UDC 666.266.6;666.651.2;623.4.08

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THERMODYNAMIC ANALYSIS OF REACTIONS OF THE CELSIAN PHASE FORMATION DURING THE SYNTHESIS OF THERMAL SHOCK RESISTANCE CERAMICS BASED ON EUTECTIC GLASSES OF THE BaO–Al_2O_3–SiO_2 SYSTEM

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The search for effective ways of obtaining densely sintered celsian ceramics at low firing temperatures usually requires a large volume of experimental research. The object of our research is the reactions of the formation of the celsian phase with the participation of glass components of eutectic compositions of the BaO–Al_2O_3–SiO_2 system under low-temperature firing conditions. In this case, thermodynamic analysis was used as a tool to assess the probability of chemical reactions. This paper reports the results of theoretical and experimental studies into the features of the course of chemical reactions with the participation of glass components of eutectic compositions of the BaO–Al_2O_3–SiO_2 system. It was revealed that once the stoichiometric ratio is maintained, the final product of the interaction between the components of eutectic glasses E-4, E-5 and E-6 with crystalline fillers is the celsian phase. The most probable is the formation of celsian when the components of eutectic glasses interact with $Al_2O_3 \cdot 2SiO_2$, which is a product of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) dehydration. It was found that barium orthosilicate, in comparison with other barium silicates, exhibits the highest activity when interacting with charging components in the direction of formation of the celsian phase already at the temperature of 750^{0}C. At the temperature of 900^{0}C, such a composition is noted to have an active transition of hexagonal celsian to monoclinic celsian. As a result, the content of monoclinic celsian increases significantly. The determined patterns allow making a reasonable choice of glasses in the BaO–Al_2O_3–SiO_2 system with the lowest melting temperatures for the subsequent production of low-temperature celsian ceramics.

Keywords: celsian ceramics, eutectic glass, BaO–Al_2O_3–SiO_2 system, thermodynamic analysis, X-ray phase analysis.

DOI: 10.32434/0321-4095-2023-148-3-63-71

Introduction

Thermal shock resistance glass-crystalline and ceramic materials are high-temperature dielectrics used in metallurgy, mechanical engineering, instrument engineering, high-frequency aviation, and rocket technology. Such materials are characterized by a high degree of sintering. Along with high thermal shock resistance, they have resistance to high-temperature oxidation, high erosion resistance, and mechanical strength [1]. The most common types of thermal shock resistance materials are quartz ceramics [1], as well as glass-crystalline and ceramic materials in the R_2O (RO)–Al_2O_3–SiO_2 system, where R_2O is Li_2O, and RO is MgO or BaO [2–4].

A quartz ceramic obtained from quartz glass shows one of the highest thermal shock resistances.

At temperatures above 1200°C, quartz glass intensively crystallizes. Therefore, it is difficult for quartz ceramics to achieve a high degree of sintering without deteriorating its thermal performance. As a result, due to porosity, the material needs to be sealed for use in a humid environment [1,5].

Using glass-crystalline and ceramic materials based on various aluminosilicate systems makes it possible to achieve a high degree of sintering and bring the density of materials closer to the theoretical one. At the same time, effective use of lithium aluminosilicate materials (spodumene, $Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, and eucryptite, $Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$) is limited up to the temperature of 900°C [2,6]. The operating temperature of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) glass ceramics and ceramics traditionally does not exceed 1100°C [3,7].

Further expansion of the areas of application of glass and ceramic materials dictates stricter requirements for functional properties. It is advisable to use glass-crystalline and ceramic materials of celsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) composition to achieve high-temperature resistance. At the same time, such materials have low dielectric losses, sufficiently high mechanical strength, chemical resistance, thermal shock resistance, and resistance to high temperatures (up to 1400°C and higher). The set of necessary functional parameters is achieved thanks to the properties of the main crystalline phase, monoclinic celsian. The melting temperature of celsian (1740°C) is much higher than the melting temperature of eucryptite and spodumene (1380°C), as well as cordierite (1465°C) [8].

Densely sintered glass-crystalline materials based on celsian are traditionally obtained by classical glass and ceramic (powder) technologies. Melting of glasses of celsian composition is carried out at high temperatures (1600–1650°C), which is a significant drawback of the mentioned methods [1,8].

For dense sintering of celsian ceramics, which is obtained by powder technology from traditional raw materials (barium carbonate, kaolin, aluminum, and silicon (IV) oxides), it is necessary to perform firing at a temperature above 1450°C [4,8].

