The search for effective modifiers of the structure of densely baked cordierite ceramics to reduce the firing temperature is a relevant task but typically requires a large amount of experimental research. The object of this study is the reaction of the formation of the cordierite phase with the participation of glass components of the eutectic compositions of the $MgO–Al_2O_3–SiO_2$ system under low-temperature firing conditions. In this case, thermodynamic analysis was used as a tool to assess the probability of chemical reactions. Thermodynamic analysis can significantly reduce the volume of the experimental sample.

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 $MgO–Al_2O_3–SiO_2$ system. It was revealed that once the stoichiometric ratio is maintained, the resulting product of the interaction between the components of eutectic glasses of the $MgO–Al_2O_3–SiO_2$ system with charging components is cordierite. Changes in the mineralogical composition of cordierite compositions depending on the firing temperature have been determined. The formation of the cordierite phase is preceded by the process of transformation of meta kaolinite $Al_2O_3•2SiO_2$, which is a product of kaolin dehydration, into mullite $3Al_2O_3•2SiO_2$. Subsequently, the formation of cordierite (in addition to crystallizing directly from eutectic glasses) occurs with the participation of the mullite phase. The formation of the cordierite phase occurs in several stages and is completed at a temperature of 1300 °C. The established features of the reactions of cordierite formation make it possible to determine the most optimal compositions for glasses of the $MgO–Al_2O_3–SiO_2$ system to obtain low-temperature cordierite ceramics with a high degree of sintering. At the same time, it is also possible to control the phase composition of ceramics and its properties

Keywords: cordierite ceramics, eutectic glass, $MgO–Al_2O_3–SiO_2$ system, thermodynamic analysis, X-ray phase analysis

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DETERMINING PATTERNS IN THE FORMATION OF CORDIERITE PHASE DURING THE SYNTHESIS OF DENSITY-SINTERED LOW-TEMPERATURE CERAMICS BASED ON GLASSES OF THE $MgO–Al_2O_3–SiO_2$ SYSTEM

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1. Introduction

Heat-resistant ceramic materials are widely used in the manufacture of radio engineering devices, in electrical engineering as dielectric materials, as carriers of catalysts, heat exchangers, refractories, as well as means of radio support in aviation and rocket technology [1, 2].

The range of heat-resistant ceramic and glass crystalline materials is quite wide. At the same time, taking into account the complexity of the technological process of production, the cost of raw materials, as well as the harsh operating conditions of heat-resistant materials, the most affordable are quartz ceramics and glass crystalline materials of aluminosilicate composition.

Quartz ceramics is characterized by one of the highest rates of heat resistance. This ceramic also exhibits stable dielectric properties in a wide temperature range [3]. The main difficulty in the manufacture of quartz ceramics is to achieve a high degree of sintering. As a result, due to the presence of porosity, the material needs to be sealed for use in a humid environment. In addition, despite various methods aimed at strengthening quartz ceramics, mechanical strength remains relatively low [4, 5].

More promising from the point of view of achieving a high degree of sintering is the use of glass crystalline and ceramic materials based on various aluminosilicate systems. As a result, products of complex shapes of various sizes can

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be obtained, the porosity of which is close to zero. However, there are certain limitations in this case. In particular, for lithium-aluminum silicate materials, the temperature of effective use due to insufficient temperature stability of dielectric and mechanical properties does not exceed 900 °C [6, 7].

To achieve the required level of high-temperature resistance of materials, it is advisable to use alkaline-free or low-alkaline aluminosilicate systems. In this case, heat-resistant materials are made on the basis of $BaO–Al_2O_3–SiO_2$ (BAS) and $SrO–Al_2O_3–SiO_2$ (SAS) systems, which contain the crystalline phases of monoclinic celsian [8] and strontium anorthite [9]. These materials can operate in the temperature range exceeding 1100 °C. At the same time, such glass ceramics have a number of disadvantages (relatively high values of specific weight and temperature coefficient of linear expansion (TCLE)), which limits the scope of application [10–12].

Cordierite glass ceramics surpasses strontium-anorthite and celsian ceramics, primarily in heat resistance and strength indicators [13–15]. In addition, cordierite is characterized by low specific weight. Therefore, ceramic and glass-ceramic materials based on cordierite are successfully used for the manufacture of heat-resistant materials of a wide range [16].

