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PHYSICO-CHEMICAL PROPERTIES AND STRUCTURAL TRANSFORMATIONS IN THE SYNTHESIS OF BOROALUMOSILICATE GLASS-CRYSTAL MATERIALS

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The aim of this work is to study the areas of glass formation and metastable liquation of the pseudo-ternary system ($MgO{\cdot}Al_2O_3$)-B_2O_3-SiO_2, and study of the crystallization process of glasses of cordierite composition. The crystallization process of glasses of cordierite composition containing B_2O_3 by a single-stage heat treatment at 1000 °C and 1200 °C, the nature of crystallization, the thermal properties of glasses and glass crystalline materials of the system ($MgO{\cdot}Al_{12}O_3$)-B_2O_3-SiO_2 were studied. It revealed that during the isolation of a boron -containing solid solution, the residual glassy phase enriched with oxides of MgO and Al_2O_3, which lead to an increase in the thermal expansion coefficient of the glass phase. The research results provide possibility to synthesize glass-ceramics with certain thermophysical parameters by stopping further glass crystallization at the stage of formation of a certain amount and ratio of the required crystalline and glassy phases.

Keywords: glass formation, liquidus temperature, metastable segregation, glass crystallization, thermal expansion

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА И СТРУКТУРНЫЕ ПРЕВРАЩЕНИЯ ПРИ СИНТЕЗЕ БОРОАЛЮМОСИЛИКАТНЫХ СТЕКЛОКРИСТАЛЛИЧЕСКИХ МАТЕРИАЛОВ

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Целью данной работы является исследование областей стеклообразования и метастабильной ликвации *псевдотройной системы ($MgO{\cdot}Al_2O_3$)-B_2O_3-SiO_2 и исследование процесса кристаллизации стекол кордиеритового состава. Изучены процессы кристаллизации стекол кордиеритового состава, содержащего B_2O_3, одноступенчатым режимом термообработки стекол при 1000 °C и 1200 °C; последовательность и характер кристаллизации, термические свойства стекол и стеклокристаллических материалов системы ($MgO{\cdot}Al_2O_3$)-B_2O_3-SiO_2. Показано, что при выделении борсодержащего твердого раствора остаточная стеклообразная фаза обогащается оксидами MgO и Al_2O_3, приводящими к увеличению коэффициента термического расширения стеклофазы. Результаты исследования дают возможность синтезировать ситаллы с определенными теплофизическими параметрами путем прекращения дальнейшей кристаллизации стекла на стадии образования определенного количества и соотношения необходимых кристаллических и стеклообразной фаз.*

Ключевые слова: стеклообразование, температура ликвидуса, метастабильная ликвация, кристаллизация стекла, термическое расширение

BOROALUMOSILIKATLI SHISHA-KRISTALLI MATERIALLAR SINTEZIDAGI FIZIK-KIMYOVIY XUSUSIYATLAR VA KONSTRUKTIV TRANSFORMATSIYALAR

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Ushbu ishning maqsadi ($MgO{\cdot}Al_2O_3$)-B_2O_3-SiO_2 tizimida shisha hosil bo'lishi va metastabil suyuqlanish maydonlarini va kordiyerit tarkibli shishalarning kristallanish jarayonini o'rganishdan iborat. Tarkibida B_2O_3 bo'lgan kordiyerit tarkibli shishalarning kristallanish jarayonini 1000 va 1200 °Cda bir bosqichli rejimda termik ishlov berish orqali, kristallanish ketma-ketligi vatabiati, ($MgO{\cdot}Al_2O_3$)-B_2O_3-SiO_2 tizimidafi shisha va shishakristall materiallarning termir xossalari o'rganilgan. Bor saqlovchi qattiq eritma ajralish vaqtida qoldiq shishasimon faza $MgO{\cdot}$va Al_2O_3 oksidlari bilan keladi. Tadqiqot natijalari ma'lum miqdordagi va kerakli kristalli va shishasimon fazalarning nisbati hosil bo'lish bosqichda shishaning keyingi kristallanishini to'xtatish orqali ma'lum termofisik parametrlarga ega sitallarni sintez qilishga imkon beradi.

