies for obtaining porous glass-ceramic materials from rocks in one heating of raw materials is an important task of modern materials science. One of the solutions to this problem is the production of porous glass ceramics by the method of alkaline activation of components [11–13]. With this method, zeolite-containing rocks are mixed with a high concentration NaOH aqueous solution, granulated and fired. As a result, a porous glass-ceramic material in the form of granules was obtained in one heating of the charge without the use of additional foaming components. The literature describes in detail the mechanism by which the foaming of the material occurs. When heated, zeolite group minerals are dehydrated in the charge and surface hydroxyl groups are clogged in micropores [12, 19]. With a further increase in the heating temperature, the charge softens, and the hydroxyl groups condense with the release of water vapor, which forms a porous structure of the material. However, during the production of porous glass ceramics using this technology, equipment quickly wears out as a result of exposure to alkalis, and harmful substances are released into the atmosphere [20]. Because of this, this technology has not found wide application.

In our early works, a method for obtaining porous glass ceramics in one heating of a charge from siliceous (zeolite-containing) rocks by powder foaming was proposed [21, 22]. Pre-dried siliceous rock with a zeolite content of no more than 25% was ground together with soda ash or thermonatrite in a planetary ball mill. The resulting charge was poured into molds or onto a conveyor belt and fired. As a result, glass-ceramic materials with a uniform fine-porous structure were obtained, which surpass foam glass in many properties. We have described the mechanisms that occur in the charge during grinding, as well as when it is heated [23]. However, the presented mechanisms and dependencies were obtained using a siliceous rock of the same chemical and mineralogical composition. It is known that rocks, including siliceous (zeolite-containing) rocks, have different chemical and mineralogical composition [12, 24]. Samples of porous glass ceramics obtained from different raw materials have different structure, phase composition and properties [22]. For example, with an increase in the composition of glass ceramics $Fe_2O_3$ and $CaO$, the limiting temperature of its operation decreases [7, 25], and with an increase in the amount of $Al_2O_3$, on the contrary, increases [26]. $MgO$ in the composition of glass ceramics radically changes its phase composition [27, 28]. Impurities (for example, $NaCl$) that enter the glass ceramics together with the fins can also affect the structure and properties of the material [21]. The influence of the composition of the charge for porous glass ceramics from siliceous rocks on the processes occurring during its heating has not been sufficiently studied in the literature. Therefore, the purpose of the study is to establish the influence of the chemical and mineralogical composition of the charge of siliceous (zeolite-containing) rocks and corrective additives on the processes of foaming and crystallization of porous glass ceramics samples during heating.

Tasks:

– by thermal (TA), X-ray phase (XRD) and other methods of analysis to establish the effect of $CaCO_3$, $Mg(OH)_2$, $MgCO_3$, $Al_2O_3$ in the composition of the charge mixture on the phase transformations in it during heating, as well as the temperature intervals of its foaming;

– to determine the effect of $CaO$, $MgO$, $Al_2O_3$ on the temperature ranges of crystallization and the phase composition of glass ceramic samples by the X-ray method;

– to establish the effect of the charge composition on the properties of porous glass ceramics samples.

## 2. Methods

### 2.1. Materials

The following components were used for experimental studies: siliceous rocks (zeolite-containing tripoli from three deposits and diatomite), calcined soda and corrective additives (magnesium hydroxide, magnesium carbonate, aluminum oxide and potassium chloride). The characteristics of the components are presented below. The chemical and mineralogical composition of siliceous rocks is given in Tables 1 and 2.

**Table 1. The chemical composition of the rocks.**

| Composition No. | Chemical composition, % mass | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | CaO | $Al_2O_3$ | $Fe_2O_3$ | $K_2O$ | MgO | $TiO_2$ | $Na_2O$ | $SO_3$ | Other |
| R1 | 70.9 | 2.4 | 12.4 | 3.5 | 1.7 | 1.7 | 0.5 | 0.1 | 0.0 | 6.8 |
| R2 | 67.9 | 7.7 | 7.6 | 2.0 | 1.6 | 1.1 | 0.3 | 0.2 | 0.1 | 11.5 |
| R3 | 62.3 | 11.3 | 6.7 | 2.0 | 1.4 | 0.9 | 0.3 | 0.1 | 0.0 | 15.0 |
| R4 | 81.5 | 1.5 | 5.3 | 2.0 | 1.0 | 0.9 | 0.3 | 0.2 | 1.8 | 5.5 |

**Table 2. The mineralogical composition of the rocks.**

| Composition No. | Mineralogical composition, % mass | | | | | | |
|---|---|---|---|---|---|---|---|
| | Quartz | Calcite | Heulandite | Muscovite | Cristobalite | Tridymite | Amorphous phase |
| R1 | 27.8 | 0.0 | 18.6 | 16.1 | 16.2 | 1.3 | 20.0 |
| R2 | 10.8 | 12.8 | 19.2 | 14.4 | 21.1 | 1.7 | 20.0 |
| R3 | 8.5 | 21.3 | 19.6 | 9.9 | 19.2 | 1.5 | 20.0 |
| R4 | 10.9 | 0.0 | 0.0 | 8.1 | 0.0 | 0.0 | 80.0 |

- Soda ash ($Na_2CO_3$) with a concentration of the main substance in the composition of more than 99 %.
- Corrective additives: Magnesium hydroxide ($Mg(OH)_2$), magnesium carbonate ($MgCO_3$), aluminum oxide ($Al_2O_3$), potassium chloride (KCl) with a concentration of the main substance in the composition of more than 97 %.