Modifying additives are introduced to reduce the firing temperature and obtain a dense structure of celsian ceramics.

Huang et al. [9] and Zaichuk et al. [10] established the effective modifying effect of glasses of the $Li_2O-B_2O_3$ and $Li_2O-Al_2O_3-B_2O_3-SiO_2$ (LABS) systems on the sintering processes of celsian ceramics. The feasibility of using LABS glass of spodumene composition was also confirmed in the synthesis of densely sintered strontium-anorthite ceramics [11]. In addition, it is noted the effective mineralizing effect of Li^+ ions on the sintering process and the modification transition of hexagonal celsian to monoclinic celsian in glass-ceramics obtained by the sol-gel method [12]. However, lithium aluminosilicates are formed in firing of these types of ceramics and glass ceramics, which lowers the temperature of the effective use of such materials and slightly increases their dielectric losses.

Tong et al. [13] synthesized densely sintered celsian glass ceramics based on the eutectic glass of the $BaO-Al_2O_3-SiO_2$ (BAS) system with the addition of $BaAl_2O_4$ and $SrAl_2O_4$ powders. However, such ceramics have high values of the temperature coefficient of linear expansion (LCTE not lower than $49{\cdot}10^{-7}$ deg^{-1}), which worsens the thermal shock resistance of the material. In addition, preliminary synthesis of $BaAl_2O_4$ and $SrAl_2O_4$ powders is necessary.

Thus, existing methods for obtaining densely sintered celsian ceramics do not allow them to fully achieve the necessary functional properties. A significant amount of experimental research is necessary in the quest for alternative methods to modify the structure of celsian ceramics to reduce the sintering temperature. Considering the above, the application of thermodynamic studies as a tool for analyzing the reactions of the formation of the celsian phase under conditions of low-temperature firing determines the relevance of the direction of these studies.

This study aims at carrying out a thermodynamic analysis of the reactions of formation of the celsian phase at the eutectic points in the $BaO-Al_2O_3-SiO_2$ system, which will enable a well-informed selection of glasses in the BAS system with the lowest melting temperatures for the subsequent production of low-temperature celsian ceramics.

Methodology of the experiment

Thermodynamic calculations were performed to establish the possibility of the formation of the celsian phase with the participation of eutectic glass components of the BAS system. The eutectic points of the BAS system were considered, in which one of the crystalline phases is celsian. During the thermodynamic analysis, changes in the Gibbs energy were determined for possible reactions of the formation of the celsian phase with the participation of glass components of the eutectic composition of the BAS system. Metakaolinite ($Al_2O_3{\cdot}2SiO_2$), which is a product of mineral kaolinite dehydration, was one of the initial components of the reactions considered. The clay component (kaolin) consists of the mineral kaolinite. Kaolin in the composition of celsian ceramics is a suspending additive and allows obtaining products with a shape of various complexity.

The temperature of softening and crystallization of the BAS glass was determined using differential thermal analysis (DTA, Netzsch 404PC) in the temperature range of 20–1000⁰C at a heating rate of 10⁰C/min.

The mineralogical composition of the crystallized glasses and celsian compositions was determined by X-ray phase analysis (XRD) using a DRON-3 diffractometer in Co-K_α radiation.

Enriched kaolin (zref-1 brand; Ukraine), technical alumina ($Al_2O_3 \geq 98.0$ wt.%), and silicon dioxide ($SiO_2 \geq 99.5$ wt.%) were used as raw components of celsian compositions glasses of eutectic compositions of the BAS system. Celsian compositions were prepared by combining wet grinding of the raw materials. The firing was carried out in the electric furnace in the air at temperatures of 750⁰C and 900⁰C.

The following raw materials were used for making glasses of eutectic compositions: barium carbonate ($BaO \geq 77.0$ wt.%), technical alumina ($Al_2O_3 \geq 98.0$ wt.%), silicon dioxide ($SiO_2 \geq 99.5$ wt.%), and boric acid ($H_3BO_3 \geq 99.8$ wt.%). The addition of B_2O_3 (10 wt.% parts over 100 wt.%) to the eutectics composition of the BAS system provides a reduction in the glass melting temperature. At the same time, the mineralogical composition does not change during the crystallization of the $BaO-Al_2O_3-B_2O_3-SiO_2$ (BABS) glass. BABS glasses were melted in corundum crucibles at 1300⁰C for 1 h.