Kalit so'zlar: shisha xosil bo'lish, likvidus harorati, metastabil likvatsiya, shishaning kristallanishi, termik kengayish

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Introduction

The results of the analysis of the state in the field of synthesis of glass-ceramic materials based on aluminum borosilicate system systems indicate that glass-ceramics are promising materials in the field of innovations for aviation, rocket and rocket-space technologies, as well as, microelectronics, where materials with high mechanical and dielectric properties are required [1-3]. To obtain materials with high parameters and low temperatures of synthesis, the primary task is to study and reveal the general regularities of the dependence of the physical and chemical properties of both the initial glasses and glass-crystalline materials on their complex composition and structure.

With the development of science and technology, glass-crystalline materials (sitalls), in terms of their complex of unique properties and as new structural materials, have an increasingly important place in materials science. Consequently, the study of the dependence of physicochemical and thermophysical properties on their composition, in particular, changes in the thermal expansion of bodies of complex composition and structures are remained an urgent task now [4-8]

The primary part of technical glass-ceramics is synthesized on the basis of glasses of aluminosilicate systems $Me_2O(MeO)$-Al_2O_3-SiO_2, where other chemical elements can be added to modify the composition and control the phase transformations, as well as, to obtain the glass-ceramic with the required structure and properties. Recently, transparent nano-glass ceramics with a low temperature coefficient of linear expansion (TCLE) and high dielectric characteristics based on glasses of the Li_2O (MgO)-Al_2O_3-SiO_2 systems have been intensively developed.

For directional crystallization, up to 4.0 mol. % TiO_2 and ZrO_2 are introduced into the glass composition. It is possible to significantly reduce the melting temperature (1600 °C) and crystallization of glasses (1600 °C), and obtain glass-ceramic materials with crystal sizes less than 100 nm by introducing oxides of alkaline earth metals, ZnO and P_2O_5 into the aluminosilicate system [8-12].

Glass-ceramics, obtained by directional crystallization of glass with certain chemical composition, are polycrystalline microheterogeneous materi-

als with the concentration of the crystalline phase varied within wide limits (from 30% or more). When passing from a homogeneous glass to a multiphase glass-crystalline material, the properties are sharply changed, especially, the TCLE, the softening temperature of the residual glassy phase, the electrical and mechanical characteristics, and etc. This rapidly developing group of transparent materials includes cordierite nano-glass ceramics based on the $(MgO \cdot Al_2O_3)$-B_2O_3-SiO_2 system. The high temperature significantly complicates the development of new glass compositions for glass-ceramics. To reduce the liquidus temperature, B_2O_3 added into the initial MgO-Al_2O_3-SiO_2 system. It also contributes the possibility to decrease the melting temperature and an expansion of the glass formation region. The additional introduction of MgF_2 and CaF_2 fluorides sharply decrease the spontaneous phase separation of the glasses, and it becomes possible to carry out a controlled process of self-catalyzed crystallization without adding the TiO_2, ZrO_2 and other crystallizers [13-16].

The aim of this work is to study the areas of glass formation and metastable liquation of the pseudo-ternary system $(MgO \cdot Al_2O_3)$-B_2O_3-SiO_2); study of the crystallization process of glasses of cordierite composition by one-stage heat treatment of glasses at 1000 °C and 1200 °C; the detection of the cordierite-like and boron-containing solid solutions formation; study of the thermal properties of glasses and glass-crystalline materials, which are having the compositions in the region of metastable liquation along the section with a constant $MgO \cdot Al_2O_3$ content of 28.6 mol. %; determination of the experimental and calculated TCLE values of the glass ceramics depending on the parameters of the precipitated crystalline phases and the temperature of isothermal heat treatment of glasses.