For the synthesis of densely baked cordierite ceramics, high temperatures are necessary. At the same time, at temperatures above 1450 °C, the crystal structure of cordierite is destroyed, followed by incongruent melting. As a result, ceramic material contains up to 20 wt. % of impurity phases (spinel, mullite, clinoenstatite). Such crystalline phases impair the performance properties of cordierite ceramics [17, 18].

Finding ways to modify the structure of cordierite ceramics to reduce the sintering temperature mainly requires a large amount of experimental research. Taking into account the above, the use of thermodynamic studies, as a tool for analyzing the reactions of the formation of the cordierite phase in conditions of low-temperature firing, determines the relevance of the direction of our research.

2. Literature review and problem statement

Heat-resistant cordierite materials for high-frequency use should have a density close to theoretical, as well as minimal water absorption (less than 0.1 %). Densely baked glass crystalline materials based on cordierite are traditionally obtained using two technologies: classical glass and ceramic (powder). Powder technology of glass crystalline materials in comparison with the classic glass one makes it possible to significantly expand the range of compositions of resulting glasses and the range of products that are manufactured [19]. At the same time, a significant disadvantage of these techniques is the baking of cordierite glass in the $MgO–Al_2O_3–SiO_2$ (MAS) system at high temperatures (1550–1600 °C) [20, 21].

The synthesis of densely sintered cordierite from a mixture of initial oxides has difficulties due to a narrow sintering interval of 10–20 °C at temperatures of 1450–1550 °C and degradation of the crystalline structure of the material. If the firing temperature is below 1450 °C, the degree of sintering is not satisfactory. Equally important is also the duration of exposure at the optimum temperature. Long duration leads to the destruction of the crystal structure and the formation of glass phase [17].

To reduce the firing temperature and obtain a dense structure of cordierite ceramics, modifying additives are introduced.

In [22, 23], the effect of cations of transition elements Cu and Co is investigated; and in [24] – of Ni and Mo on the processes of formation of the cordierite phase and sintering of ceramics. The effective role of such cations has been established. The value of the ionic radius of the studied transition elements is close to the ionic radius of Mg^{2+} (0,74 Å). As a result of the substitution of Mg^{2+} ions in the structure of cordierite, isomorphic solid solutions are formed at low temperatures. However, if the concentration of additives exceeds the solubility limit, additional phases are formed in the form of spinel and silicates. New crystalline phases can significantly change the properties of cordierite ceramics. First of all, the dielectric properties deteriorate, which are important in the case of using materials for radio engineering.

Another mechanism of action is observed with the introduction of alkali metal oxides, in particular K_2O. Alkali metal oxides contribute to the formation of glass phase, which reduces the sintering temperature to 1450 °C. However, K_2O increases the dielectric losses of cordierite ceramics in the case of high-frequency use [25]. Liquid-phase sintering of cordierite ceramics is also observed with the administration of bismuth(III) oxide. A dense microstructure is formed after firing at a temperature of 1350–1400 °C for 2 hours, but the properties are also insufficient for the use of materials as high-frequency dielectrics [26].

In [27], the results of research on the search for ways to reduce the sintering temperature of cordierite ceramics by optimizing the technological process of manufacturing are given. The synthesis was carried out both from the starting materials ($MgCO_3$, Al_2O_3 and SiO_2) in stoichiometric ratio, and from pre-obtained spinel ($MgAl_2O_4$) and forsterite (Mg_2SiO_4). It was established that the greatest decrease in sintering temperature (up to 1350 °C) was achieved with the simultaneous use of spinel and forsterite with the addition of aluminum oxides and silicium. The advantage of this technique is explained by the fact that $MgAl_2O_4$ has the highest degree of symmetry of the crystal lattice (cubic). This leads to a decrease in energy costs in the formation of cordierite crystals. However, obtaining these results required a large amount of experimental research. In addition, the manufacture of such materials occurs by semi-dry pressing, which imposes significant restrictions on the complexity of the shape of the products.

Thus, existing methods for producing densely sintered cordierite ceramics are typically based on high temperature firing or do not make it possible to achieve a set of necessary physical, technical, and technological indicators.

