Modification of barium aluminosilicate glass-ceramics with zirconium oxide additives

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Abstract. Barium aluminosilicate glass-ceramics modified with zirconium oxide (ZrO$_2$) in the presence and without of stabilizing yttrium oxide was synthesized by the sol-gel method. The influence of the concentration of zirconium oxide on gelation, phase formation and sintering of materials were investigated. It was found that modification with zirconium oxide leads to a reduction in the gelation time of the initial solutions. It was shown that the introduction of ZrO$_2$ in an amount of up to 10 wt.% leads to the intensification of sintering of glass-ceramics. However, with a further increase in the ZrO$_2$ content to 15 wt.%, it is necessary to increase the sintering temperature to 1600°C. But this is not permissible, since it leads to not a desired metastable phase – hexacelsian becoming predominant in all samples. Only glass-ceramics modified with 10 wt.% ZrO$_2$ contains only the monocelsian phase in the entire sintering temperature range. The use of the sol-gel method made it possible to synthesize glass-ceramics with a fine-crystalline structure and a uniform volume distribution of ZrO$_2$ grains.

1. Introduction
Barium aluminosilicate glass-ceramics is promising to use in aerospace technology as a structural material as a structural material that is operated at high temperatures and in aggressive environments [1-13]. This is because the crystalline phase dominant in this glass-ceramics – monocelsian (BaAl$_2$Si$_2$O$_8$), has a low density (3.39 g/cm$^3$) and a high melting point – 1760°C [14]. However, low fracture toughness (critical stress intensity factor $K_{IC} < 2.5$ MPa$\cdot$m$^{1/2}$) significantly limits the use of these materials. A possible way to solve this problem is to modify barium aluminosilicate glass-ceramics with various fillers, that is, the creation of glass-ceramic composite materials [15-17]. The most promising fillers are particles of refractory oxides, in particular zirconium oxide. The uniqueness of zirconia is its ability to perform a local martensitic phase transformation from the tetragonal phase to the monoclinic phase under the action of tensile stresses in the region of microconcentrators (in the region of microcracks, at the boundaries of particles of strengthening phases, etc.). During synthesis of materials it is necessary to ensure the stabilization of the high-temperature tetragonal form of ZrO$_2$, including with the use of stabilizing oxides (Y$_2$O$_3$, MgO, CeO$_2$). The local phase transition is accompanied by the development of shear and volume deformations that ensure stress relaxation and closure of the crack surface. As a result, microcracks become stable while maintaining the level of external load. This effect was called transformational reinforcement [18, 19].

Works on the use of ZrO$_2$ particles as a reinforcing fillers were carried out back in the 1980s on the example of aluminum oxide ceramics and magnesium aluminum silicate glass-ceramics (cordierite...
glass-ceramics). For example, it was shown in [18] that the introduction of 10-15 vol.% Y_2O_3-stabilized (2.2-2.5 mol% Y_2O_3) ZrO_2 made it possible to increase the fracture toughness of cordierite glass-ceramics by more than 50% and the change of the dielectric properties of material were insignificant. Reinforcement of aluminum oxide ceramics with particles of Y_2O_3 stabilized (3 mol% Y_2O_3) ZrO_2 in an amount of 15% by weight using the sol-gel method resulted in an increase in its critical stress intensity factor and bending strength up to 9.23 MPa·m^{1/2} and 856 MPa, respectively, which is 2.4 and 1.3 times higher in comparison with the initial ceramic [19].

The most promising method for the synthesis of modified barium aluminosilicate glass-ceramics is the sol-gel method, since it allows one to obtain materials with a fine crystalline structure and uniform distribution of modifying oxides in glass-ceramics, which provides their higher mechanical and thermal properties.

The goal of our study was sol-gel synthesis of barium aluminosilicate glass-ceramics modified with zirconium oxide (ZrO_2) in the presence and without of stabilizing yttrium oxide and study of the influence of the concentration of zirconium oxide on gelation, phase formation and sintering of materials.

2. Experimental

For the synthesis of sol-gel solutions, we used the composition of monocelsian (BaO·Al_2O_3·2SiO_2, BAS) with ZrO_2 additives in an amount of 5-15 wt.% in the presence and without stabilizing yttrium oxide (in an amount of 3 mol.% of the contents of ZrO_2). Solutions were prepared by sequentially adding components.