### 2.2. Compositions and fabrication of samples

In the work, the 6 composition of the charge for the production of porous glass ceramics was studied. The compositions are given in Table 3.

**Table 3. Charge compositions.**

| Composition No. | Composition of the charge, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Rock R1 | Rock R2 | Rock R3 | Rock R4 | $Na_2CO_3$ | $Mg(OH)_2$ | $MgCO_3$ | $Al_2O_3$ | KCl |
| C1 | 81.5 | – | – | – | | – | – | – | |
| C2 | – | 81.5 | – | – | | – | – | – | |
| C3 | – | – | 81.5 | – | 18.2 | – | – | – | 0.3 |
| C4 | – | – | 63.5 | 15 | | 3 | – | – | |
| C5 | – | – | 62.1 | 15 | | – | 4.4 | – | |
| C6 | – | – | 60.5 | 15 | | 3 | – | 3 | |

The charge was prepared as follows. The components were dried to a moisture content of no more than 1 %, dosed (according to Table 3) and ground together in a Retsch PM 400 planetary ball mill (Germany) for 30 minutes at overloads inside the mill cups equal to 20g.

### 2.3. Analytical techniques

The phase transformations occurring in the charge during heating were determined by thermal analysis methods: differential thermal analysis (DTA) and differential thermogravimetry (DTG). The studies were performed on the TGA/DSC1 device (Switzerland) according to the following methodology. A charge weighing 20±0.1 mg was poured into an alund crucible with a volume of 150 µl. The crucible together with the charge was placed in the device and heated at a speed of 10 °C/min from 30 to 850 °C, and then cooled at a speed of 10 °C /min to 30 °C. The device recorded changes in the mass and temperature of the sample. The experimental data obtained were processed using the STARe software (Mettler-Toledo, Switzerland).

The temperature intervals of foaming of the charge for porous glass ceramics were determined on samples of cylinders with a diameter of 12±0.1 mm and a height of 12±1 mm according to the following procedure. The samples were made by pressing the charge (weight 5 g) in a mold under a pressure of 1 MPa. The resulting cylinder samples were mounted vertically on a ceramic plate and placed in a muffle furnace. In the furnace, the samples were fired at a speed of 6 °C/min to a set temperature and kept at a maximum temperature for 10 minutes. After the samples cooled down together with the furnace to room temperature, their photofixation was carried out and the apparent density of the samples was determined. The arithmetic mean of the test results of three samples of each composition was taken as the final result.

The change in the phase composition of the charge during heating, as well as the beginning and end of crystallization of glass ceramic samples were determined by X-ray phase analysis. The studies were performed on an Empyrean PANalytical device (Netherlands) with a PIXcel$^{3D}$ semiconductor detector. A thin layer of 15 g of charge was poured onto a rectangular ceramic plate with dimensions of 150×150×5 mm. The plate with the sample was placed in a muffle furnace and heated at a speed of 6 °C/min to a predetermined temperature and kept at a maximum temperature for 10 minutes. In order to fix the phase composition of the charge at a given temperature, it was quickly removed from the furnace, transferred from a ceramic plate to a rectangular steel plate with dimensions of 300×300×50 mm and covered with a second steel plate with dimensions of 300×300×20 mm. After complete cooling of the charge, it was crushed in an agate mortar with an agate pestle to a fraction <90 microns. The obtained powders were examined on an Empyrean PANalytical device in the mode of linear scanning by a detector in CuK$_\alpha$ radiation in the range of angles $2\theta$ = 5–55°. The sampling rate is 0.0131 °/minute with an integration time at each point of 150 seconds. The phase composition of the samples was determined by the Hanawalt method using an open database of crystallography.

The method of determining the physical and mechanical properties (apparent density, bending and compressive strength) and thermophysical properties (thermal conductivity coefficient and operating temperature limit) of porous glass ceramics samples is presented in detail in our previous work [22].