In [28], a technological process is proposed, which makes it possible to obtain densely baked ceramics of cordierite composition. The essence of the technique is that part of the components of cordierite ceramics is introduced using a relatively low-melting glass with eutectic composition, which is synthesized in the pseudo-triple system $MgO–Al_2O_3–SiO_2$. By changing the content of glass and its composition, it is possible to control the microstructure and phase composition of ceramic materials. The formation of cordierite partially occurs due to the process of fine crystallization of the experimental glass, which helps increase the mechanical strength of ceramics. In addition, the principle of reaction formation of the microstructure of ceramics is implemented. 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. The implementation of that approach required a significant amount of energy-intensive experimental research. At the same time, the issues of determining the most optimal compositions of the glass of the MAS system for obtaining low-temperature cordierite ceramics with a high degree of sintering remained unresolved.

Fig. 1 shows part of the $MgO–Al_2O_3–SiO_2$ system, indicating the temperatures of the invariant points at which one of the crystalline phases is cordierite [29]. Invariant points are characterized by the lowest melt formation temperatures in the system, which is advisable to use in the design of cordierite ceramics compositions using MAS glasses.

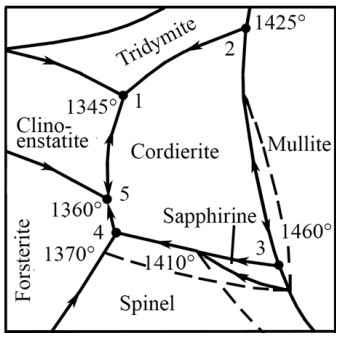

Fig. 1. Part of the $MgO–Al_2O_3–SiO_2$ system with invariant points (1–5) in which one of the crystalline phases is cordierite

Given that invariant points 1–5 are represented by different crystalline phases, there are a large number of variants of the course of chemical reactions in the implementation of the principle of reaction formation of the structure of cordierite ceramics. This requires a significant amount of experimental research to select invariant points that will provide the most rational technological conditions for the formation of cordierite ceramics. The above allows us to assert the expediency of using thermodynamic studies as an effective method for assessing the probability of chemical and physical-chemical processes. In this case, the volume of energy-intensive experimental research is significantly reduced.

3. The aim and objectives of the study

The aim of this study is to determine the patterns of formation of the cordierite phase at the invariant points of the $MgO–Al_2O_3–SiO_2$ system in the synthesis of densely baked cordierite ceramics with low sintering temperatures. This will allow for a reasonable choice of glasses in a MAS system with the lowest baking temperatures. Selected glasses will be used as components for the manufacture of heat-resistant cordierite ceramics at low temperatures.

To accomplish the aim, the following tasks have been set:

– to calculate the change in Gibbs energy $\left(\Delta G_T^0\right)$ for the reactions of the formation of the cordierite phase at the invariant points of the $MgO–Al_2O_3–SiO_2$ system;

– to check the calculated data using X-ray phase analysis (XPA) by assessing the change in the mineralogical composition of cordierite compositions depending on the firing temperature.

4. The study materials and methods

This work is aimed at determining the patterns of formation of the cordierite phase with the participation of glass components of eutectic compositions of the $MgO–Al_2O_3–SiO_2$ system under low-temperature firing conditions. To establish the possibility of the formation of the cordierite phase, thermodynamic calculations were used. The invariant points of the $MgO–Al_2O_3–SiO_2$ system were considered, in which one of the crystalline phases is cordierite. During thermodynamic analysis, changes in Gibbs energy were determined for possible reactions of cordierite phase formation with the participation of components of experimental MAS glasses. Meta kaolinite acted as one of the initial components of the reactions under consideration ($Al_2O_3{\cdot}2SiO_2$), which is a product of the dehydration of the mineral kaolinite. The mineral kaolinite is represented by the clay material kaolin. It is this component of cordierite ceramics that ensures its ability to mold by almost all traditional methods.

The mineralogical composition of cordierite compositions was determined using X-ray phase analysis (XPA) on the Philips APD-15 diffractometer in Co-Kα radiation.