The gelation of solutions was studied by constructing kinetic curves of viscosity changes. The gelation time was determined visually by the meniscus deflection for 1 min. when tilting the glass with the gel at an angle of 45°. As the main methods of study were used differential scanning calorimetry and thermogravimetry (DSC/TG), X-ray phase analysis (XRD), and dilatometric method for determining the shrinkage during sintering. The analysis of the microstructure of materials was carried out by using scanning electron microscopy and energy dispersive X-ray spectroscopy. Apparent density was measured by using the Archimedes principle.

3. Results and discussion

A study of the kinetic curves of the change in the viscosity of solutions during gelation (Fig. 1) showed that two sections are observed on all curves. The first one, almost parallel to the abscissa axis, corresponds to a uniform course of hydrolysis of silicon alcoholes and condensation of the resulting monomers into dimers. The second, characterized by an intensive increase in viscosity, is associated with the polycondensation reaction with the formation of a three-dimensional network structure via ≡Si–O–Si≡ bonds.

It was found that the introduction of ZrO_2 in an amount of 5 wt.% contributes to a significant reduction in the time of hydrolysis and condensation. This leads to a decrease in the total gelation time from 380 h to 23 h (Figure 1). However, with an increase in the content to 15 wt.%, This effect weakens. The presence of yttrium oxide has little effect on the kinetics of viscosity changes.
After hydrolysis and polycondensation were completed, the gels were dried. Studying the dried gels by the DSC/TG method showed that in the temperature range 100-1000 °C crystallization water and solvent are removed from them, and inorganic salts of the starting elements decompose as well. The occurring physicochemical transformations are accompanied by significant mass losses (about 45%), which stabilize only at a temperature of 1000°C. In the temperature range 1020-1450 °C, gel crystallization is observed with the formation of monocelsian through successive transformations of barium silicates and hexacelsian. With the introduction of refractory zirconium oxide, the crystallization peaks in the thermograms of the samples become blurred, which makes their identification difficult.

According to the DSC/TG results, the dried gels were calcined and heat treated at temperatures of 1000°C and 1500°C, respectively. The resulting powders were ground in a planetary mill to a particle size of 3 μm.

The study of the curves of linear shrinkage of samples during heat treatment in the temperature range 25–1600 °C (Figure 2) showed that their sintering occurs due to the mechanism of viscous flow and is accompanied by shrinkage of 7–13% in the temperature range 1300–1600 °C. The maximum sintering speed is achieved in the range of 1500-1600 °C. It was found that the introduction of up to 10 wt.% ZrO₂ leads to an intensification of the sintering process of glass-ceramics. So, for example, the shrinkage achieved during sintering of barium aluminumsilicate glass-ceramics with 10 wt.% zirconium oxide increases by 1.7 times. However, a further increase in the concentration of zirconium oxide, characterized by a high melting point (2715°C), up to 15 wt.% leads to a shift in the maximum sintering speed to a higher temperature region.
Figure 2. Linear shrinkage curves of samples containing zirconium and yttrium oxides depending on the concentration of the additive.

The results of studying the sintering of modified glass-ceramics by isothermal firing of samples in the temperature range 1500-1650 °C are consistent with the data of high-temperature dilatometry. Thus, it was shown that the introduction of ZrO$_2$ up to 10 wt.% helps to reduce the open porosity of barium aluminosilicate glass-ceramics. With the joint introduction of zirconium and yttrium oxides, this effect is enhanced. For samples containing up to 10 wt.% zirconium oxide additives in the presence and without yttrium oxide, the maximum density can be achieved by sintering at 1550°C. With an increase in the ZrO$_2$ content to 15 wt.%, it is necessary to increase the sintering temperature to 1600°C.