# 3. Results and Discussion

## 3.1. Phase transformations in the charge during heating and temperature intervals of its foaming

The processes occurring in the charge during heating are determined by the methods of thermal analysis (DTA and DTG) and X-ray phase analysis (XRD). The obtained thermograms of the charge samples are shown in Fig. 1.
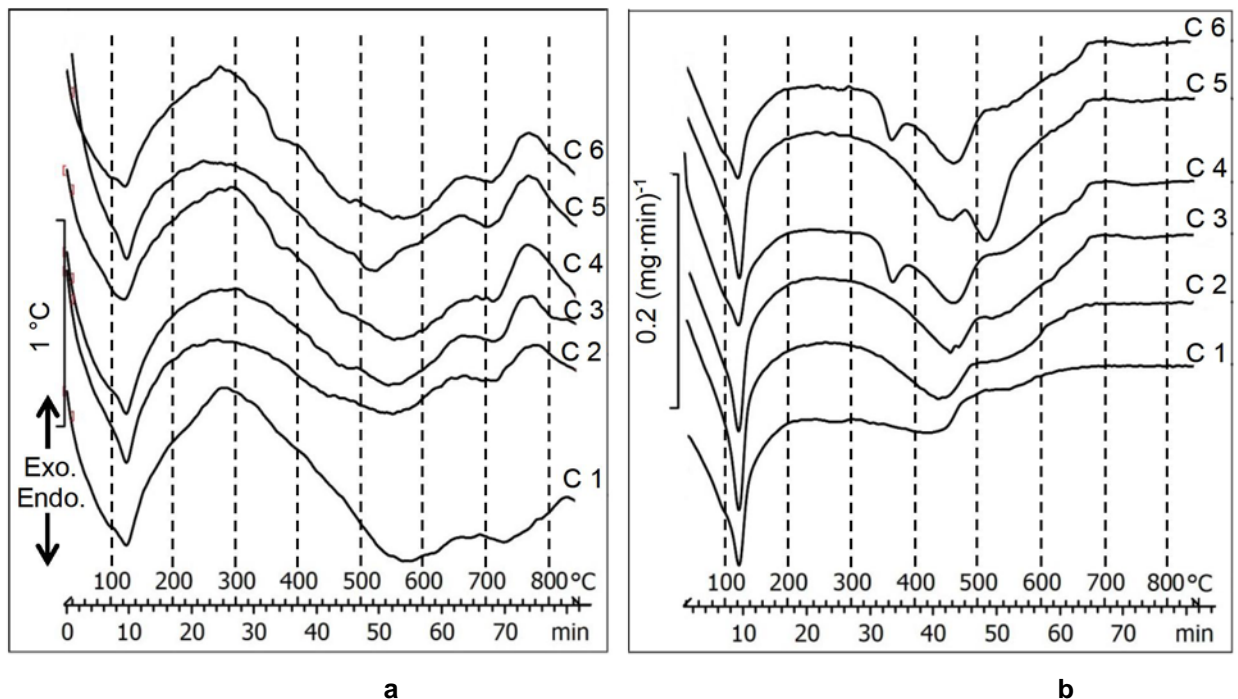


**Figure 1. DTA (a) and DTG (b) curves of charge mixture samples.**

As a result of the mechanochemical activation of a charge mixture of siliceous rocks, soda ash and additives, a new mineral wegscheiderite ($Na_5[CO_3](HCO_3)_3$) is formed in it. The presence of this mineral in all the studied charge samples is evidenced by the endothermic effect and mass loss of samples with a

maximum at a temperature of ≈120 °C (Fig. 1). This conclusion is confirmed by the results of the XRD of the charge before and after its firing at a temperature of 200 °C (Fig. 2). According to Fig. 2, the X-ray image of the charge sample (C3) shows the lines characteristic of the wegscheiderite mineral [$Na_5[CO_3](HCO_3)_3$, Code: 96-900-7682] before firing, and after firing them at a temperature of 200 °C, the lines disappeared. Similar data were obtained from the results of the X-ray analysis of all the studied samples of the charge mixture (X-ray patterns are not given). According to literature sources, decomposition of sodium hydrosilicates is also possible in the charge mixture for glass ceramics from siliceous rocks in this temperature range [12]. As a result of our research (Fig. 1 and 2), this conclusion was not confirmed.
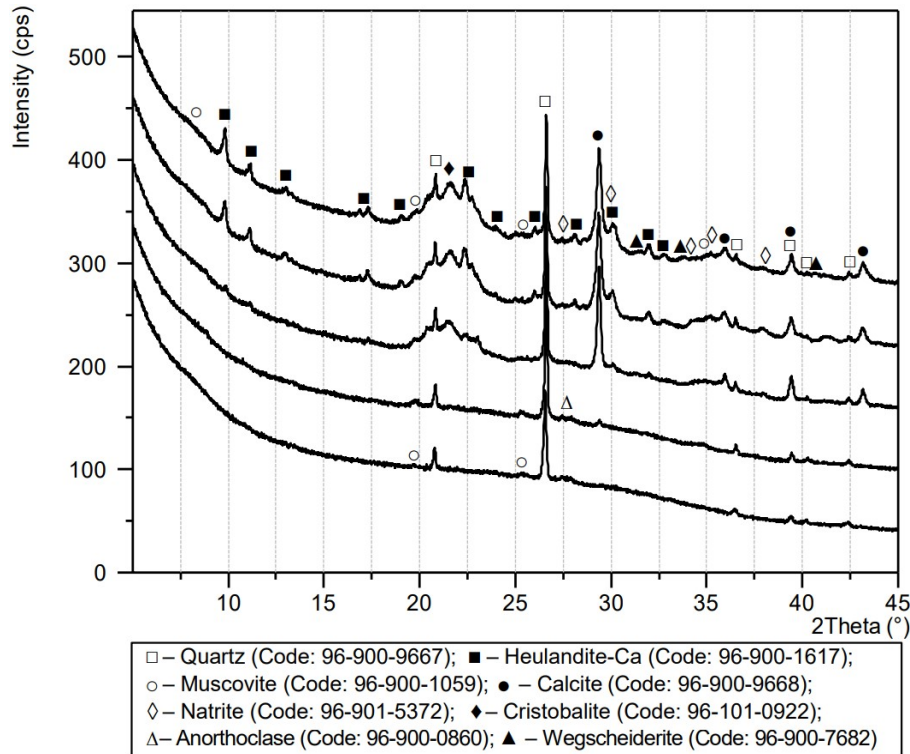


