Structure and properties of porous glass ceramics from siliceous rocks with the addition of Mg(OH)₂

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Abstract. Porous glass-ceramic materials are widely used in the construction, reconstruction and repair of objects for various purposes. The article establishes the influence of $Mg(OH)_2$ and together with Al_2O_3 in the composition of a charge of siliceous rocks and soda ash on the structure and properties of porous glass-ceramic materials. A joint mechanochemical activation of the components was carried out in a planetary ball mill, and then the resulting charge was fired at a maximum temperature of 825 °C. The influence of the type and quantity of additives on the structure and properties of porous glass ceramics was established by thermal analysis (TA), X-ray phase analysis (XRD), etc. From the charge with the addition of $Mg(OH)_2$ in glass ceramics, instead of wollastonite, diopside is formed, and instead of devitrite, combeite is formed. The influence of the phase composition of the samples on their properties has been established. The developed porous glass ceramics has an apparent density of 135-235 kg/m³, bending and compressive strength up to 1.6 and 4.2 MPa, respectively, a thermal conductivity coefficient of 0.05-0.067 W/m·°C, thermal resistance of 170 °C, maximum operating temperature up to 870 °C, high chemical resistance. The developed materials are superior in many respects to foam glass and other analogues and can be used in the insulation of industrial and civil facilities.

Keywords: glass ceramic; construction material; thermal insulation; siliceous rocks; $Mg(OH)_2$; compressive strength; thermal conductivity

Introduction

Foam glass and porous glass-ceramic materials have a range of unique properties. They are light, durable, do not burn, have good thermal and acoustic insulating properties, high chemical resistance, etc. [1,2]. They are used in the construction, reconstruction and repair of walls of buildings and structures [3]. They insulate the structures of the floor, roof, and facades [2]. These materials have proved efficient in finishing works [4]. Porous glass ceramics are widely used in industry as refractory thermal insulation materials [5], anticorrosive materials [6], acoustic insulation of industrial equipment [7], etc.

Glass-ceramic materials made of solid waste are often used in construction of buildings and structures [7,8]. Numerous studies were aimed at developing compositions and technologies for obtaining porous glass ceramics from different types of industrial waste: ferrous and non-ferrous slags [4,9,10], red mud [11], fly ash [1,2,12,13], etc. A separate group of building materials includes glass ceramics from siliceous rocks (diatomite, tripoli,

opoka) [14–17]. Depending on the raw materials used, porous glass-ceramic materials are obtained using different technologies: by foaming colloidal suspension [18], powder method [1,2], etc. Foaming components are added to the charge to form the porous structure of the resulting glass-ceramic material with such production methods: carbonates [1,2,19], carbon with various additives [3,20], etc. Glass ceramics for construction is obtained from siliceous rocks mainly by the method of alkali activation of components followed by annealing [14,15]. This production method does not require foaming components. This technology yielded good results in the production of granular material. In our early works, we described the specifics of obtaining block-shaped porous glass ceramics from zeolite-containing tripoli [21–23]. Combined mechanochemical activation of dry components (tripoli and soda ash) was carried out at the first stage, and then the resulting charge was annealed at a temperature of no more than 850 °C. The charge foams and crystallizes during annealing. The obtained block-shaped materials have a homogeneous fine structure, low density, relatively high strength, high chemical resistance, elevated service temperature, etc.

The chemical and mineralogical composition of raw materials as well as the production technology have a direct impact on the composition, structure and properties of the resulting glass-ceramic material [15,19]. The chemical and mineralogical composition of the charge components affects the structure and phase composition of glass ceramics, which in turn affect the properties of the finished product. Several studies discovered found that the density of glass ceramics from industrial waste is significantly influenced by the amount of CaO in the composition of the material. The density of the material increases with an increase in CaO fraction [24,25]. The strength properties of glass ceramics improve with an increase in of Al$_2$O$_3$ content in the charge composition [26]. A similar effect was also established for an increase of Fe$_2$O$_3$ in the composition of the material [27]. The maximum service temperature of glass ceramics sharply decreases with an increased content of Na$_2$O, Fe$_2$O$_3$ and CaO in the charge [28,29]. The reverse effect was established with an increase in Al$_2$O$_3$ content in the charge composition [29,30].

We established the influence of chemical and mineralogical composition of charge prepared from siliceous rocks and soda ash on the structure and properties of porous glass-ceramic materials in our earlier studies. A homogeneous fine structure of glass-ceramic materials from siliceous rocks with a high calcite content in the composition was obtained by introducing a small amount of chlorides into the charge [21]. The phase composition of glass ceramics has practically not changed. A large amount of mineral nepheline is produced when porous glass ceramics are prepared from siliceous rocks with a high aluminum oxide content in the charge, increasing the resistance of the material to sudden temperature variations and its maximum service temperature from 850 to 930 °C, but decreasing the chemical resistance of the samples [22]. No results are available in the literature for the combined effect from introducing Mg(OH)$_2$ and it Al$_2$O$_3$ into charge composition on the structure and properties of porous glass ceramics from siliceous rocks and soda ash.

The goal of the study was to establish the combined effect of magnesium hydroxide and aluminum oxide in the composition of a mechanochemically activated charge from siliceous rocks and soda ash on the structure and properties of porous glass-ceramic materials.

Objectives:
– to determine the combined effect of Mg(OH)$_2$ and Al$_2$O$_3$ on the phase transformations in the charge under heating and the phase composition of annealed porous glass ceramics by thermal analysis (TA) and X-ray diffraction phase analysis (XRD);
– to establish the effect of additives in the charge composition on the macrostructure of porous glass ceramics;

– to determine the effect of phase composition and macrostructure of porous glass ceramic samples on their physico-mechanical and thermophysical properties, as well as chemical resistance.

Methods

Materials. The following components were used for experimental studies: siliceous rocks (zeolite-containing tripoli and diatomite), soda ash, magnesium hydroxide, aluminum oxide and potassium chloride. Characteristics of the components:

– Zeolite-containing tripoli from Engalychevskoye deposit (Russia, Republic of Mordovia) with the following chemical composition: 62.35 % SiO_2, 11.27 % CaO, 6.67 % Al_2O_3, 2.05 % Fe_2O_3, 1.38 % K_2O, 0.94 % MgO, 0.30 % TiO_2, 0.10 % Na_2O, 0.18 % P_2O_5, 0.03 % SO_3, 0.06 % SrO, 14.67 % PPP. Mineralogical composition of the rock: 19.2 % cristobalite; 19. 6 % heulandite; 8.5 % quartz; 21.3 % calcite; 9.9 % muscovite; 20.0 % amorphous phase. The rock was dried to a moisture content of less than ≤ 2 % and crushed to a fraction of ≤ 5 mm.