As raw materials in the preparation of cordierite compositions, we used glass of eutectic compositions; enriched kaolin, brand zref-1 (Ukraine); magnesium oxide, grade; technical alumina, grade G-0. Cordierite compositions were prepared by the method of compatible wet grinding of the original raw materials. Firing was carried out in an electric furnace in an air environment in the temperature range of 900–1300 °C.

The following raw materials were used for baking glasses of eutectic compounds: talc, grade 5SSW (India); technical alumina, grade G-0; silicon dioxide, grade A; boric acid (H_3BO_3≥99.8 wt. %). The introduction into the MAS system of boron oxide (10 wt. p. over 100 wt. %) provides a decrease in the baking temperature of experimental silicate glasses and, at the same time, does not change their mineralogical composition during the crystallization process [30, 31]. Glass baking in the $MgO–Al_2O_3–B_2O_3–SiO_2$ (MABS) system was carried out in an electric furnace with carbide silicon heaters at temperatures of 1375–1400 °C for 1 hour. Corundum crucibles were used for baking.

5. The results of research on cordierite ceramics

5. 1. The results of thermodynamic research

The purpose of thermodynamic calculations is to find changes in Gibbs energy reactions $\left(\Delta G_T^0\right)$. The fundamental possibility and probable direction of the course of any physicochemical process is determined by the magnitude and sign of the change in Gibbs energy. 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 $\left(\Delta G_T^0\right)$.

To select glasses as components of low-temperature cordierite ceramics, it is necessary to determine the thermodynamic conditions for the formation of the cordierite phase at the invariant points of the $MgO–Al_2O_3–SiO_2$ system. According to data from [29], in the MAS system there are five invariant points at which one of the crystalline phases is cordierite (Fig. 1). Finely dispersed crystallization of the cordierite phase from glass provides high rates of mechanical strength of ceramics [28]. The lowest temperatures (below 1400 °C) of melt formation in the MAS system

characterize invariant points 1 (1345 °C), 4 (1370 °C), and 5 (1360 °C). Invariant points 1 and 5 are eutectic, that is, they simultaneously crystallize the three phases. In addition to cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), tridymite ($SiO_2$) and clinoenstatite ($MgO{\cdot}SiO_2$) crystallize at point 1, and at point 5 – forsterite ($2MgO{\cdot}SiO_2$) and clinoenstatite. The invariant point 4 is the double lifting point at which the crystallization process is not completed. The crystallization process is completed at eutectic point 5, which is bounded by the field of the elementary triangle $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$–$MgO{\cdot}SiO_2$–$2MgO{\cdot}SiO_2$. Given this, the thermodynamic analysis for the formation of the cordierite phase was carried out for reactions involving forsterite, clinoenstatite, and tridymite, which are products of crystallization of glass of eutectic compositions (E-1 and E-5) of the MAS system. The initial components of chemical reactions were also meta kaolinite, MgO, and Al_2O_3 (Table 1).

Table 1

Compounds that are the initial components of reactions in compositions C-1 and C-5

Composition numbers and starting components for synthesis	
C1-	C5-
Glass E-1 (SiO_2, $MgO{\cdot}SiO_2$)*, $Al_2O_3{\cdot}2SiO_2$, MgO, Al_2O_3	Glass E-5 ($2MgO{\cdot}SiO_2$, $MgO{\cdot}SiO_2$)*, $Al_2O_3{\cdot}2SiO_2$, MgO

*Note: * – those phases are indicated in brackets, which, along with $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, are products of the crystallization of glasses E-1 and E-5*

Thermodynamic calculations of ΔG_T^0 were carried out in the temperature range of 873–1573 K for chemical reactions given below:

$$2(MgO{\cdot}SiO_2)+Al_2O_3{\cdot}2SiO_2+ +Al_2O_3+SiO_2=2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (1)$$

$$2(MgO{\cdot}SiO_2)+2(Al_2O_3{\cdot}2SiO_2)= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2+SiO_2, \quad (2)$$

$$MgO{\cdot}SiO_2+2(Al_2O_3{\cdot}2SiO_2)+MgO= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (3)$$

$$3(MgO{\cdot}SiO_2)+Al_2O_3{\cdot}2SiO_2+2Al_2O_3= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2+MgO{\cdot}Al_2O_3, \quad (4)$$