Results and discussion

An effective technological method was proposed in the work [7], which makes it possible to obtain densely sintered cordierite ceramics at a reduced temperature of 1350⁰C. This technique implies that thr part of the components of cordierite ceramics are introduced using a low-melting glass eutectic composition, which is synthesized in the pseudo-ternary system $MgO-Al_2O_3-SiO_2$. Glass is a thermodynamically unstable phase, which determines its high thermal activity when interacting with crystalline compounds. As a result, the cordierite phase is formed during the sintering process due to the interaction of part of the components of the experimental glass with crystalline fillers. Such an interaction occurs much more intensively than the course of reactions in the solid phase. In addition, the formation of cordierite is the result of finely dispersed crystallization of the glass, which helps increase the mechanical strength of ceramics. Implementing that approach in synthesizing celsian ceramics required a significant amount of energy-intensive experimental research. Therefore, for a justified selection of glasses as components of low-temperature celsian ceramics, it is necessary to determine the thermodynamic conditions for the formation of the celsian phase at the eutectic points of the $BaO-Al_2O_3-SiO_2$ system. The eutectic points represent the temperature at which the mixture of components reaches the lowest melt formation temperature, indicating the lowest possible melting temperature of glass in the system.

Figure 1 presents a segment of the $BaO-Al_2O_3-SiO_2$ system, with the eutectic points and corresponding temperatures highlighted, where celsian is one of the crystalline phases [14].

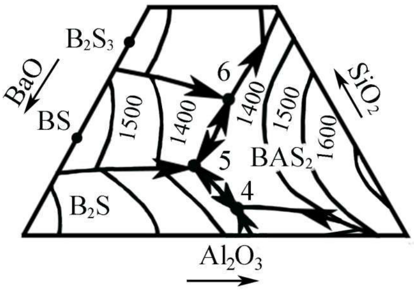


Fig. 1. Area of the $BaO-Al_2O_3-SiO_2$ system with eutectic points 4–6

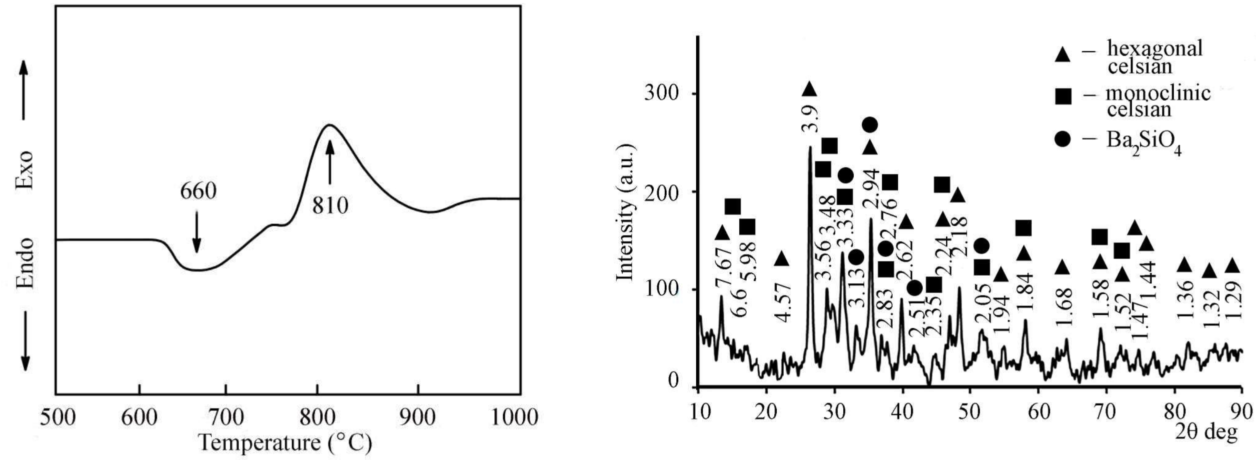
As eutectic points 4–6 correspond to different crystalline phases, there are many variants of the course of chemical reactions during the interaction of glass components with crystalline fillers. Consequently, thermodynamic studies can be useful in assessing the likelihood of chemical and physicochemical processes, thereby reducing the need for energy-intensive experimental research.

When conducting thermodynamic calculations, the change in Gibbs energy of reactions is found (ΔG_T^0). Of the different processes that can occur in the system, the thermodynamically most likely is the one that is accompanied by the greatest drop in ΔG_T^0. At the same time, calculations were performed for the same number of moles of the initial components (glass crystallization products). In this case, the values ΔG_T^0 can be compared.