Research methods

The synthesis of glasses was carried out in platinum and corundum crucibles in an electric furnace in an air atmosphere at temperatures ~ 200 ... 250 °C higher than the liquidus temperature of the system for 60 min. The raw materials were chemically pure reagents - $MgCO_3$, $Al(OH)_3$, H_3BO_3 and SiO_2. Fluorides (MgF_2, CaF_2) were added into the glass composition from 5.0 mol. % over 100%. The region of metastable liquation was determined from the value of the opalescence formation temperatures. At a glass viscosity of ~10^7 *Pa·s*, the appearance of opalescence and phase separation occur at ~ 30 minutes exposure. The differential thermal analysis (DTA) of glasses was carried out in a platinum crucible on a Q-1500 derivatograph (Al_2O_3 standard), heating rate – 15 °min^{-1}. The glass transition temperature of the residual glass phase in the glass-ceramics was determined from the DTA curve at the point corresponding to the "onset" of the endothermic effect in the glass transformation region, and the degree of crystallinity of the glass-ceramic was determined by the effect area. The measurement error due to the change in the baseline path and the temperature range of crystallization was 3%. TCLE was measured on a DKV-4 dilatometer at a heating rate of ~ 5 °C min^{-1}, the accuracy of determination was $\alpha \pm 3{,}0 \cdot 10^{-7}$ °C^{-1}.

Thermal expansion of glass-crystalline materials (glass-ceramic) is one of its main parameters used simultaneously as structural and functional materials characterization. This work presents both experimental and calculated data on the thermal expansion of glass-ceramic, depending on their composition and degree of crystallinity. The glass-ceramic heterogeneous compositions provided lack of porosity and discontinuities between phases, a statically uniform distribution of phases, and the absence of anisotropy, the TCLE consists of the thermal expansion of the constituent phases, and the simple additivity rule is not met [17]. TCLE of glass-ceramic (a) are calculated by the following formula;

$$a = S^n_i a_i ([(E_i/(1-2m_i)] (P_i/r_i) / S^n_i [(E_i/(1-2m_i)] (P_i/r_i),$$

where: E_i , m_i - elastic modulus and Poisson's ratio of the i-th phase; a_i - TCLE of i-th phase; P_i - mass fraction and r_i - density of the i-th phase. The modulus of elasticity varies within 85 ... 100 GPa for the most aluminosilicate glasses but the Poisson's ratio of the aluminosilicate ceramics and glasses is 0.25 ... 0.3, which is greatly simplifies the preliminary calculations. Using the above formula, it is required to know the phase composition of the glass -ceramic, the mass ratios between the phases and the composition of the residual glassy phase. As shown by preliminary studies, in the preparation of glass-ceramic based on cordierite glasses containing B_2O_3, crystallization of the initial glasses occurs stepwise, and the sequence of phase separation and phase transitions is the same for all glasses [18-21]. Therefore, if assumed a certain mass percentage of the crystalline phases content in the glass ceramic, which is easily determined from the thermal analysis curve, it is possible to calculate the chemical composition of the residual glass phase and its physical parameters.

The values of the physical parameters of the precipitated phases necessary for calculation of the TCLE of glass-ceramics were taken from the literature [17, 22, 23], and the calculation of the physical parameters of the residual glass phase in the glass-ceramics and boron-containing solid solutions was carried out by the Appen method [24].

Results and discussion

Figure 1 shows diagrams of the glass formation regions, metastable segregation of the $(MgO \cdot Al_2O_3)$-B_2O_3-SiO_2 system, and the state diagram of a partial section of the $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ - $2(MgO \cdot Al_2O_3)5B_2O_3$ system (content MgO Al_2O_3 28.6 mol. %). The region of