$$2(MgO{\cdot}SiO_2)+2(Al_2O_3{\cdot}2SiO_2)+3Al_2O_3+ +SiO_2=2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2+3Al_2O_3{\cdot}2SiO_2, \quad (5)$$

$$MgO{\cdot}SiO_2+MgO=2MgO{\cdot}SiO_2, \quad (6)$$

$$2(MgO{\cdot}SiO_2)+2Al_2O_3+3SiO_2=2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (7)$$

$$2MgO{\cdot}SiO_2+2(Al_2O_3{\cdot}2SiO_2)= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (8)$$

$$2(2MgO{\cdot}SiO_2)+Al_2O_3{\cdot}2SiO_2+3Al_2O_3+ +SiO_2=2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2+2(MgO{\cdot}Al_2O_3), \quad (9)$$

$$2MgO{\cdot}SiO_2+2Al_2O_3+4SiO_2=2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (10)$$

$$2MgO{\cdot}SiO_2+SiO_2=2(MgO{\cdot}SiO_2), \quad (11)$$

$$2MgO{\cdot}SiO_2+Al_2O_3=MgO{\cdot}SiO_2+MgO{\cdot}Al_2O_3, \quad (12)$$

$$Al_2O_3{\cdot}2SiO_2+2Al_2O_3=3Al_2O_3{\cdot}2SiO_2, \quad (13)$$

$$3MgO+Al_2O_3{\cdot}2SiO_2= =MgO{\cdot}Al_2O_3+2(MgO{\cdot}SiO_2), \quad (14)$$

$$5MgO+Al_2O_3{\cdot}2SiO_2= =MgO{\cdot}Al_2O_3+2(2MgO{\cdot}SiO_2), \quad (15)$$

$$3(Al_2O_3{\cdot}2SiO_2)=3Al_2O_3{\cdot}2SiO_2+4SiO_2, \quad (16)$$

$$2MgO+2Al_2O_3+5Al_2O_3= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (17)$$

$$2MgO+2(Al_2O_3{\cdot}2SiO_2)+SiO_2= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (18)$$

$$2SiO_2+3Al_2O_3=3Al_2O_3{\cdot}2SiO_2, \quad (19)$$

$$6(MgO{\cdot}SiO_2)+2(3Al_2O_3{\cdot}2SiO_2)+ +5SiO_2=3(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2), \quad (20)$$

$$3(MgO{\cdot}SiO_2)+3Al_2O_3{\cdot}2SiO_2= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2+MgO{\cdot}Al_2O_3, \quad (21)$$

$$4(MgO{\cdot}SiO_2)+3Al_2O_3{\cdot}2SiO_2+ +Al_2O_3+4SiO_2=2(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2), \quad (22)$$

$$3(MgO{\cdot}SiO_2)+3Al_2O_3{\cdot}2SiO_2= =3(MgO{\cdot}Al_2O_3)+5SiO_2, \quad (23)$$

$$3(2MgO{\cdot}SiO_2)+2(3Al_2O_3{\cdot}2SiO_2)+8SiO_2= =3(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2, \quad (24)$$

$$2MgO{\cdot}SiO_2+3Al_2O_3{\cdot}2SiO_2+MgO+2SiO_2= =2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2+MgO{\cdot}Al_2O_3, \quad (25)$$

$$6MgO+2(3Al_2O_3{\cdot}2SiO_2)+11SiO_2= =3(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2). \quad (26)$$

The temperature range in which thermodynamic calculations of reactions were carried out with the participation of $Al_2O_3{\cdot}2SiO_2$ was limited by the maximum temperature of existence of this compound (1173 K).

There are no thermodynamic constants for minerals in the literature, which are products of crystallization of experimental glasses, in the vitreous state. According to the data from [32], various crystalline modifications of SiO_2 and SiO_2 in the form of glass have similar values of thermodynamic constants. For example, the value of $\Delta H^0_{298,15}$ (β-quartz)=–911.58 kJ/mol, $\Delta H^0_{298,15}$ (α-tridymite)=–905.98 kJ/mol, $\Delta H^0_{298,15}$ (SiO_2 glass)= =–902.86 kJ/mol. Considering minor differences in the values of thermodynamic constants for different silicates in the crystalline and vitreous state, there is an insignificant difference in the results of thermodynamic calculations. Therefore, available thermodynamic constants for crystalline compounds were used.