To select glasses compositions for the low-temperature synthesis of celsian ceramics, it is necessary to determine the thermodynamic conditions for the formation of the celsian phase at the eutectic points of the $BaO-Al_2O_3-SiO_2$ system. According to data from [14], in the BAS system, there are three eutectic points at which one of the crystalline phases is celsian (Fig. 1). Finely dispersed crystallization of the celsian phase from glass provides high rates of mechanical strength of ceramic materials. Simultaneous crystallization of three phases should occur at eutectic points 4–6. In addition to celsian and barium metasilicate ($BaO{\cdot}SiO_2$), the compound $2BaO{\cdot}SiO_2$ crystallizes at point 5, and the compound $2BaO{\cdot}3SiO_2$ crystallizes at point 6. At the eutectic point 4, according to Belyankin et al. [14], together with celsian and $2BaO{\cdot}SiO_2$, a solid solution based on the ternary compound $3BaO{\cdot}3Al_2O_3{\cdot}2SiO_2$ ($B_3A_3S_2$) crystallizes. These authors note that the $B_3A_3S_2$ phase has a non-stoichiometries composition and melts incongruently at a temperature of 1550°C. No other data on the presence of the $B_3A_3S_2$ phase were found in the literature. X-ray phase analysis studies of a crystallized glass of eutectic composition E-4 (Fig. 2) also did not reveal the presence of the $B_3A_3S_2$ phase. The mode of heat treatment of E-4 glass (two-hour exposure at temperatures of 660°C and 810°C) was chosen based on the results of the differential thermal analysis (Fig. 2,a). The DTA curve shows an endothermic effect at 660°C, as well as an exothermic effect with a maximum at 810°C, which are responsible for the softening and crystallization of glass. Crystallization products of E-4 glass are hexagonal form celsian ($d{\cdot}10^{10}$=7.67; 3.90; 2.94; 2.62; and 2.18 m) and monoclinic form celsian ($d{\cdot}10^{10}$=6.6; 3.56; 3.48; 3.33; and 2.76 m). In addition, barium orthosilicate $2BaO{\cdot}SiO_2$ ($d{\cdot}10^{10}$=3.33; 3.13; 2.83; 2.51; and 2.05 m) was detected.

Thus, celsian is the only thermodynamically stable ternary compound in the BAS system. Considering the above, the thermodynamic analysis of the formation of the celsian phase was carried out for reactions involving the double compounds $2BaO{\cdot}3SiO_2$, $BaO{\cdot}SiO_2$, and $2BaO{\cdot}SiO_2$. Such barium silicates are products of the crystallization of glasses of eutectic compositions (E-4, E-5, and E-6) of the BAS system. The initial components of chemical reactions were also $Al_2O_3{\cdot}2SiO_2$, Al_2O_3, and SiO_2 (Table 1).

Thermodynamic calculations ΔG_T^0 were carried out in the temperature range of 873–1173 K. The temperature range in which thermodynamic calculations of reactions were carried out was limited by the maximum temperature of the existence of the compound $Al_2O_3{\cdot}2SiO_2$ (1173 K). Metakaolinite acted as one of the main starting compounds in the reactions of celsian formation. In addition, the polymorphic transformation α-quartz→α-tridymite, which occurs at the temperature of 870°C, was



a b

Fig. 2. DTA curve (a) and XRD pattern (b) of E-4 glass

Table 1

Compounds that are the initial components of reactions in celsian compositions.

Compositions number and starting components for synthesis		
B-4	B-5	B-6
Glass E-4 ($2BaO{\cdot}SiO_2$)*, $Al_2O_3{\cdot}2SiO_2$, Al_2O_3, SiO_2	Glass E-5 ($BaO{\cdot}SiO_2$, $2BaO{\cdot}SiO_2$)*, $Al_2O_3{\cdot}2SiO_2$, Al_2O_3, SiO_2	Glass E-6 ($BaO{\cdot}SiO_2$, $2BaO{\cdot}3SiO_2$)*, $Al_2O_3{\cdot}2SiO_2$, Al_2O_3, SiO_2

Note: * – those phases are indicated in brackets, which, along with $BaO{\cdot}Al_2O_3{\cdot}2SiO_2$, are products of the crystallization of glasses E-4, E-5, and E-6.

considered.

There are no thermodynamic constants for minerals in the literature, which are products of the crystallization of experimental glasses in the vitreous state. Therefore, thermodynamic constants for crystalline compounds were used. A slight difference between the thermodynamic constants for different silicates in the crystalline and vitreous states does not lead to noticeable changes in the final result.

The values of the thermodynamic constants of the initial individual compounds and the resulting products of chemical reactions at the standard temperature are given in Table 2.