**Figure 2. X-ray patterns of a sample of charge C3 after firing at different temperatures.**

As a result of the conducted research (Fig. 1 and 2), the temperature ranges of decomposition of the minerals of the charge mixture were established. The endothermic decomposition reaction of sodium began at a temperature of ≈300 °C and ended up to 500 °C. Calcite decarbonization, on the contrary, began intensively at a temperature of >500 °C, and ended at 670 °C. This is evidenced by a gradual decrease in the X-ray lines characteristic of natrite [$Na_2CO_3$, Code: 96-901-5372] and calcite [$CaCO_3$, Code: 96-900-9668]. The endothermic effect and mass loss in charge samples C4 and C6 in the temperature range from 350 °C to 370 °C is associated with dehydration of $Mg(OH)_2$. $MgCO_3$ in the C5 sample was decarbonized in the temperature range from 460 °C to 560 °C. Dehydration of the heulandite mineral (endoeffect) in all samples, the charge was completed at a temperature of ≈500 °C (Fig. 1), which is confirmed by the results of the XRD (Fig. 2). On the X-ray of the charge samples after firing at 450 °C, the lines characteristic of the heulandite mineral [$Na_{1.30}K_{0.12}Ca_{3.70}(Si_{27.11}Al_{8.89})O_{72.76}\times24H_2O$, Code: 96-900-1617] are practically absent. The endothermic decomposition reaction of muscovite in all charge samples began at temperatures up to 450 °C and continued up to >700 °C. The X-ray pattern of the charge mixture samples after firing at a temperature of 700 °C preserved muscovite lines [$KAl_2(Si_3Al)O_{10}(OH)_2$, Code: 96-900-1059] of weak intensity.

According to literature sources, when firing a charge mixture for glass ceramics from zeolite-containing rocks to a temperature of ≈670 °C, it is compacted with blockage in micropores of surface hydroxyl groups (Si–O–H). With a further increase in temperature, the charge mixture begins to soften, and the hydroxyl groups condense into water vapor and foam it [12, 23]. The beginning of softening of all the samples studied by us from the charge with calcite in the composition began at a temperature of ≈660 °C (C2–C6), and without calcite ≈680 °C (C1). The beginning of the endothermic effect without loss of mass in the samples was recorded on the DTA curves (Fig. 1). This endoeffect is associated with an increase in the heat capacity of an amorphous material as a result of its softening. At the temperature of the beginning of softening of the charge mixture, the process of its foaming begins. The foaming component is most likely water vapor condensed from hydroxyl groups of the mineral muscovite. As noted above, after firing the charge mixture at a temperature of 700 °C, the lines of this mineral were preserved on the X-ray pattern (Fig. 2). As a result of foaming, the charge mixture increases in volume, and the thermal conductivity of the

sample decreases. Consequently, its heat absorption coefficient decreases. On the thermograms (Fig. 1a), the DTA curves are directed upwards. According to the maxima of thermal effects, it is possible to determine the temperature of the completion of the foaming process. A further increase in the firing temperature of the charge samples led to the stabilization of the heat flow. DTA curves are directed downwards.

With an increase in the amount of calcite in the charge mixture, the foaming intensity increases, and the process completion temperature decreases. According to Fig. 1a, the samples of the charge mixture without calcite in the composition (C1) continue to foam slowly to a temperature of ≈825 °C. Foaming of charge samples (C3–C6) from the rock with the maximum amount of calcite (R3, calcite 21.3 %) was completed at a temperature of ≈750 °C. It was not possible to establish the effect of corrective additives ($Mg(OH)_2$, $MgCO_3$, $Al_2O_3$) in the composition of the charge mixture on the intensity and temperature intervals of its foaming by thermal and X-ray phase analysis.