The values of the thermodynamic constants of the initial individual compounds and the resulting products of chemical reactions (1) to (26) at the standard temperature are given in Table 2.

The results of ΔG_T^0 calculations for reactions (1) to (26) in the temperature range of 873–1573 K are given in Table 3.

Table 2

Initial thermodynamic constants [33]

Compound	$-\Delta H^0_{298,15}$, kJ/mol	$-\Delta G^0_{298,15}$, kJ/mol	$\Delta S^0_{298,15}$, J/mol·K	$C_p=a+b\cdot T+c\cdot T^{-2}$, J/mol·K			Temperature range
				a	$b\cdot10^3$	$c\cdot10^{-5}$	
MgO	601.78	569.53	27.08	42.61	7.28	–6.19	298–2100
$MgSiO_3$	1548.92	1462.10	67.86	102.77	19.84	–26.29	298–1800
Mg_2SiO_4	2171.91	2052.93	95.19	149.90	27.38	–35.66	298–1800
γ-Al_2O_3	1637.98	1542.12	52.54	106.68	17.79	–25.5	298–1600
α-tridymite	905.98	852.19	43.53	57.10	11.05	0	390–2000
$Al_2Si_2O_7$	3316.15	3102.29	124.24	229.68	36.84	–14.57	298–1173
$Al_6Si_2O_{13}$	6857.09	6462.90	251.16	485.16	46.88	–154.88	298–2000
$MgAl_2O_4$	2300.78	2175.90	80.58	154.05	26.79	–40.94	298–1800
$Mg_2Al_4Si_5O_{18}$	9158.36	8648.19	407.10	602.22	108.03	–161.62	298–1650

Table 3

Estimated ΔG^0_T values for chemical reactions (1) to (26)

Reaction No.	ΔG^0_T value for reactions (kJ/mol) at the temperature, K							
	873	973	1073	1173	1273	1373	1473	1573
1	–266.3	–272.5	–278.5	–284.6	–	–	–	–
2	–425.6	–433.9	–442.0	–450.2	–	–	–	–
3	–461.6	–469.0	–476.4	–483.7	–	–	–	–
4	–300.9	–309.1	–317.3	–325.6	–	–	–	–
5	–556.7	–565.3	–573.9	–582.7	–	–	–	–
6	–22.5	–22.9	–23.3	–23.8	–24.3	–24.9	–25.5	–26.1
7	–107.1	–111.0	–115.0	–119.1	–123.3	–127.5	–131.7	–136.1
8	–439.1	–446.1	–453.0	–459.9	–	–	–	–
9	–362.4	–370.3	–378.1	–386.0	–	–	–	–
10	–120.5	–123.3	–126.0	–128.8	–131.7	–134.6	–137.6	–140.6
11	–13.5	–12.3	–10.9	–9.7	–8.4	–7.1	–5.9	–4.6
12	–48.0	–48.9	–49.8	–50.7	–51.6	–52.5	–53.4	–54.4
13	–290.4	–292.9	–295.4	–298.1	–	–	–	–
14	–301.7	–303.4	–305.2	–307.0	–	–	–	–
15	–346.7	–349.2	–351.9	–354.6	–	–	–	–
16	–608.9	–615.7	–622.4	–629.1	–	–	–	–
17	–178.9	–181.3	–183.7	–186.2	–188.8	–191.6	–194.5	–197.4
18	–493.2	–499.8	–506.4	–512.9	–	–	–	–
19	–131.1	–131.4	–131.9	–132.5	–133.3	–134.1	–134.9	–135.8
20	–	–	–	–	–103.3	–114.3	–125.4	–136.6
21	–	–	–	–	–33.1	–38.8	–44.4	–50.1
22	–	–	–	–	–113.3	–120.9	–128.6	–136.4
23	–	–	–	–	3.8	–1.9	–7.8	–13.6
24	–	–	–	–	–128.6	–135.8	–143.0	–150.4
25	–	–	–	–	–74.3	–77.9	–81.6	–85.3
26	–	–	–	–	–299.9	–306.6	–313.5	–320.7