The results of ΔG^0_T calculations for chemical reactions (1)–(21) in the temperature range 873–1173 K are summarized in Table 3. These results showed that the formation of the celsian phase from the components of eutectic glasses of the BAS system is most likely when interacting directly with $Al_2O_3{\cdot}2SiO_2$. The values ΔG^0_T of reactions (1), (7), and (10) indicate that celsian is the only final product of the interaction of the initial components. The lowest ΔG^0_T values (–1385÷–1744 kJ/mol) in the temperature range 873–1173 K are characteristic of the formation of celsian with $2BaO{\cdot}SiO_2$ according to reaction (10). Further, the formation of celsian with the participation of $2BaO{\cdot}3SiO_2$ (reaction (7)) and $BaO{\cdot}SiO_2$ (reaction (1)) is possible.

To verify the data thermodynamic calculations, celsian compositions were obtained based on glasses of eutectic compositions E-4, E-5, and E-6. The chemical compositions of BABS glasses are presented in Table 4.

The content of glass in the compositions is as follows (wt.%): B-4 64.4; B-5 63.9; and B-6 70.9. The content of the glasses was determined by the need to fully bond the components of such glasses into stoichiometric celsian due to the addition of crystalline fillers (Table 1). The compositions were fired at temperatures of 750°C and 900°C with subsequent X-ray phase analysis of the products obtained (Figs. 3 and 4).

X-ray phase analysis confirmed the results of thermodynamic calculations. It was established that the final mineralogical composition of compositions B-4, B-5, and B-6 is represented only by the celsian

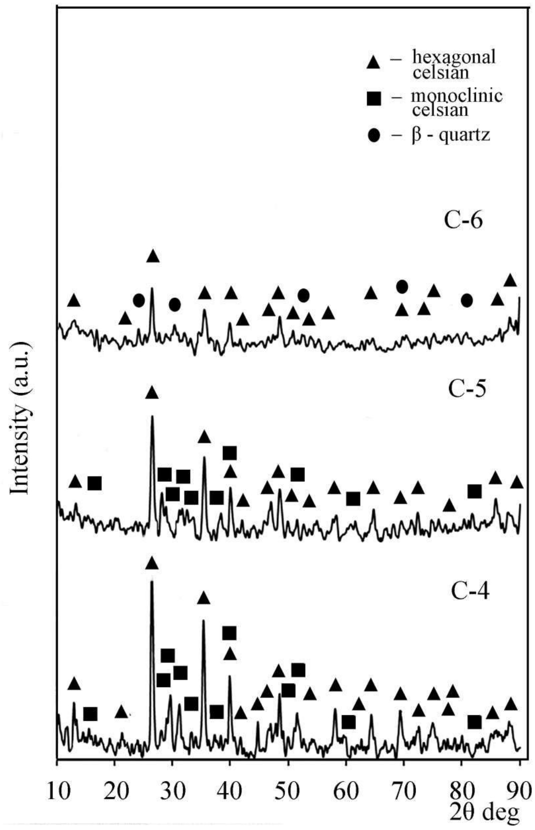


Fig. 3. X-ray patterns of celsian compositions fired at the temperature of 750°C

Table 2

Initial thermodynamic constants [15]

Compounds	$-\Delta H^0_{298.15}$, kJ/mol	$-\Delta G^0_{298.15}$, kJ/mol	$S^0_{298.15}$, J/mol·K	$C_p = a + b \cdot T + c \cdot T^{-2}$, J/mol·K		
				a	$b{\cdot}10^3$	$c{\cdot}10^{-5}$
$BaSi_2O_5$	2532.94	2395.8	154.05	172.8	13.08	–28.96
$Ba_2Si_3O_8$	4196.34	3973.64	266.23	211.52	38.43	–0.7
$BaSiO_3$	1629.10	1545.00	112.18	102.56	24.69	0
Ba_2SiO_4	2298.24	2184.39	182.89	144.42	33.49	0
γ-Al_2O_3	1637.98	1542.12	52.54	106.68	17.79	–25.5
α-quartz	911.50	857.08	41.86	60.32	8.13	0
α-tridymite	905.98	852.19	43.53	57.10	11.05	0
$Al_2Si_2O_7$	3316.15	3102.29	124.24	229.68	36.84	–14.57
$Al_6Si_2O_{13}$	6857.09	6462.90	251.16	485.16	46.88	–154.88
$BaAl_2Si_2O_8$	4257.77	4196.64	205.04	287.39	41.86	–63.59

Table 3

Calculated ΔG_T^0 values for chemical reactions (1)–(21)