Visual confirmation of the influence of the chemical and mineralogical composition of the charge mixture on the sintering processes and the temperature intervals of its foaming are given below. The study was performed on cylindrical samples with a diameter of 12±0.1 mm and a height of 12±1 mm according to the procedure described above. Fig. 3 shows a photo of cylindrical samples before and after firing.
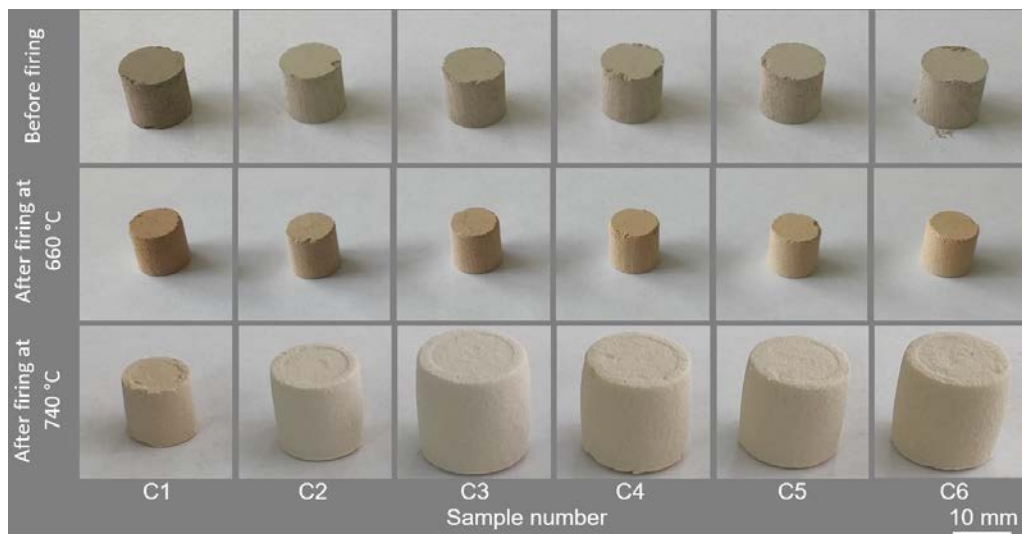


**Figure 3. Photos of samples before and after firing.**

It can be seen that the charge of siliceous rocks, soda ash and corrective additives after firing at a temperature of 660 °C was sintered (Fig. 3). The volume of cylindrical samples decreased by almost 3 times. The color of the samples changed from light gray to light brown. The photo after firing the charge at a temperature of 740 °C shows already foamed cylindrical samples. The volume of samples increased to varying degrees depending on the composition. The dependences of the change in the apparent density of the charge samples on the firing temperature are shown in Fig. 4. The results of the studies are presented in the temperature range from 620 °C to 840 °C.
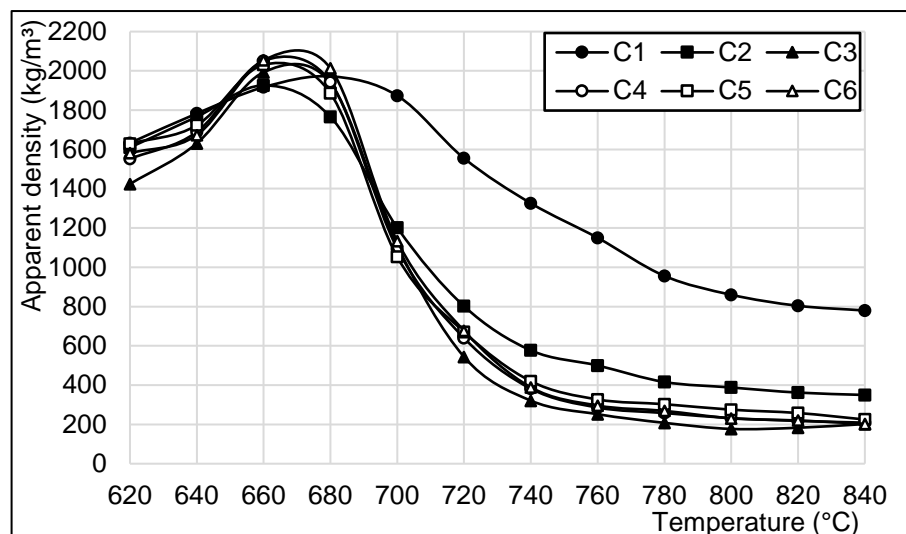