The study of sintered samples by XRD showed that, regardless of the concentration of ZrO$_2$ after firing at 1550°C, the main phase in the samples is monocelsian (m-BaAl$_2$Si$_2$O$_8$), which is consistent with the previously considered DSC results. However, in most samples there is also a metastable form – hexacylsian (h-BaAl$_2$Si$_2$O$_8$), which becomes predominant with an increase in firing temperature to 1600°C. According to published data, the hexacylsian phase is undesirable for high-temperature glass-ceramics, since it is characterized by a high thermal expansion coefficient (∼ (8.0 × 10$^{-6}$) K$^{-1}$) and polymorphic transformation into an orthorhombic modification at a temperature of about 300°C, which is accompanied by a volume change of ∼ 3% [13]. Thus, it was found that the sintering temperature of the modified barium aluminosidicate glass-ceramics should not exceed 1550°C. It was also revealed that glass-ceramics modified with 10 wt.% ZrO$_2$ is the most promising, since only the monocelsian is present in it at all sintering temperatures (Figure 3). It was established that, regardless of its concentration, zirconium oxide is present in glass-ceramics in monoclinic and tetragonal modifications.
Figure 3. XRD results of samples containing 10 wt.% ZrO$_2$ after sintering at 1550°C and 1600°C (m – monoclinic, t – tetragonal).

A study by scanning electron microscopy (Figure 4) showed that all samples, regardless of ZrO$_2$ concentration and sintering temperatures (1550°C or 1600°C), are characterized by a fine-crystalline structure with elongated celsian grains and zirconium grains. The grain sizes are at the level of micrometer units and increase slightly with increasing sintering temperature. All samples contain pores with sizes from 1 to 10 μm.

![Scanning electron microscopy images of glass-ceramic samples modified with 10 wt.% zirconium oxide obtained by sintering at 1550°C and 1600°C.](image)

Figure 4. Scanning electron microscopy images of glass-ceramic samples modified with 10 wt.% zirconium oxide obtained by sintering at 1550°C and 1600°C.

According to the results of the study of sintered samples by energy dispersive X-ray spectroscopy (Fig. 5), it was found that the use of the sol-gel method made it possible to create uniform distribution of zirconium oxide grains in the volume of glass-ceramics. It was shown that yttrium oxide is also distributed over the volume of materials; however, foci of its concentration near zirconium oxide grains are observed. This confirms the effect of Y$_2$O$_3$ as a stabilizer of the tetragonal form of ZrO$_2$ in glass-ceramics.
4. Conclusions

Thus, the barium aluminum silicate glass-ceramics modified with zirconia additives in the presence and without stabilizing yttrium oxide were synthesized by the sol-gel method, and the influence of the ZrO$_2$ concentration on gelation, phase formation, and sintering of materials was studied.

It was found that the introduction of ZrO$_2$ reduces the gelation time of solutions. This is manifested to the greatest extent with the introduction of small amounts of ZrO$_2$ (5 wt.%). Crystallization of gels occurs in the temperature range 1020-1450 °C with the formation of monocelsian through successive transformations of barium silicates and hexacelsian. With the introduction of refractory zirconium oxide, the crystallization peaks in the thermograms of the samples become blurred, which makes their identification difficult.

It was shown that the introduction of ZrO$_2$ in an amount of up to 10 wt.% leads to an intensification of sintering of barium aluminosilicate glass-ceramics. With the joint introduction of zirconium and yttrium oxides, this effect is enhanced. For samples containing up to 10 wt.% zirconium oxide additives in the presence and without yttrium oxide, the maximum density can be achieved by sintering at 1550°C. With an increase in the ZrO$_2$ content to 15 wt.%, it is necessary to increase the sintering temperature to 1600°C. However, according to the XRD results, this is not permissible, since it leads to the predominance of an undesirable hexacelsian phase in all samples. Glass-ceramics modified by the addition of 10 wt.% ZrO$_2$ is characterized by the presence of only the monocelsian phase in the entire temperature range of sintering.

It is shown that the synthesized samples are characterized by a fine-crystalline structure with grain sizes at the level of micrometer units. The use of the sol-gel method made it possible to ensure uniform distribution of zirconium oxide grains in the volume of glass-ceramics. It was established that yttrium oxide is predominantly concentrated near zirconium oxide grains. This confirms the effect of Y$_2$O$_3$ as a stabilizer of the tetragonal form of ZrO$_2$ in glass-ceramics.

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