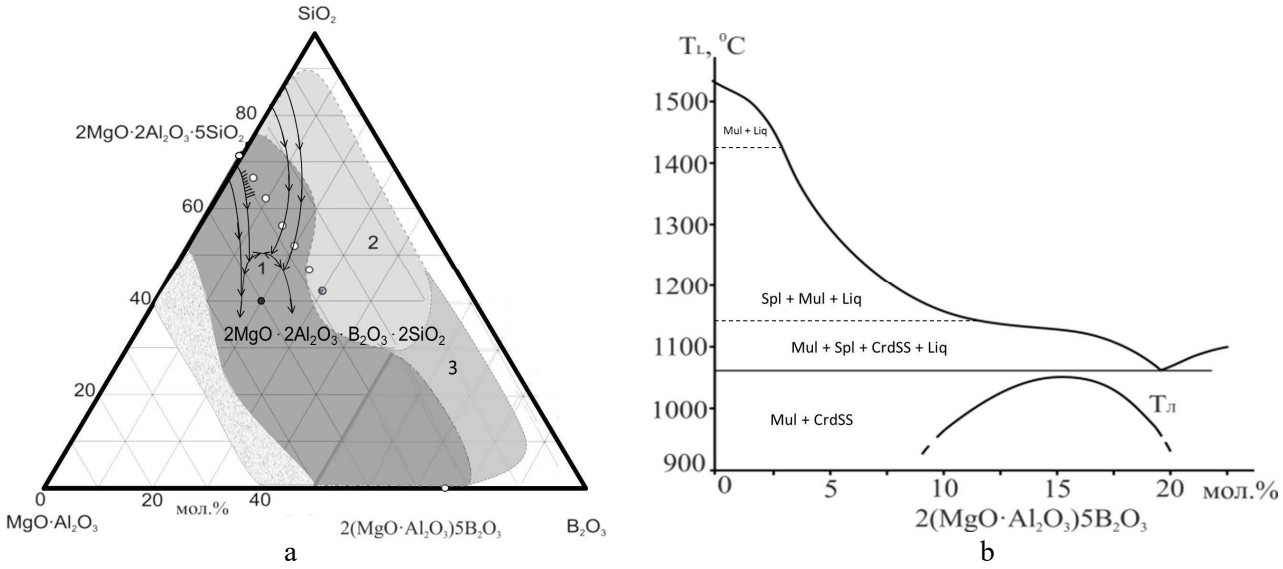

Figure 1. Diagrams of glass formation, metastable liquation (a) and system state ($MgO·Al_2O_3$)-B_2O_3-SiO_2 the section $2MgO·2Al_2O_3·5SiO_2$-$2(MgO·Al_2O_3)5B_2O_3$ (b): a - area of formation of transparent glasses (1), metastable liquation (2), crystallization of the melt during the casting (3); b - Crd- cordierite -$2MgO·2Al_2O_3·5SiO_2$, Mul- mullite - $3Al_2O_32SiO_2$, Spl- spinel $MgO·Al_2O_3$, Liq- liquid.

glass formation is uninterrupted and located between the pseudo-binary systems of the concentration triangle. In the SiO_2 - $MgO·Al_2O_3$ and B_2O_3 - $MgO·Al_2O_3$ systems, the glasses are formed in the range of compositions containing - 0 ... 38 mol. % $MgO·Al_2O_3$ (for the SiO_2 - $MgO·Al_2O_3$ system) and 0 ... 52 mol. % $MgO·Al_2O_3$ (for the B_2O_3-$MgO·Al_2O_3$ system). The glass formation region expands up to 55 mol. % $MgO·Al_2O_3$ in the pseudo-ternary system. The continuity and expansion of the glass formation region of transparent glasses in the ternary system are explained by the joint introduction of Al_2O_3 and B_2O_3 , as well as, besides the aluminate complexes $[AlO_{4/2}]_2^-Mg^{2+}$ due to the possibility of the formation of $[BO_{4/2}]_2^-Mg^{2+}$ borate complexes groups in the system of silicate glass. The high ionic bonds with the Mg^{2+}cation make possible to build a single spatial glass framework with aluminate and silicate groups [4]. Glass formation stops due to a sharp increase in the liquidus temperature and the insolubility of $MgO·Al_2O_3$ in a high-viscosity borosilicate melt.