**Figure 4. Change in the apparent density of samples from the firing temperature**

According to the data (Fig. 4), it was found that with an increase in the firing temperature of cylindrical charge samples with calcite in the composition from 620 °C to 660 °C (C2–C6) and without calcite to 680 °C (C1), their apparent density increased on average from 1570 kg/m³ to 2000 kg/m³. A further increase in the firing temperature to 760 °C led to a sharp decrease in the apparent density of charge samples with an increased calcite content (C3–C6) to ≈300 kg/m³. With an increase in the firing temperature of a sample without calcite in the composition (C1) to 820 °C, its apparent density slowly decreases to ≈800 kg/m³. The obtained results are consistent with the data of thermal and X-ray phase analysis of charge samples. Foaming of charge samples with calcite in the composition begins at a temperature of 660 °C. The process proceeds intensively and ends at a temperature of ≈760 °C. Charge samples without calcite in the composition are foamed slowly in the temperature range of 680–820 °C. Additives used in the work as part of the charge mixture (Mg(OH)$_2$ ≤3 %, MgCO$_3$ ≤4.4 %, Al$_2$O$_3$ ≤3 %) do not significantly affect the foaming processes when it is heated.

### 3.2. Temperature ranges of crystallization and phase composition of glass ceramic samples

The influence of the chemical and mineralogical composition of the charge on the temperature intervals of crystallization of porous glass ceramics samples is shown in Fig. 5.
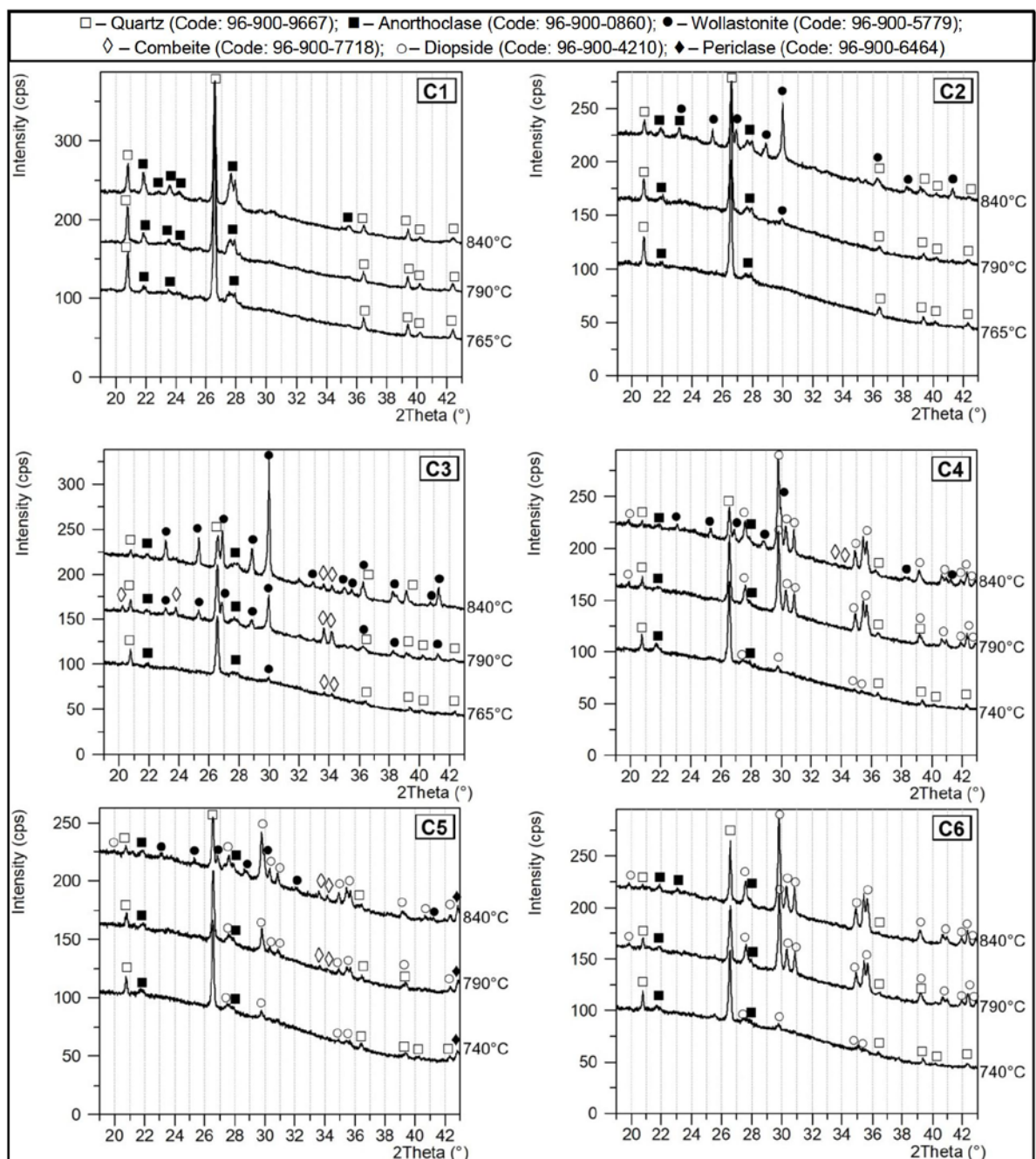


**Figure 5. X-ray patterns of glass ceramic samples after firing at different temperatures.**

According to the data obtained (Fig. 5), all fired charge samples consist of an amorphous and crystalline phase. The presence of an amorphous phase is characterized by a non-monotonic change in the background on all X-ray patterns in the range of angles up to 37° (2θ). The amount of amorphous phase decreased slightly with an increase in the firing temperature of the charge. The influence of the chemical and mineralogical composition of the charge on the change in the amorphous phase of glass ceramics has not been established.