Reaction number	Chemical reactions	ΔG_T^0 value for reactions (kJ/mol) at the temperature, K			
		873	973	1073	1173
1	$BaO\cdot SiO_2+0.5(Al_2O_3\cdot 2SiO_2)+0.5Al_2O_3=BaO\cdot Al_2O_3\cdot 2SiO_2$	–668	–726	–785	–844
2	$BaO\cdot SiO_2+0.33(Al_2O_3\cdot 2SiO_2)=0.33(2BaO\cdot 3SiO_2)+0.33(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–250	–269	–286	–303
3	$BaO\cdot SiO_2+0.5(Al_2O_3\cdot 2SiO_2)=0.5(BaO\cdot 2SiO_2)+0.5(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–371	–400	–430	–459
4	$BaO\cdot SiO_2+Al_2O_3+SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2$	–584	–641	–699	–761
5	$BaO\cdot SiO_2+0.33Al_2O_3+0.66SiO_2=0.33(2BaO\cdot 3SiO_2)+0.33(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–179	–196	–213	–232
6	$BaO\cdot SiO_2+0.5Al_2O_3+SiO_2=0.5(BaO\cdot 2SiO_2)+0.5(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–287	–315	–344	–376
7	$2BaO\cdot 3SiO_2+0.5(Al_2O_3\cdot 2SiO_2)+1.5Al_2O_3=2(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–1248	–1372	–1496	–1621
8	$2BaO\cdot 3SiO_2+2Al_2O_3+SiO_2=2(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–1164	–1286	–1410	–1539
9	$2BaO\cdot 3SiO_2+Al_2O_3+SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+BaO\cdot 2SiO_2$	–571	–635	–699	–769
10	$2BaO\cdot SiO_2+Al_2O_3\cdot 2SiO_2+Al_2O_3+SiO_2=2(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–1385	–1503	–1622	–1744
11	$2BaO\cdot SiO_2+Al_2O_3\cdot 2SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+BaO\cdot SiO_2$	–802	–862	–922	–983
12	$2BaO\cdot SiO_2+Al_2O_3\cdot 2SiO_2+0.5SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+0.5(2BaO\cdot 3SiO_2)$	–803	–860	–916	–975
13	$2BaO\cdot SiO_2+Al_2O_3\cdot 2SiO_2+SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+BaO\cdot 2SiO_2$	–792	–851	–911	–974
14	$2BaO\cdot SiO_2+2Al_2O_3+3SiO_2=2(BaO\cdot Al_2O_3\cdot 2SiO_2)$	–1217	–1333	–1449	–1579
15	$2BaO\cdot SiO_2+Al_2O_3+2SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+BaO\cdot SiO_2$	–634	–692	–750	–817
16	$2BaO\cdot SiO_2+Al_2O_3+2.5SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+0.5(2BaO\cdot 3SiO_2)$	–635	–690	–744	–809
17	$2BaO\cdot SiO_2+Al_2O_3+3SiO_2=BaO\cdot Al_2O_3\cdot 2SiO_2+BaO\cdot 2SiO_2$	–624	–681	–738	–808
18	$3(Al_2O_3\cdot 2SiO_2)=3Al_2O_3\cdot 2SiO_2+4SiO_2$	–626	–633	–640	–629
19	$2BaO\cdot SiO_2+SiO_2=2(BaO\cdot SiO_2)$	–50	–51	–51	–56
20	$2BaO\cdot SiO_2+2SiO_2=2BaO\cdot 3SiO_2$	–54	–49	–39	–40
21	$2BaO\cdot SiO_2+3SiO_2=2(BaO\cdot 2SiO_2)$	–31	–30	–28	–38

Table 4

Chemical compositions of BABS glasses (wt.%)

Glass numbers	SiO_2	Al_2O_3	BaO	B_2O_3
E-4	20.4	13.2	57.3	9.1
E-5	23.6	9.1	58.2	9.1
E-6	29.1	9.1	52.7	9.1