– Diatomite from Atemarskoye deposit (Russia, Republic of Mordovia) with the following chemical composition: 81.56 % SiO_2, 1.51 % CaO, 5.35 % Al_2O_3, 2.05 % Fe_2O_3, 0.97 % K_2O, 0.89 % MgO, 0.25 % TiO_2, 0.20 % Na_2O, 1.76 % SO_3, 1.46 % PPP. Mineralogical composition of the rock: 10.9 % quartz, 8.1 % muscovite, 80.0 % amorphous phase. The diatomite was dried to a moisture content of ≤ 2 % and crushed to a fraction of ≤ 5 mm.

– Soda ash (Na_2CO_3) with the main ingredient concentration of more than 99 %.

– Magnesium hydroxide ($Mg(OH)_2$) with the main ingredient concentration of more than 97 %.

– Aluminum oxide (Al_2O_3) with the main ingredient concentration of more than 97 %.

– Potassium chloride (KCl) with the main ingredient concentration of more than 97 %.

Sample compositions and preparation procedure At the first stage, dosing and combined mechanochemical activation of components (siliceous rocks, soda ash, magnesium hydroxide, aluminum oxide and potassium chloride) were carried out in a Retsch PM 400 planetary ball mill. Activation mode: overload inside mill cups was 20 g, duration 30 min. The required number of components for each charge composition is taken in accordance with Table 1.

Table 1. Charge compositions

Composition	Charge composition, %					
	Zeolite-containing tripoli	Diatomite	Na_2CO_3	$Mg(OH)_2$	Al_2O_3	KCl
C1	76.5	5.0		–	–	
C2	75.0	5.0		1.5	–	
C3	73.5	5.0		3.0	–	
C4	71.5	10.0		–	–	
C5	70.0	10.0		1.5	–	
C6	68.5	10.0	18.2	3.0	–	0.3
C7	66.5	15.0		–	–	
C8	65.0	15.0		1.5	–	
C9	63.5	15.0		3.0	–	
C10	62.5	15.0		3.0	1.0	
C11	61.5	15.0		3.0	2.0	
C12	60.5	15.0		3.0	3.0	

After mechanochemical activation, the charge was annealed in rectangular metal molds with face sizes of 120 × 120 × 260 mm under the following conditions: heating to a temperature of 640 °C at a rate of 6 °C/min, exposure at a temperature of 640 °C for 1 hour, heating to a temperature of 825 °C at a rate of 6 °C/min, exposure at a temperature of 825 °C for 30 min.

The molds with the resulting material were cooled together with the furnace to room temperature. Then they were removed from the furnace and disassembled, and the foamed material was cut into samples of the required sizes and tested.

Analytical methods. The effect of Mg(OH)$_2$ and Al$_2$O$_3$ on phase transformations in the charge under heating and the phase composition of the annealed porous glass ceramics were established by thermal analysis methods (differential thermal analysis (DTA) and thermogravimetric analysis (TGA)) and X-ray diffraction analysis (XRD):

– DTA and TGA of charge samples were carried out with the TGA/DSC1 system (Switzerland). The charge in the amount of 20 ± 0.1 mg was poured into an alundum crucible (150 µl volume) and compacted by tapping the crucible against a table. The sample was placed in the device and heated from 30 to 850 °C at a speed of 10 °C/min. 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).

– XRD of porous glass ceramic samples was carried out on an Empyrean PANalytical diffractometer (Netherlands) using a PIXcel^{3D} semiconductor detector. Samples of porous glass ceramics were crushed to a fraction of less than 90 µm. XRD patterns were recorded in linear scanning mode with CuK$_\alpha$ radiation in the angle range $2\Theta = 10 - 45°$. The recording rate was 0.0131 °/min, the integration time 150 s. The qualitative phase composition of the samples was determined by the Hanawalt method using an open database on crystallography.

The effect of additives in the charge composition on the macrostructure of porous glass ceramics was established by scanning the surface of the samples at a resolution of 600×600 dpi.

The influence of the phase composition and macrostructure of porous glass ceramic samples on the physical properties (density and porosity), mechanical properties (density under bending and compression), thermophysical properties (thermal conductivity, thermal resistance, maximum service temperature), as well as chemical resistance in water and aqueous solutions of acids and alkalis were established by the following methods:

– The true density of porous glass ceramics (ρ_0, g/cm^3) was determined using a pycnometer on samples crushed to a fraction of < 90 µm. During the experiment, 2 samples of each composition were tested. The arithmetic mean of the test results of the samples was taken as the final result for each composition.

– The open, closed and total porosity of glass ceramics was determined for cubic samples with the face size of 50 ± 5 mm. The testing procedure is described in detail in [22].

– The bending strength of the materials was determined for dry samples shaped as a rectangular prism with the face dimensions of $120 \times 30 \times 30$ mm. The samples were placed horizontally on two cylindrical supports (the diameter of the supports was 6 ± 0.1 mm) located 100 ± 1 mm from each other. A rod (6 ± 0.1 mm in diameter) through which force was applied to the sample was placed over the entire width of the sample at an equal distance from the supports. The force application rate was the same for all samples. The force at which failure occurred in the sample was controlled as a result of the experiment. The bending strength was determined by the standard formula. The arithmetic mean of the test results for three samples of each composition was taken as the final result.

– The compressive strength of porous glass ceramics was determined for cubic samples with a face size of 90 ± 5 mm. The samples were pre-dried and then subjected to a press test. The maximum value of the force at which cracks appeared in the sample or the height of the sample decreased by 10 % from the initial value was recorded in the experiments. The arithmetic mean of the test results for five samples of each composition was taken as the final result.

– The thermal conductivity of the samples was determined using an MIT–1 portable thermal conductivity meter (Russia) by the probe method. A hole with a diameter of 6 mm and a depth of 50 to 60 mm was drilled in the center of the face in dry cubic samples

($90 \times 90 \times 90$ mm). Before the test, the prepared samples and the measuring device were kept in the laboratory at a temperature of 24 ± 1 °C for 2 days. During the test, the probe of the device was immersed in the hole and readings were taken. The arithmetic mean of the test results for five samples of each composition was taken as the final result.