The pseudo-binary system SiO_2 - $MgO·Al_2O_3$ has not been fully studied but practically important for the preparation of high-temperature ceramics and glass-ceramics. One ternary compound $2MgO·2Al_2O_3·5SiO_2$ is formed from SiO_2 and the $MgO·Al_2O_3$ spinel. Complex polymorphism and a limited number of solid solutions characterize the formation. The given eutectic and peritectic compositions are the beginning of the boundary curves of the primary crystallization fields for the cordierite - SiO_2 and cordierite - $MgO·Al_2O$ regions which are based on the results of experimental and calculated phase diagrams, taking into account the existence of a large number of intermediate structural states of cordierite solid solutions [25].

The $2MgO2Al_2O_35SiO_2$ (cordierite) compound is located in the glass formation region of the binary system of $MgO·Al_2O_3$-SiO_2, which melts incongruently at 1160 °C with the formation of mullite and melt. Such a phase transition in the presence of a liquid phase complicates the production of the stoichiometric composition of the $2MgO2Al_2O_35SiO_2$ glass due to the occurrence of a peritectic reaction and the formation of mullite (or mullite and spinel) and a high- siliceous melt [26]. In the crystal structure of cordierite, the three aluminum atoms are in octahedral coordination, and the fourth one replaces one silicon atom in the ring structure, forming the $AlSi_5O_1$ groups.

The columns of the rings connected by AlO_4 tetrahedrons and MgO_6 octahedrons. When solid solutions formed, isomorphic substitutions can occur according to the following schemes: $2Al^{3+}$+ Mg^{2+} ↔ Si^{4+} and $2B^{3+}$ + Mg^{2+}↔ Si^{4+}→$2B^{3+}$. As a result of such heterovalent isomorphism, the cordierite solid solutions with an excess or deficiency of both SiO_2 and Al_2O_3 can be formed [27-29]. Such substitutions can cause contraction or stretching of the lattice, and a change in the TCLE of the crystal. In the ternary system, starting from the cordierite compound, a limited number of solid solutions are formed, going towards the new identified compound of the $2(MgO·Al_2O_3)B_2O_32SiO_2$ composition, which is melting congruently at 1220 °C.

In the binary system, along the $2MgO·2Al_2O_3·5SiO_2$ -$2(MgO·Al_2O_3)5B_2O_3$ particular section, only a eutectic is formed in the studied region at a content of 20 mol. % magnesium aluminoborate (Fig. 1b). The liquidus temperature at additions of $Mg_2Al_4B_{10}O_{23}$ decreases from 1550 °C (complete melting of a mixture of cordierite composition) to a eutectic composition. By the nature of the change in the liquidus temperature curve of the