phase. Celsian is intensively formed in the firing process already at the temperature of 750^0C. At the same time, the hexagonal form of celsian dominates the phase composition. The maximum content of this crystalline phase is observed for the B-4 composition. This is confirmed by the highest intensity of the main diffraction maxima of the hexagonal celsian in the corresponding X-ray pattern (Fig. 3) and is fully consistent with the results of thermodynamic calculations (Table 3). Composition B-4 is obtained based on eutectic glass E-4, the crystallization product of which, along with the celsian phase, is $2BaO\cdot SiO_2$. Barium orthosilicate, in comparison with other barium silicates, shows the greatest activity when interacting with crystalline fillers in the direction of the formation of the celsian phase. However, the firing temperature of 750^0C is inadequate for complete binding of the initial components of composition B-6 in celsian, as evidenced by the presence of a small amount of b-quartz in the phase composition ($d\cdot 10^{10}$=4.27; 3.37; 2.05; and 1.55 m). Accordingly, the composition B-6 is characterized by the lowest content of hexagonal celsian. Composition B-6 is obtained based on eutectic glass E-6. The crystallization products of such glass, along with the celsian phase, are $BaO\cdot SiO_2$ and $2BaO\cdot 3SiO_2$. Reactions for the formation of the celsian phase from the specified barium silicates are characterized by a higher value of ΔG_T^0 than $2BaO\cdot SiO_2$ (Table 3). Similar dynamics are also observed for the change in the content of the monoclinic form of celsian ($d\cdot 10^{10}$=6.54; 3.69; 3.55; 3.35; 3.14; 2.73; and 1.80 m) in the B-4 and B-5 compositions (Fig. 3). For the B-6 composition at a temperature of 750^0C, the transition of the hexagonal celsian into the monoclinic form does not occur.

The formation of the celsian phase is fully completed at the temperature of 900^0C. This is evidenced by the absence of diffraction maxima from

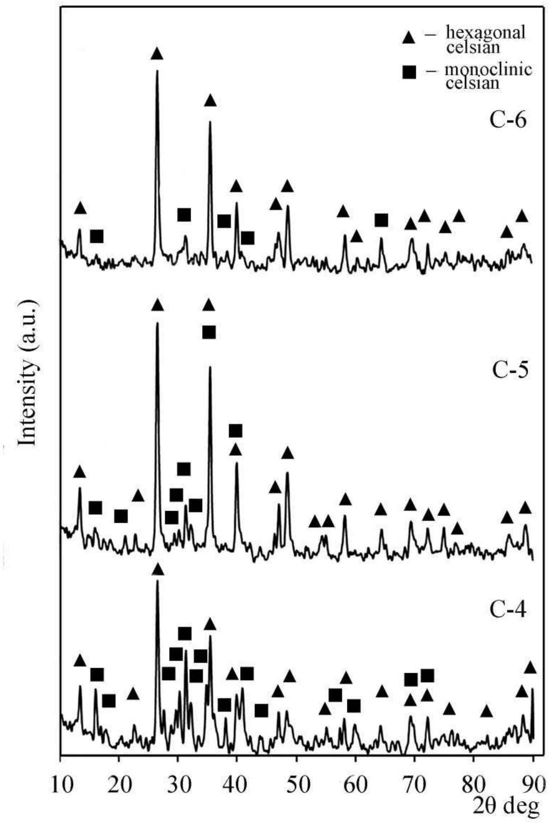


Fig. 4. X-ray patterns of celsian compositions fired at the temperature of 900^{0}C

the initial compounds in X-ray patterns. The phase composition of compositions B-5 and B-6 is dominated by the hexagonal form of celsian ($d\cdot10^{10}$=7.56; 3.86; 2.92; 2.60; 2.16; 1.83; and 1.67 m) (Fig. 4). For composition B-4, an active transition from hexagonal celsian→monoclinic celsian is observed. As a result, the content of monoclinic celsian increases significantly due to the decrease in the content of hexagonal celsian. For celsian ceramics, it is desirable to form the monoclinic celsian shape, which is characterized by higher electrical insulating, thermal and mechanical properties than the hexagonal shape.

Considering the above, using eutectic glass E-4 to obtain densely sintered celsian ceramics at low temperatures is the most appropriate. Crystallization of such glass occurs with the formation of the celsian phase and barium orthosilicate.

Conclusions

Thermodynamic calculations determined the conditions for the formation of the celsian phase at the eutectic points of the $BaO-Al_2O_3-SiO_2$ system. The most probable is the formation of celsian when the components of eutectic glasses interact with $Al_2O_3\cdot2SiO_2$, which is a product of kaolinite dehydration. It was established that the final product of the interaction between the components of glasses of eutectic compositions E-4, E-5 and E-6 with crystalline fillers is celsian. Compared with other barium silicates, barium orthosilicate was determined to show the greatest activity when interacting with crystalline fillers. In addition, at the temperature of 900^{0}C, the content of monoclinic celsian increases significantly due to a decrease in the content of hexagonal celsian. The determined regularities allow making a reasonable choice of glasses in the $BaO-Al_2O_3-SiO_2$ system with the lowest melting temperatures for the subsequent production of low-temperature celsian ceramics.