– The thermal stability of the materials was determined for cubic samples with a face length of 50 ± 5 mm. Cracking in the samples was monitored under abrupt cooling. At the beginning of the experiment, the samples were dried, and then placed for 2 hours in a thermostat with a temperature of 110 °C. After holding at a given temperature, the samples were removed from the thermostat in less than 10 seconds and immersed in a container with water (the water temperature was 20 ± 2 °C). The samples were kept in water for 65 ± 5 s. Cracked samples were removed from the test, and the experiment was repeated with the remaining ones the temperature of the thermostat increased by 10 °C. The experiment was repeated until cracks appeared in all samples. The thermal stability of each sample was calculated by the formula

$$\Delta T = T_T - T_w - 10, \tag{1}$$

where T_T, °C, is the temperature of the thermostat at which the sample was kept; T_w, °C, is the temperature of the coolant in the container; 10 °C is the difference in the thermostat temperatures between the subsequent and the previous test.

The thermal resistance tests adopted the arithmetic mean for four samples of each composition as the final result.

– The maximum service temperature of porous glass ceramics was determined for samples shaped as rectangular prisms with face sizes of $90 \times 40 \times 40$ mm. The variation in sample sizes after heating was monitored. At the beginning of the experiment, the height and width of the samples were measured with an accuracy of 0.01 mm, and then they were mounted vertically in a muffle furnace. The samples in the furnace were heated under the following conditions: heating to a temperature 50 °C less than the set temperature at a rate of 10 °C/min, heating to a set temperature at a rate of 2 °C/min, exposure at a set temperature for 2 hours. The heating rate set was increased by 10 °C and the experiment was repeated if the sample sizes changed by < 1 % after the test. The arithmetic mean of the test results for three samples of each composition was taken as the final result.

– Chemical resistance of materials was determined for samples crushed to a fraction of $0.315 - 0.630$ mm. The change in the mass of the samples after boiling in distilled water, an aqueous solution of acid and alkali was monitored. At the beginning of the experiment, the samples were dried, and then 5 ± 0.0005 g of the sample was poured into a flask. 100 ± 0.5 cm^3 of reagent (distilled water, 6N HCl aqueous solution, 1N Na$_2$CO$_3$ aqueous solution + 1N NaOH aqueous solution) were poured into the flask, which was then connected to a reflux condenser and the reagent was boiled. After 3 hours of boiling, aggressive fluid was poured out of the flask, and the sample was washed with distilled water at least 5 times. Distilled water was filtered through a paper ashless filter. The filter, together with the sample remaining on it, was placed in a ceramic crucible and calcinated in a muffle furnace at a temperature of 800 ± 10 °C for 1 hour. After the sample was dried in a desiccator with CaCl$_2$ to room temperature, it was weighed and the mass variation was determined. The arithmetic mean of the test results for two samples of each composition was taken as the final result.

Results and Discussion
Phase transformations in the charge and the phase composition of porous glass ceramics.
The combined effect of Mg(OH)$_2$ and Al$_2$O$_3$ on phase transformations in the charge under heating was established by methods of differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The results of the study are presented in Fig. 1.
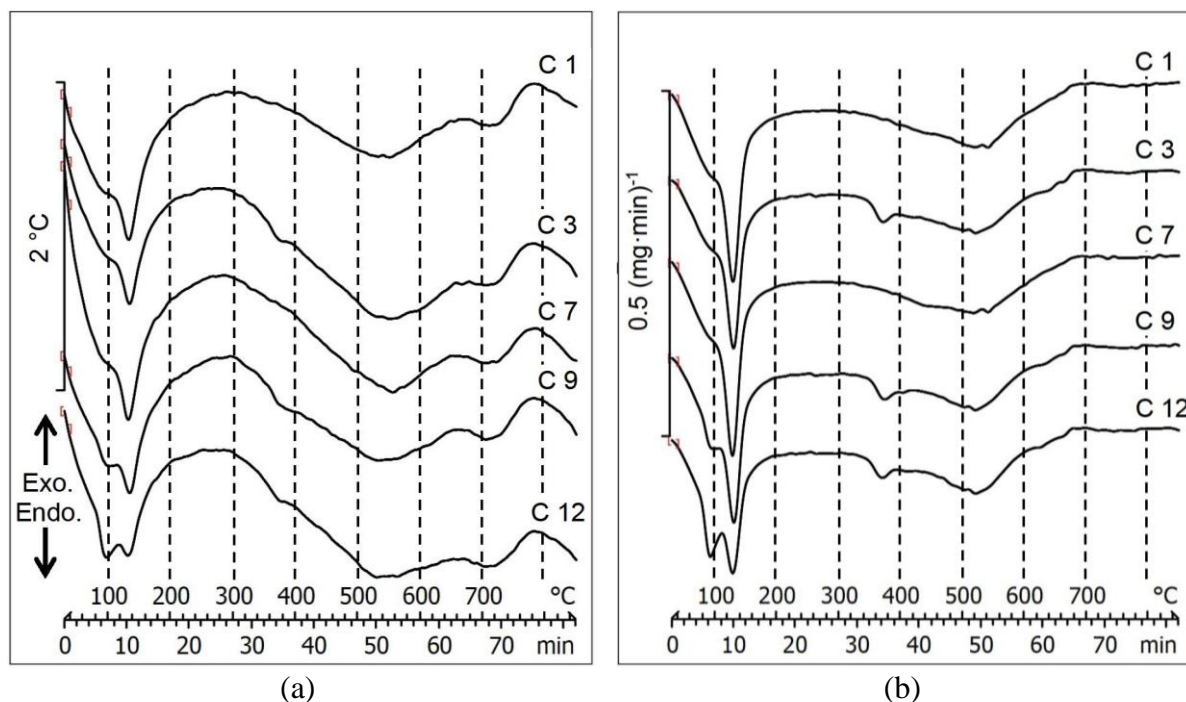
Fig. 1. DTA (a) and TGA (b) curves of charge samples

The data obtained (Fig. 1) can be used to assess the processes occurring in the charge from siliceous rock and soda ash with additives under heating. The endothermic effect in DTA (Fig. 1(a)) and the significant mass loss in TGA (Fig. 1(b)) observed in the curves of all tested samples at temperatures from 100 to 160 °C are likely associated with dehydration of hydrosilicates or sodium bicarbonates formed during grinding of the charge. The release of water from hydrosilicates in this temperature range was also observed by other authors [31]. The following endothermic effect and mass loss of samples C3, C9, C12 in the temperature range from 350 to 380 °C are associated with dehydration of Mg(OH)$_2$. A smooth endothermic effect in a large temperature range from 300 to 670 °C, accompanied by a significant loss of mass in all samples, is associated with decarbonization of minerals in the charge (calcite, natrite), as well as with the dehydration of minerals of the zeolite group (heulandite) and mica (muscovite). Formation of sodium silicates occurs in this temperature range [15,31]. According to the literature, surface hydroxyl groups are blocked in the micropores simultaneously with the formation of sodium silicates; as the charge is further softened, the micropores produce water vapor and foam it [15,31]. The softening of the charge, accompanied by an endothermic effect in the DTA curves of all tested samples, begins at a temperature of ≈ 680 °C. The reaction proceeds without changing the mass of the samples and ends with an exothermic crystallization effect. The temperature at which crystallization starts in all samples is ≈ 710 °C. The crystallization intensity decreases when the samples are heated above 780 °C.