The crystal phase of glass ceramic samples from siliceous rock R1 (without calcite and corrective additives) consists of quartz [$SiO_2$, Code: 96-900-9667] and anorthoclase [$(Na_{0.85}K_{0.15})(AlSi_3O_8)$, Code: 96-900-0860] (Fig. 5 C1). The presence of quartz in C1 glass ceramics is due to its presence in large quantities in the rock. Anorthoclase, according to Fig. 2, begins to crystallize in glass ceramics at a temperature of ≈600 °C. The amount of this mineral increased almost linearly with an increase in the firing temperature of the samples to 840 °C. When firing porous glass ceramics C2 from siliceous rock R2 (12.8 % calcite) at a temperature of ≈790°C the wollastonite phase additionally begins to form [$CaSiO_3$, Code: 96-900-5779]. The temperature of the beginning of crystallization of wollastonite decreased to 765 °C with an increase in the amount of calcite (C3) in the charge mixture. In parallel with wollastonite, combeite also begins to crystallize at a temperature of 765 °C [$Na_2Ca_2Si_3O_9$, Code: 96-900-7718]. On the X-ray of the C3 sample after firing at a temperature of 840 °C, the intensity of the combeite lines decreased, and wollastonite sharply increased. This indicates the recrystallization process in the material. This is also confirmed by the exothermic effect on the DTA curve of sample C3 (Fig. 1a) with a maximum at a temperature of 830–840 °C. In earlier studies, we found an increase in open porosity to >70% in glass ceramic samples with an increase in the composition of the calcite charge mixture [21, 22]. Which may also be a consequence of the recrystallization process in the material.

When magnesium-containing additives ($Mg(OH)_2$ are introduced into the charge mixture and $MgCO_3$) the crystallization process of glass ceramics differs from additive-free formulations (C4–C6). Instead of wollastonite in the material at a temperature of 740°C diopside begins to form [$Mg_{0.56}Ca_{0.44}SiO_3$, Code: 96-900-4210]. The process of crystallization of this mineral in samples with the addition of $Mg(OH)_2$ (C4 and C6) was almost completely completed at a temperature of 790 °C, and in samples with the addition of $MgCO_3$) – at 840 °C. Periclase crystallizes in parallel with diopside in samples of glass ceramics from the charge with the addition of $MgCO_3$ [MgO, Code: 96-900-6464]. With an increase in the firing temperature of samples C4 and C5 to 840 °C on the X-ray patterns (Fig. 5 C4 and C5), the intensities of the diopside lines did not change and additionally there were lines of wollastonite and combeite of low intensity. This effect was not observed when the charge was simultaneously introduced into the composition with magnesium-containing additives $Al_2O_3$ (Fig. 5 C6). According to the data obtained, it can be concluded that in diopside glass ceramics from siliceous rocks, the recrystallization of diopside into wollastonite does not occur. Wollastonite and combeite are formed as a result of crystallization of the amorphous phase. This effect can be prevented by introducing $Al_2O_3$ additives into the charge mixture. The data obtained correlate with the results of studies on the production of glass-ceramic materials from fly ash and industrial waste [27, 28].

### 3.3. Properties of porous glass ceramics samples

The physico-mechanical and thermophysical properties of porous glass ceramics samples from siliceous rocks of different chemical and mineralogical composition, soda ash and corrective additives ($Mg(OH)_2$, $MgCO_3$, $Al_2O_3$) are shown in Table 1.

**Table 4. Properties of porous glass ceramics samples.**

| Composition No. | Properties | | | | |
|---|---|---|---|---|---|
| | Apparent density, kg/m$^3$ | Compressive strength, MPa | Bending strength, MPa | Coefficient of thermal conductivity, W/m·°C | Maximum operating temperature, °C |
| C1 | 298.4 | 3.31 | 1.52 | 0.080 | 870 |
| C2 | 252.6 | 3.3 | 1.25 | 0.067 | 860 |
| C3 | 174.2 | 1.83 | 1.03 | 0.057 | 840 |
| C4 | 158.7 | 0.9 | 0.65 | 0.055 | 850 |
| C5 | 208.6 | 2.25 | 0.94 | 0.063 | 850 |
| C6 | 154.6 | 0.84 | 0.57 | 0.054 | 870 |

The chemical and mineralogical compositions of siliceous rocks and corrective additives have a significant effect on the apparent density of porous glass ceramic samples. With an increase in the amount of calcite in the composition of siliceous rocks to 21.3 %, the apparent density of glass ceramic samples decreased from 298.4 kg/m$^3$ to 174.2 kg/m$^3$. When 3 % $Mg(OH)_2$ was introduced into the charge mixture,

as well as 3 % $Al_2O_3$ together with it, the apparent density of glass ceramic samples decreased further to 158.7 kg/m³ and 154.6 kg/m³, respectively.