Given the results of thermodynamic calculations (Table 3), at the first stage the most likely is the formation of mullite from meta kaolinite (16). It is (16) that is characterized by the lowest ΔG^0_T values. It has been established that the further formation of the cordierite phase from the components of glasses E-1 and E-5 ($MgO\cdot SiO_2$, $2MgO\cdot SiO_2$ and SiO_2) can mainly occur with the participation of $3Al_2O_3{\cdot}2SiO$. It should be noted that cordierite will be the only resulting product of the interaction between the components of eutectic glasses E-1 and E-5 with charging components. In the temperature range of 1273–1573 K, the lowest ΔG^0_T values (–299.9÷–320.7 kJ/mol) were observed for the reaction of cordierite formation involving tridymite (26). Subsequently, the formation of cordierite from forsterite $2MgO\cdot SiO_2$ and clinoenstatite $MgO\cdot SiO_2$ is likely. Forsterite interacts with mullite for (24). In the case of $MgO\cdot SiO_2$, cordierite formation is most likely according to (20) for composition C-5. For composition C-1, which contains Al_2O_3 as a charging component, the formation of cordierite with the participation of $MgO\cdot SiO_2$ can occur according to reaction (22) or (7). Reactions of cordierite formation from forsterite and clinoenstatite, based on ΔG^0_T values in the temperature range of 1273–1573 K are almost equivalent.

5. 2. The results of studies of crystal-phase composition

In order to verify the data of our thermodynamic calculations, cordierite compositions were compiled. Cordierite compositions C-1 and C-5 contained, respectively, eutectic glasses E-1 and E-5. The content of glasses E-1 and E-5 was the same and amounted to 30 wt. %. Charging components were administered in the amount required for the formation of stoichiometric cordierite. Firing of the compositions was carried out in the temperature range of 600–1300 °C, followed by X-ray phase analysis of the products obtained (Fig. 2, 3).

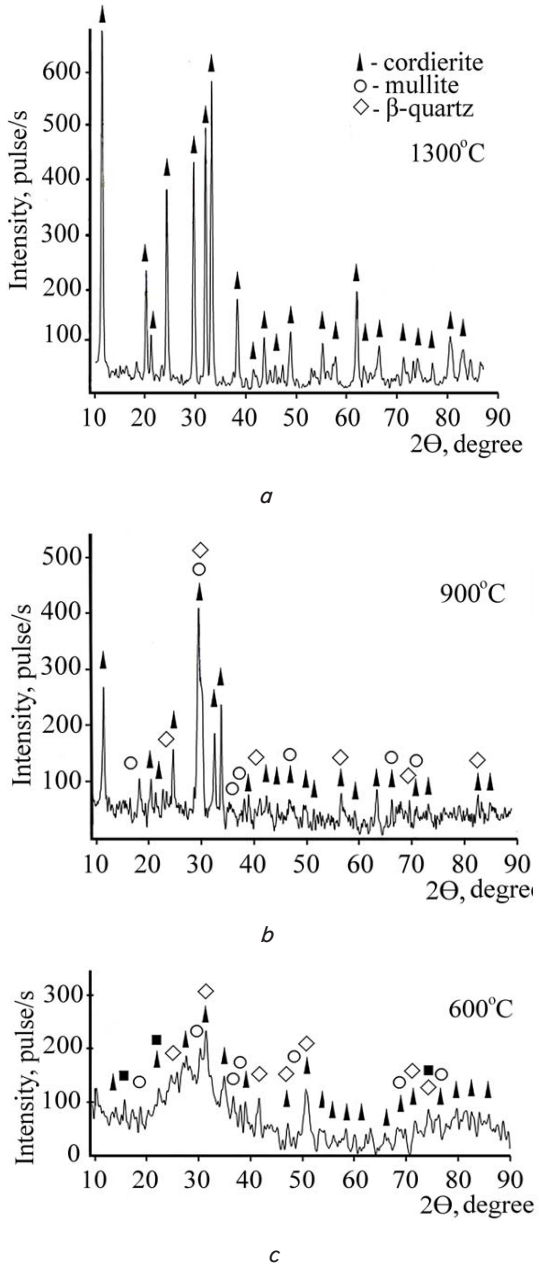

Fig. 2. Radiographs of cordierite compositions C-1, fired at different temperatures: *a* — 1300 °C, *b* — 900 °C, *c* — 600 °C