It was established through thermal analysis of the charge samples that introducing up to 3 % Mg(OH)$_2$ combined with up to 3 % Al$_2$O$_3$ into its composition does not significantly affect the phase transformations in the charge under heating. Figure 2 shows XRD patterns of glass ceramic samples whose compositions are given in Table 1.

Analyzing the XRD patterns of the samples (Fig. 2), we determined the combined effect of Mg(OH)$_2$ and Al$_2$O$_3$ on the qualitative phase composition of glass ceramics. All tested samples consist of an amorphous and crystalline phase. The presence of an amorphous phase in the samples is evidenced by a non-monotonic change in the background (halo) in all XRD patterns in the angle range from 17 to 37° (2θ). The type and amount of additives in the charge composition had no apparent effect on the variation of the amorphous halo. The crystalline

phase in the samples obtained from the charge without $Mg(OH)_2$ and Al_2O_3 additives (C1, C7) consists of quartz [SiO_2, Code: 96-900-9667], wollastonite [$CaSiO_3$, Code: 96-900-5779], devitrite [$Na_2Ca_3Si_6O_{16}$, [32]] and anorthoclase [$(Na_{0.85}K_{0.15})(AlSi_3O_8)$, Code: 96-900-0860]. If up to 3 % $Mg(OH)_2$ is added to the charge, wollastonite in the glass ceramics composition is replaced by diopside [$Mg_{0.56}Ca_{0.44}SiO_3$, Code: 96-900-4210], and devitrite is replaced by combeite [$Na_2Ca_2Si_3O_9$, Code: 96-900-7718] (XRD patterns C2, C3, C8, C9 in Fig. 2). If diatomite content in the charge is increased from 5 to 15 %, practically no replacement of devitrite with combeite is observed. The effect can be explained by the introduction of chemically active SiO_2 in the amount necessary for crystallization of devitrite into the charge composition with diatomite. Conversely, the absence of this component in the charge composition leads to crystallization of combeite in glass ceramics containing two times less SiO_2. If up to 3 % $Mg(OH)_2$ combined with Al_2O_3 is added to the charge composition (C12), the anorthoclase content in the glass ceramics composition increases slightly. As we established in earlier studies [22], if Al_2O_3 is added to the charge, this leads to an increase of anorthoclase content in the composition of glass ceramics from siliceous rocks.
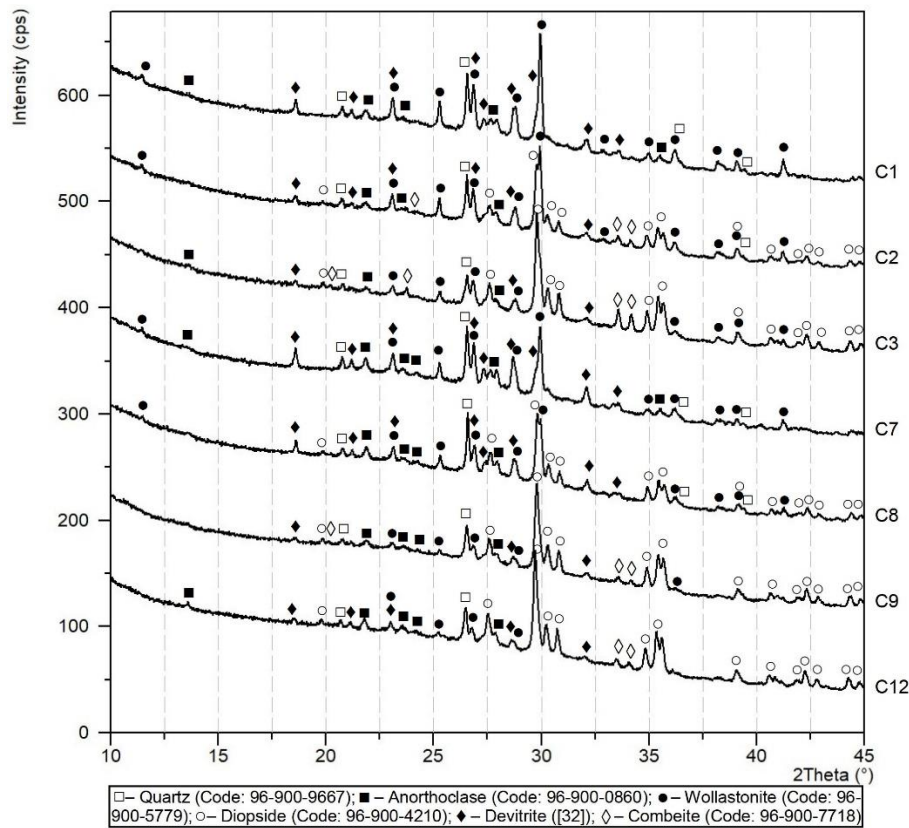

Fig. 2. XRD patterns of glass ceramic samples

Macrostructure of porous glass ceramics. The surface of the porous glass ceramic samples was scanned to illustrate the combined effect of $Mg(OH)_2$ and Al_2O_3 in the charge composition on the macrostructure. Figure 3 shows sample surface scans for all 12 compositions tested in the study.