The bending and compressive strength, as well as the thermal conductivity coefficient of porous glass ceramic samples are linearly dependent on their apparent density. The effect of magnesium-containing additives and $Al_2O_3$ on these properties has not been established. The highest bending strength (1.52 MPa) and compression strength (3.31 MPa), as well as the coefficient of thermal conductivity (0.080 W/m·°C) samples of composition C1 (apparent density 298.4 kg/m³). The lowest bending strength (0.57 MPa) and compression strength (0.84 MPa), as well as the coefficient of thermal conductivity (0.054 W/m·°C) in C6 samples with the lowest apparent density of 154.6 kg/m³.

The dependence of the maximum operating temperature of porous glass ceramics samples on their phase composition is established. Anorthoclase glass ceramics (C1) and diopside glass ceramics (C6) can be operated at a maximum temperature of up to 870 °C, and wollastonite glass ceramics (C2) – up to 850 °C. With an increase in the amount of the mineral combeite in the glass ceramic samples, the maximum temperature of their operation decreases to 840 °C. This is probably due to the recrystallization of combeite into wollastonite, the process of which is described above. According to the physicomechanical and thermophysical properties, the developed porous glass ceramics from siliceous rocks surpasses many analogues [1, 2, 4, 29, 30].

## 4. Conclusions

Porous glass-ceramic materials were obtained by powder foaming from a charge based on siliceous rocks of different chemical and mineralogical composition, soda ash and corrective additives ($Mg(OH)_2$, $MgCO_3$ and $Al_2O_3$). The components of the charge mixture were ground together in a planetary ball mill and fired. Thermal, X-ray phase and other analysis methods have established the effect of additives, as well as the chemical and mineralogical composition of siliceous rocks on the processes of foaming and crystallization of porous glass ceramics samples during heating:

- Sintering of charge mixture samples without calcite in the composition is completed at a firing temperature up to ≈680 °C, and with calcite and additives up to ≈660 °C. With an increase in the firing temperature of the charge before sintering, the amount of amorphous phase in the sample increases. A further increase in the firing temperature leads to softening of the amorphous phase and foaming of the charge. The foaming component is most likely water vapor condensed from hydroxyl groups of the mineral muscovite. Charge samples without calcite and corrective additives in the composition are foamed slowly in the temperature range of 680–820 °C. Foaming of charge samples with calcite begins at a temperature of ≈660 °C. The process proceeds intensively and ends at a temperature of ≈760 °C. Additives used in the work as part of the charge mixture ($Mg(OH)_2$ ≤3 %, $MgCO_3$ ≤4.4 %, $Al_2O_3$ ≤3 %) do not significantly affect the foaming processes when it is heated.

- The chemical and mineralogical composition of the siliceous rock, as well as additives ($Mg(OH)_2$, $MgCO_3$ and $Al_2O_3$) in the charge mixture have a significant effect on the temperature ranges of crystallization and the phase composition of porous glass ceramic samples. From a charge mixture based on siliceous rocks and soda ash without calcite and additives, anorthoclase porous glass ceramics were obtained, from rocks with calcite – wollastonite and wollastonite-combeite glass ceramics. When magnesium-containing additives are introduced into the charge mixture, diopside glass ceramics crystallizes. The crystallization process of diopside porous glass ceramics is completed at a temperature of ≈790 °C, which is 50 °C less than for anorthoclase glass ceramics.

- Porous glass ceramics have been developed with an apparent density from 154.6 kg/m³ to 298.4 kg/m³, compressive strength from 0.84 MPa to 3.31 MPa, bending strength from 0.57 MPa to 1.52 MPa, with a maximum operating temperature from 840 °C to 870 °C. $CaCO_3$, $Mg(OH)_2$ and $Al_2O_3$ together with $Mg(OH)_2$ as part of a charge mixture of siliceous rocks and soda ash contribute to a decrease in the apparent density of glass ceramic samples. An increase in the composition of glass ceramics of the mineral combeite leads to a decrease in the maximum operating temperature of the material to 840 °C.

- The developed porous glass-ceramic materials are recommended to be used as a structural thermal insulation material in the construction of residential buildings and industrial facilities, as well as thermal insulation of various industrial equipment (melting boilers, furnaces, etc.) and pipelines.

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