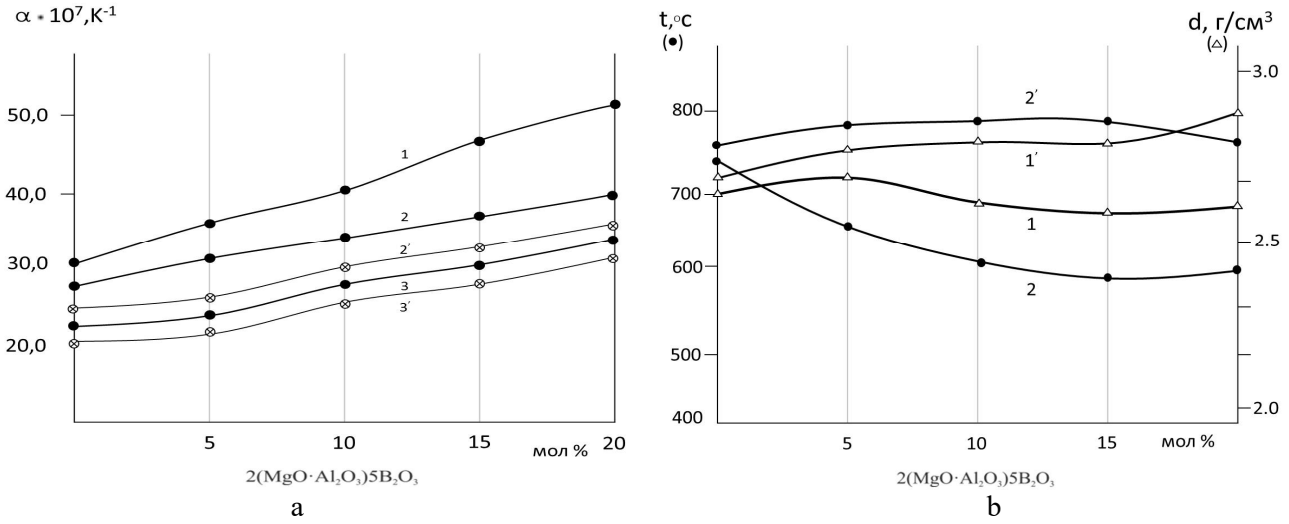

Figure 2. a - dependences of TCLE of the initial glasses (1) and glass-ceramics (~60% crystals.): experimental data at 1000 °C (2), 1200 °C (3) and calculated data - (2^I), (3^I); b - glass transition temperature (2) and density (1) initial glass and residual glass phase (2^I) и (1^I).

$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ - $2(MgO{\cdot}Al_2O_3)5B_2O_3$ pseudo -binary system, it can be noted that there is no pronounced convexity characteristic of liquidating systems with immiscible melts.

The evidence for the existence of metastable liquation in the system is the flat course of the liquidus temperature curve with the asymmetry of the dome, which indicates the unequal temperature dependence of the mutual solubility of the coexisting phases and, consequently, the tendency of the system to form solid solutions. The region of metastable segregation is located in the subsolidus region of the system within the composition range from 7,5 to 20 mol. % of aluminum borate, and an upper critical point at ~1055 °C. In the range of compositions up to 5 mol. %, above 1420 °C, the $Mg_2Al_4B_{10}O_{23}$ melt and mullite ($3Al_2O_32SiO_2$) coexist. In a wide range of lower temperatures (1420 ... 1150 °C) and compositions (up to ~15 mol. % $Mg_2Al_4B_{10}O_{23}$), the melt is in equilibrium with two crystalline phases: $3Al_2O_3{\cdot}2SiO_2$ and $MgO{\cdot}Al_2O_3$. The metastable equilibrium near the solidus line have three crystalline phases and a melt, which released the mullite and the cordierite solid solutions at complete crystallization.

For the synthesis of glass-crystalline materials with certain properties, the original glasses were subjected to a one-stage heat treatment at temperatures of the glass crystallization exo-effects (~1000 °C and ~1200 °C), determined by the DTA method, up to ~60% of the crystallinity of the glass. For glasses containing up to 20 mol. % of the $2MgO_2Al_2O_35B_2O_3$, the primary crystalline phase is μ-cordierite ($2MgO2Al_2O_36SiO_2$) with the structure of high-temperature quartz (mass fraction – 21,4 ... 32,0%) and α-cordierite (mass fraction 5,5 ... 21,5%). The concentration of SiO_2 in the solid solution decreases at higher temperature, and an increase of the content of the aluminum-magnesium component in the residual glass phase initiates the release of the $MgAl_2O_4$ spinel (mass fraction – 2,6 ... 12,3%) and sapphirine $4MgO5Al_2O_32SiO_2$ (mass fraction – 1,4 ... 10,2%). Up to 1100 °C, the ratio of the number of formed phases is practically preserved. The intensity of α-cordierite precipitation increases sharply above 1100^0C, and the amount of the metastable phase μ-cordierite and α-cordierite is comparable in the products of glass crystallization at 1200 °C. The boron-containing new phase appears (mass fraction – 0,5 ... 14,6%) in the crystallization products of glasses containing up to 20 mol. % of $2MgO_2Al_2O_35B_2O_3$, and located in the region of metastable segregation of the system. New phase forms solid solutions with cordierite with the composition of $2MgO{\cdot}2Al_2O_3{\cdot}5[(SiO_2)_{1-X}(B_2O_3)_X]$ ($x \leq 0{,}05\ldots0{,}2$), the intensive release of which occurs above 1000 °C.