According to Fig. 3, samples of porous glass ceramics obtained from the charge without $Mg(OH)_2$ additives have a homogeneous fine macrostructure (C1, C4, C7). The diameter of the cells decreases on average from 1.5 to 0.5 mm if 5 to 15 % diatomite is introduced into the charge. If up to 3 % $Mg(OH)_2$ is introduced into the composition of the charge from siliceous rock, this leads to an increase in the pore diameter to 10 mm. Samples C3 and C6 have the most

heterogeneous macrostructure. Analyzing the XRD data of the samples (Fig. 2), we can trace the direct dependence of the increase in the surface macrostructure heterogeneity with an increase in combeite mineral content in the composition. Simultaneously increasing $Mg(OH)_2$ to 3 % and diatomite to 15 % (C9) in the charge composition allowed to once again obtain a homogeneous macrostructure of glass ceramic samples with a pore diameter of no more than 2 mm. According to XRD analysis (Fig. 2), the combeite mineral content in the C9 sample is insignificant. Introducing $Mg(OH)_2$ combined with Al_2O_3 into the charge composition had no apparent effect on the surface macrostructure of samples from porous glass ceramics.
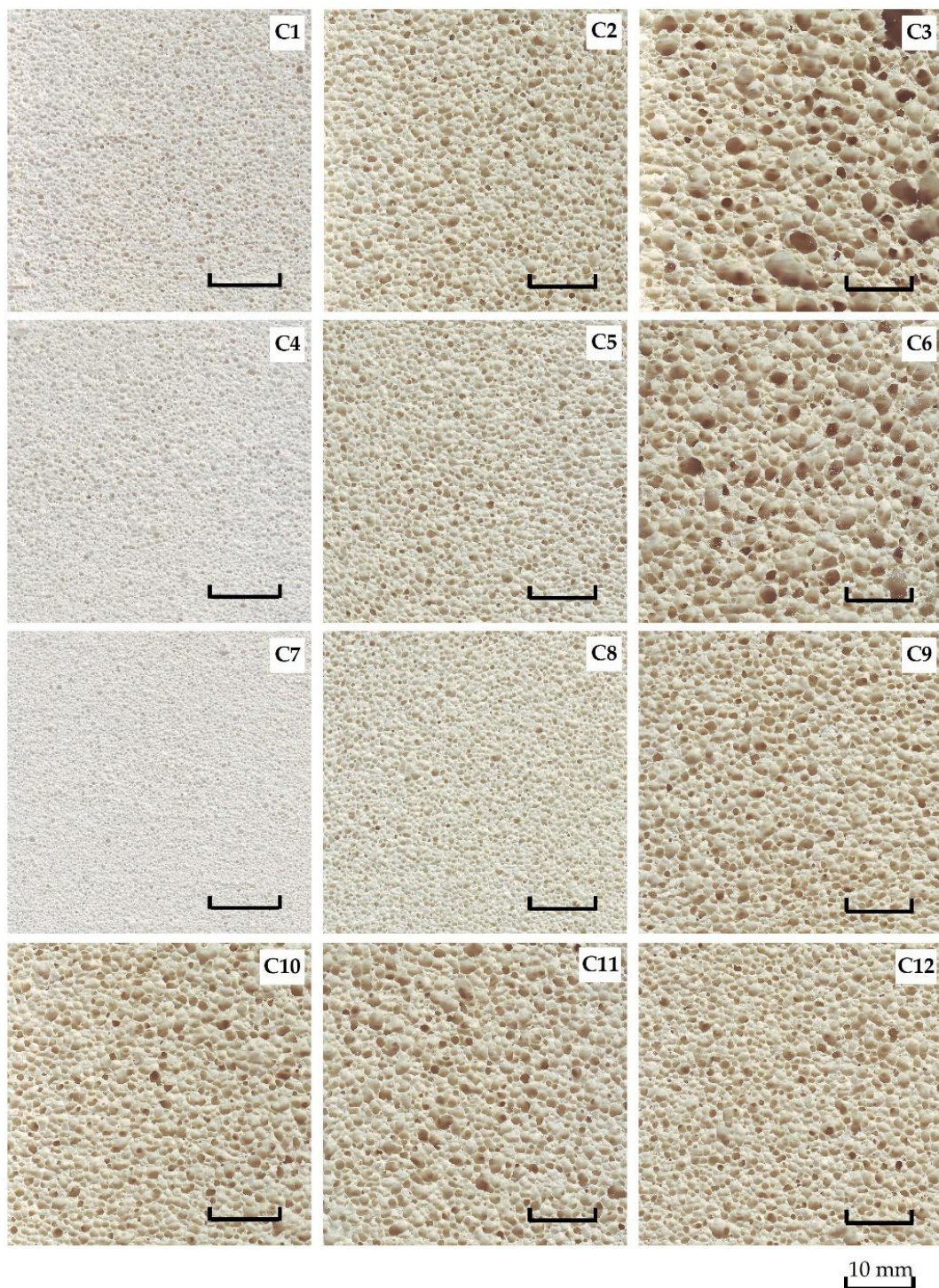

Fig. 3. Surface scan of porous glass ceramic samples

The surface color of samples from porous glass ceramics changed with an increase in $Mg(OH)_2$ in the charge composition to 3 %. The surface of the samples became more beige instead of light gray (without the $Mg(OH)_2$ additive). The effect can be associated with an increase in the diopside content in the samples (Fig. 2), as it can have different shades. According to the data given in the literature [4], the color of glass ceramics can also be influenced by the structure of the pores.

Physicomechanical properties of porous glass ceramics samples. Figure 4 shows the dependences of apparent density and porosity of glass ceramics samples on the type and content of additives ($Mg(OH)_2$, $Mg(OH)_2$ combined with Al_2O_3, diatomite) to the charge.
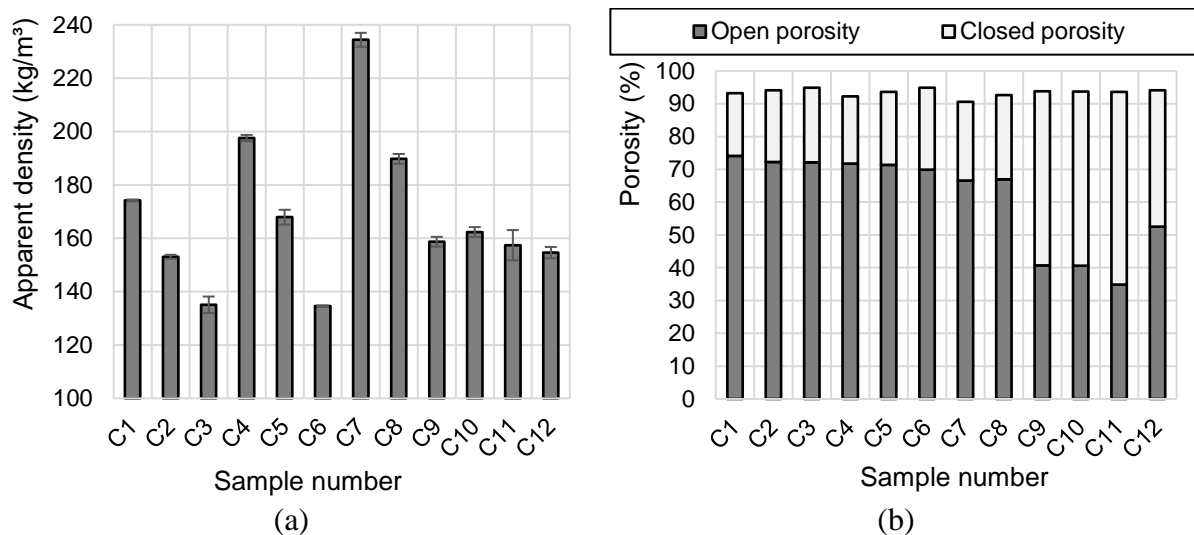