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Received 01.02.2023

ТЕРМОДИНАМІЧНИЙ АНАЛІЗ РЕАКЦІЙ УТВОРЕННЯ ЦЕЛЬЗІАНОВОЇ ФАЗИ ПРИ СИНТЕЗІ ТЕРМОСТІЙКОЇ КЕРАМІКИ НА ОСНОВІ ЕВТЕКТИЧНИХ СТЕКОЛ СИСТЕМИ $BaO–Al_2O_3–SiO_2$

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Пошук ефективних шляхів отримання щільноспеченої цельзіанової кераміки при знижених температурах випалу, як правило, потребує великого об'єму експериментальних досліджень. Об'єктом досліджень в даній роботі є реакції утворення цельзіанової фази за участю компонентів стекол евтектичних складів системи $BaO–Al_2O_3–SiO_2$ в умовах низькотемпературного випалу. При цьому, як інструмент для оцінки ймовірності перебігу хімічних реакцій, використовували термодинамічний аналіз. В статті наведені результати теоретичних і експериментальних досліджень особливостей перебігу хімічних реакцій за участю компонентів стекол евтектичних складів системи $BaO–Al_2O_3–SiO_2$. Виявлено, що у випадку дотримання стехіометричного співвідношення кінцевим продуктом взаємодії компонентів евтектичних стекол Е-4, Е-5 і Е-6 з підшихтовочними компонентами є цельзіанова фаза. Найбільш ймовірним є утворення цельзіану при взаємодії компонентів евтектичних стекол з $Al_2O_3·2SiO_2$, який є продуктом дегідратації каолініту ($Al_2O_3·2SiO_2·2H_2O$). Встановлено, що ортосилікат барію у порівнянні з іншими силікатами барію проявляє найбільшу активність при взаємодії з підшихтовочними компонентами в напрямку утворення цельзіанової фази вже при температурі 750°C. При температурі 900°C для такої композиції відмічається активний перехід гексагональний цельзіан®-моноклінний цельзіан. В результаті суттєво збільшується вміст моноклінного цельзіану. Визначені закономірності дають змогу здійснити обгрунтований вибір стекол в системі $BaO–Al_2O_3–SiO_2$ з найнижчими температурами варіння для подальшого виготовлення низькотемпературної цельзіанової кераміки.

Ключові слова: цельзіанова кераміка, евтектичне скло, система $BaO–Al_2O_3–SiO_2$, термодинамічний аналіз, рентгенофазовий аналіз.

THERMODYNAMIC ANALYSIS OF REACTIONS OF THE CELSIAN PHASE FORMATION DURING THE SYNTHESIS OF THERMAL SHOCK RESISTANCE CERAMICS BASED ON EUTECTIC GLASSES OF THE $BaO–Al_2O_3–SiO_2$ SYSTEM

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The search for effective ways of obtaining densely sintered celsian ceramics at low firing temperatures usually requires a large volume of experimental research. The object of our research is the reactions of the formation of the celsian phase with the participation of glass components of eutectic compositions of the $BaO–Al_2O_3–SiO_2$ system under low-temperature firing conditions. In this case, thermodynamic analysis was used as a tool to assess the probability of chemical reactions. This paper reports the results of theoretical and experimental studies into the features of the course of chemical reactions with the participation of glass components of eutectic compositions of the $BaO–Al_2O_3–SiO_2$ system. It was revealed that once the stoichiometric ratio is maintained, the final product of the interaction between the components of eutectic glasses E-4, E-5 and E-6 with crystalline fillers is the celsian phase. The most probable is the formation of celsian when the components of eutectic glasses interact with $Al_2O_3·2SiO_2$, which is a product of kaolinite ($Al_2O_3·2SiO_2·2H_2O$) dehydration. It was found that barium orthosilicate, in comparison with other barium silicates, exhibits the highest activity when interacting with charging components in the direction of formation of the celsian phase already at the temperature of 750°C. At the temperature of 900°C, such a composition is noted to have an active transition of hexagonal celsian to monoclinic celsian. As a result, the content of monoclinic celsian increases significantly. The determined patterns allow making a reasonable choice of glasses in the $BaO–Al_2O_3–SiO_2$ system with the lowest melting temperatures for the subsequent production of low-temperature celsian ceramics.

Keywords: celsian ceramics; eutectic glass; $BaO–Al_2O_3–SiO_2$ system; thermodynamic analysis; X-ray phase analysis.

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