Consequently, the crystallization of the studied glasses to obtain cordierite glass-ceramics proceeds as a result of the formation of intermediate phases, and with increasing temperature, mainly μ- and α-modifications of cordierite and solid solutions of aluminoborosilicate are released. A change in the composition of the metastable phases formed during the crystallization of glass to the intense release of α -cordierite significantly affects the thermal and mechanical characteristics of glass-ceramics.

The Figure 2 represents the dependencies of TCLE glass and glass-ceramics, which obtained by one-stage heat treatment of the original glasses. Distinctive peculiarity of crystallization of the $2MgO_2Al_2O_35SiO_2$ glass composition is due to the formation of metastable phases - structures of high temperature-quartz (μ-coordinates) from the stoichiometric composition, which is the reason for the complication of the technology of cordierite glass-ceramics. To change the composition of crystalline phases and the temperature range of their stability in the system, the SiO_2 partially replaced by B_2O_3. The TCLE values of glass-ceramics increase with

an increase in the content of B_2O_3 in composition. Howevwer, they are significantly low in relation to the TCLE of the initial glasses. The initial glass-ceramics of the cordierite composition - $2MgO2Al_2O_35SiO_2$ (without the glassy phase) has a rather low expansion coefficient of ~ $9{,}5\cdot10^{-7}1/^oC$ [30]. Glass-ceramics containing B_2O_3 have relatively high TCLE values, which is associated with the high content of spinel and sapphirine in the glass-crystalline material as main phases. Considering that at a temperature of ~1000 ^oC μ-cordierite is predominantly a structure of high-temperature quartz, which has a very low expansion coefficient, the relatively low TCLE values of synthesized glass -ceramics are associated with the additive effect of thermal expansions of crystalline phases composing the glass-ceramics. As can be seen from curves 2, 2^1 and 3, 3^1(Fig. 2a), the calculated data are in good agreement with the experimental results, and the deviations of the dependences from direct proportionality (additivity) are small. It is apparently due to the small difference of the parameter E/(1-2m)r in the equation for calculating the TCLE of glass-ceramics containing crystalline glassy phases with close elastic parameters. Calculations have shown that the values of this parameter vary in the range from 5,8 ... to 6,2 for aluminosilicate glasses and precipitated crystalline phases in the studied system. The introduction of $2MgO_2Al_2O_35B_2O_3$ and an increase in its content lead to a decrease in the glass transition temperature of the initial glasses, while the values of the glasses density do not change practically. An increase in the glass transition temperature and the density of the residual glass phase in the glass-ceramics is associated with the partial transition of the MgO and Al_2O_3 oxides into the glass phase at high sitallization temperatures. Thus, during the heat treatment of the original glasses, prepared glass-ceramics can contain four crystalline and residual glass phases. Crystalline phases precipitated during heat-treatment have a specific volume that is different from each other and from the glass phase, which predetermines the possibility of synthesizing glass-ceramics with certain thermophysical parameters by stopping further glass crystallization at the stage of formation of a certain amount and ratio of the required crystalline phases.

Conclusion

Based on the analysis of the glass crystallization process, it is possible to confirm the formation of stable and metastable phases with different TCLE values and specific volumes of the phases. The results of the study make it possible to synthesize glass-ceramics with certain thermophysical parameters by stopping further glass crystallization at the stage of formation of certain amounts and ratio of crystalline and glassy phases. The relatively long process of sitallization gives reason to believe that the stresses due to the difference in the specific volumes of the phases composing the glass-ceramics can completely relax during the heat treatment of the material.

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