Fig. 4. Apparent density (a) and porosity (b) of samples

The results (Fig. 4(a)) indicate that the apparent density of porous glass ceramics samples decreases almost linearly if $Mg(OH)_2$ content in the charge composition is increased to 3 %. The effect is repeated with an increase in diatomite content in the charge from 5 to 15%. If $Mg(OH)_2$ is added to the charge composition together with Al_2O_3, the apparent density of glass ceramic samples is further decreased. The highest value of apparent density is reached in samples of composition C7 (≈ 235 kg/m^3). The lowest values of apparent density are reached in samples of compositions C3 and C6 (≈ 140 kg/m^3). However, the samples of these compositions exhibit heterogeneous porosity (Fig. 3). As noted above, this disadvantage can be corrected by introducing amorphous silica into the charge.

According to Fig. 4(b), the total porosity of the tested samples of glass-ceramic materials is in the range from 90.6 to 94.9%. There is an increase in the total porosity of the samples with an increase in the composition of the charge to 3 % $Mg(OH)_2$. An increase in $Mg(OH)_2$ in the composition of the charge also contributes to an increase in the number of closed pores in the material. This effect is clearly visible with combined addition of 15 % diatomite to the charge. The number of open pores in the material decreases from ≈ 70 to 40 % (C9). This effect is likely associated with a more homogeneous phase composition of the samples, consisting of the dominant mineral diopside and a small amount of quartz, wollastonite, devitrite and combeite minerals.

Introducing up to 2 % $Mg(OH)_2$ combined with Al_2O_3 to the charge composition further reduces open porosity. A further increase in Al_2O_3 increases the number of open pores in the material. An increase in open porosity in glass-ceramic samples from siliceous rocks with added Al_2O_3 was observed in [22]. Figure 5 shows the strength characteristics of porous glass ceramic samples from siliceous rocks.
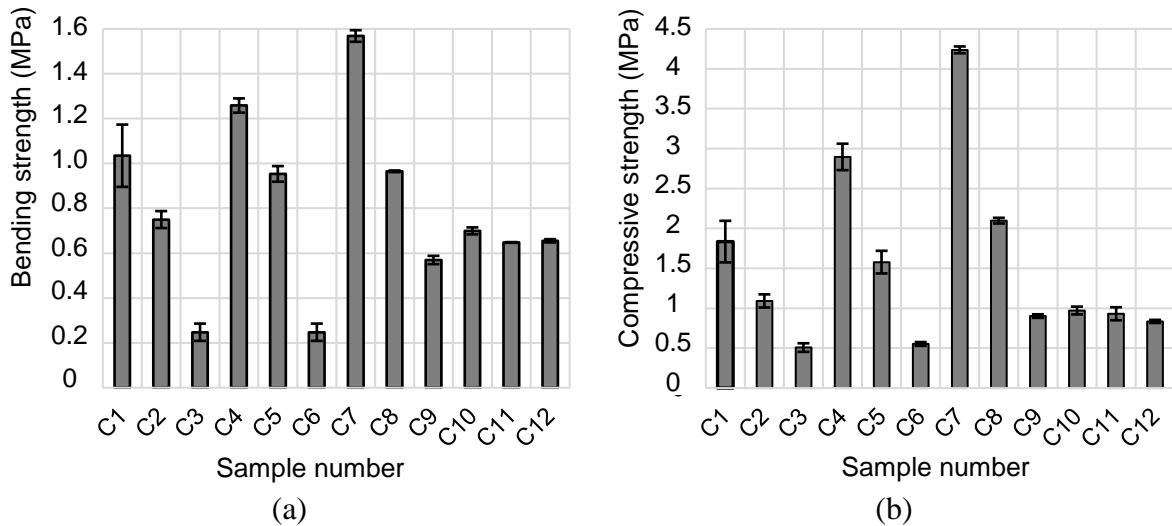
Fig. 5. Bending strength (a) and compressive strength (b) of samples

The analysis carried out (Fig. 5) indicates that bending and compressive strength of samples of porous glass-ceramic materials is linearly related to their apparent density. The apparent density of the samples and, consequently, their strength characteristics decreased as Mg(OH)$_2$ content in the charge composition was increased to 3 %. The highest value of bending strength ($\approx$ 1.6 MPa) and compression strength ($\approx$ 4.2 MPa) was observed for samples with an apparent density of $\approx$ 235 kg/m^3 (C7), the lowest strengths ($\approx$ 0.25 MPa and $\approx$ 0.5 MPa respectively) were observed for samples with a density of 135 kg/m^3 (C3, C6). It was not possible to establish the influence of the phase composition of porous glass ceramics on their strength characteristics. Introducing up to 3 % Mg(OH)$_2$ into the composition of the charge from siliceous rocks and soda ash allowed to obtain porous glass ceramic samples whose strength characteristics were superior to foam glass and glass ceramics from industrial waste with the same apparent density [1,2,8,13,28,33].

Thermophysical properties of porous glass ceramic samples. Figure 6 shows the thermal conductivities determined for porous glass ceramic samples. The relationship of thermal conductivity with the apparent density of the samples is shown.
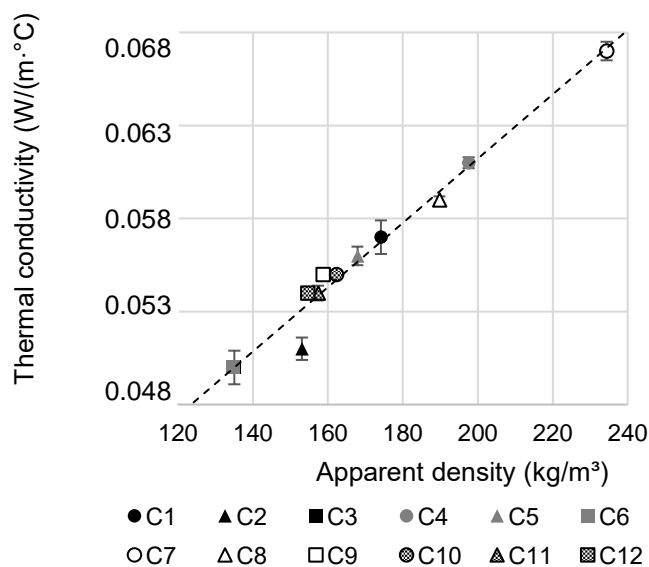

Fig. 6. Thermal conductivity of samples

The results in Fig. 6 point to a linear relationship between the thermal conductivity of porous glass ceramic samples and their apparent density. As the apparent density of glass ceramics is increased from 120 to 240 kg/m³, the thermal conductivity of the samples increases by the following formula:

$$\lambda = 1/6000 \cdot \rho + 0{,}028, \tag{2}$$

where: λ is the thermal conductivity, W/m °C, ρ is the apparent density of dry material, kg/m³. The approximation accuracy coefficient (R^2) is equal to 0.973.

It was established in the experiments that the lowest thermal conductivity (0.05 W/m·°C) is observed in dry porous glass ceramic samples of compositions C3 and C6. The apparent density of the samples is ≈ 135 W/m³. The highest thermal conductivity (0.067 W/m·°C) is observed in samples of composition C7 (apparent density ≈ 235 kg/m³). We detected no influence of the phase composition of porous glass ceramic samples on their thermal conductivity. The results obtained are in agreement with the data obtained in [34–36].
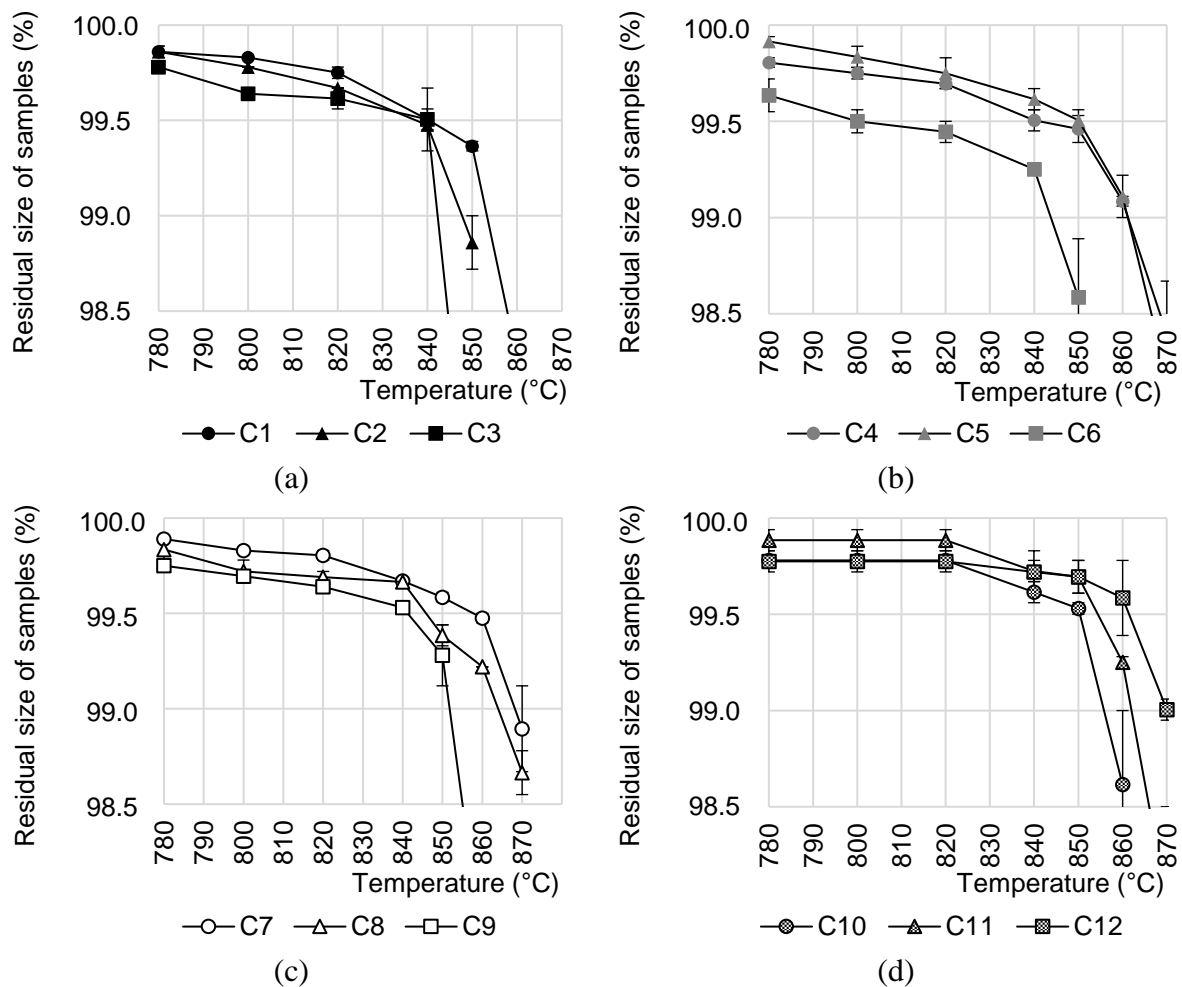
Fig. 7. Final dimensions of samples after exposure for 2 hours at a given temperature (samples from siliceous rock with added diatomite: 5 % (a); 10 % (b); 15 % (c); with added Al_2O_3 (d); C1–C12 are the composition numbers)

According to the data from [22], porous glass ceramics can be used for thermal insulation of industrial equipment. One of the main criteria for using a material as refractory thermal insulation is its maximum service temperature. This criterion is determined by the final size of the sample after exposure at a given temperature for 2 hours. Figure 7 illustrates the effect of

the type and quantity of additives ($Mg(OH)_2$, $Mg(OH)_2$ combined with Al_2O_3, diatomite) to the charge composition on the maximum service temperature of glass ceramic materials from siliceous rocks.

It was established in the experiments (Fig. 7) that the phase composition of porous glass ceramic samples has a significant effect on their maximum service temperature. The increased content of mineral combeite in the samples (Fig. 2, C2 and C3) reduces this indicator to 840 °C. If combeite and devitrite contents in the composition were decreased with a simultaneous increase in anorthoclase content, the maximum service temperature of the material increased to 870 °C (C12). This result was achieved by introducing 15 % diatomite, 3 % ($Mg(OH)_2$ and 3 % Al_2O_3 into the charge from siliceous rock and soda ash. Other studies [22,29,30] also confirmed that adding Al_2O_3 to glass ceramic materials has a positive effect on their resistance to prolonged exposure to high temperatures.

In terms of the maximum service temperature, the developed porous glass-ceramic materials from siliceous rocks (modified with $Mg(OH)_2$, Al_2O_3 and diatomite) are superior to foam glass and porous glass-ceramics from siliceous rocks obtained by alkaline charge activation [14–17,37]. They can be used as thermal insulation of melting furnaces, boiler equipment, etc.

An equally important requirement for refractory thermal insulation materials is their thermal resistance, which characterizes the ability of the material to withstand abrupt temperature changes [30]. According to experimental data, the thermal stability of the developed samples of porous glass ceramic materials virtually does not depend on the composition (Table 1) and is equal to 170 °C. This indicator is comparable with the test results for foam glass and porous glass ceramics from industrial waste [30], which once again confirms that is possible to use porous glass ceramics as thermal insulation in industrial equipment.

Chemical resistance of porous glass ceramic samples. The effect of the phase composition of porous glass ceramic samples on their chemical resistance is shown in Fig. 8. The criterion for assessing the chemical resistance of the material was the mass loss of crushed samples (fraction of 0.315–0.630 mm) after boiling for 3 hours in various chemical media.
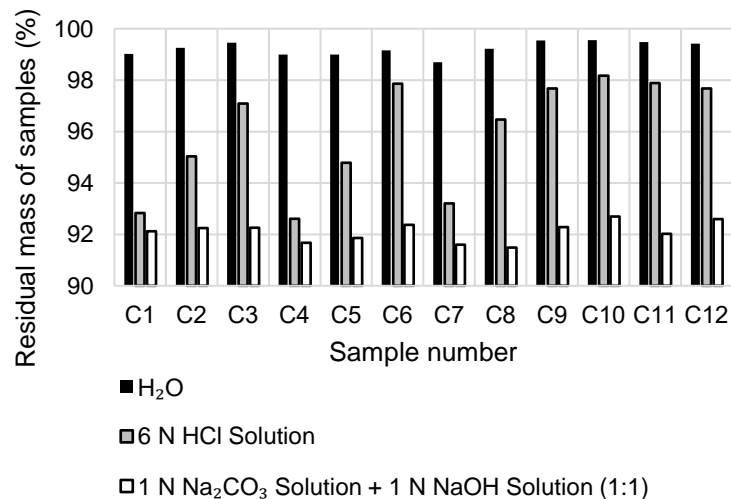
Fig. 8. Residual mass of samples after boiling in chemical media for 3 hours

According to the data obtained (Fig. 8), the developed glass-ceramic materials have high chemical resistance in water. This indicator increases with an increase in the composition of the mineral diopside samples (C3, C6, C9–C12). After boiling for 3 hours, glass ceramic samples with the maximum diopside content in the composition lost approximately 0.5 wt. %. The

results obtained make it possible to recommend the developed materials for applications in wet conditions.

We detected the influence of the phase composition of glass ceramic samples on their chemical resistance in an aqueous solution of HCl (6N). The residual mass of the samples after boiling in hydrochloric acid for 3 hours increased linearly from $\approx 93\%$ (C1, C4, C7) to $\approx 97.5\%$ (C3, C6, C9) with an increase in mineral diopside content and a consequent decrease in wollastonite in the composition of glass ceramic samples. The results obtained indicate a high chemical resistance of glass ceramics with predominant mineral diopside content. The literature also describes the insolubility of mineral diopside in acids, as well as self-gelation of wollastonite in hydrochloric acid [38].

We could detect no influence of the phase composition of glass ceramics from siliceous rocks on their resistance to alkaline solutions (Na_2CO_3(1N) + NaOH(1N)). After the samples were boiled in alkaline solution for 3 hours, their mass decreased by 7.5 – 8.5 %.

Based on our findings, we can argue that porous glass ceramics from siliceous rocks with added $Mg(OH)_2$, Al_2O_3 and diatomite have high chemical resistance. The results obtained are higher than those for many equivalents [38,39]. As a result, the developed materials can be used as insulation of pipelines, industrial installations, etc.

Conclusions

Porous glass-ceramic materials were obtained from a charge consisting of siliceous rocks, soda ash and additives. $Mg(OH)_2$, Al_2O_3 and diatomite were used as additives. Combined mechanochemical activation of the components was carried out in a planetary ball mill; next, the resulting charge was annealed at a maximum temperature of 825 °C. Thermal analysis and XRD analysis were used to establish the influence of the type and quantity of additives on the structure and properties of porous glass ceramic samples.

Main conclusions:

– Adding up to 3 % $Mg(OH)_2$ combined with up to 3 % Al_2O_3 to the composition of the charge from siliceous rock and soda ash does not significantly affect the phase transformations in the charge under heating. The annealed samples of porous glass ceramics consist of an amorphous and crystalline phase. The crystalline phase of the samples obtained from the charge without $Mg(OH)_2$ and Al_2O_3 additives consists of quartz, wollastonite, devitrite and anorthoclase. If $Mg(OH)_2$ is added to the charge, wollastonite in the composition is replaced by diopside and devitrite is replaced by combeite.

– To obtain a uniform fine structure of glass-ceramic materials from siliceous rock and soda ash with added $Mg(OH)_2$, it is necessary to minimize the mineral combeite content in the composition of annealed glass ceramics. This problem was solved by introducing diatomite into the charge. If diatomite content in the charge is increased from 5 to 15 %, practically no replacement of devitrite with combeite is observed. Consequently, glass ceramic samples have a homogeneous fine macrostructure with a pore diameter of no more than 2 mm.

– We established the influence of the phase composition of porous glass ceramic samples on their properties. If mineral diopside content in the composition was increased, the open porosity of the samples decreased, while their chemical resistance in water and aqueous hydrochloric acid solution increased. The maximum service temperature of the developed glass-ceramic materials is significantly influenced by the mineral combeite content in their composition. With its increase, the maximum service temperature of the samples decreased.

– The developed porous glass ceramics has an apparent density of 135–235 kg/m^3, bending and compressive strength up to 1.6 and 4.2 MPa, respectively, thermal conductivity of 0.050 – 0.067 W/m·°C, thermal resistance of 170 °C, maximum service temperature up to 870 °C, high chemical resistance.

– The developed materials are superior in many respects to foam glass and other counterparts and can be used as insulation in industrial and civil facilities.

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