X-ray phase studies confirmed the results of thermodynamic calculations. It was established that the resulting mineralogical composition of compositions C-1 and C-5 is formed at a temperature of 1300 °C and is represented only by cordierite ($d \cdot 10^{10}$=8.3; 4.82; 4.04; 3.34; 3.10; 3.00; 2.62; 1.68 m). This is evidenced by the absence on radiographs of lines from the initial and intermediate compounds. The formation of the cordierite phase occurs in several stages. A small amount of cordierite is formed already at a temperature of 600 °C. Mullite and β-quartz are also recorded as new formations. In addition, there is residual kaolinite, which is introduced into the composition of the compositions by a clay component (kaolin).

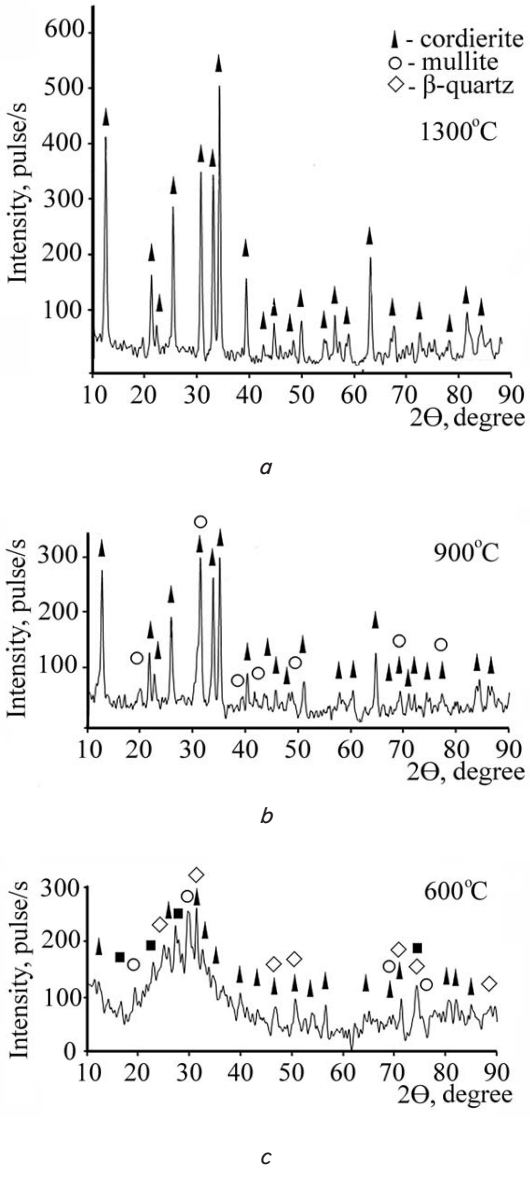

Fig. 3. Radiographs of cordierite composition C-5, fired at different temperatures: *a* — 1300 °C, *b* — 900 °C, *c* — 600 °C

Cordierite is the main crystalline phase of compositions C-1 and C-5, which were fired at a temperature of 900 °C. In addition to cordierite, there is a small amount of mullite ($d \cdot 10^{10}$=5.34; 3.40; 2.88; 2.67; 1.58 m). For composition C-1, a small amount of β-quartz is registered ($d \cdot 10^{10}$=4.22; 3.40; 2.48; 1.55; 1.33 m).

6. Discussion of the results of studies of the course of chemical reactions with the participation of glass components of eutectic compositions of the $MgO–Al_2O_3–SiO_2$ system

The choice of the composition of glasses that correspond to the invariant points of the MAS system for the production of low-temperature cordierite ceramics was carried out using thermodynamic studies. Among the invariant points at which cordierite is one of the phases in the process of crystallization, preference is given to eutectic compounds. The eutectic points E-1 and E-5 are characterized by the lowest melt formation temperatures in the MAS system (1345 °C and 1360 °C).

In the course of research, it was established that the resulting product of the interaction of the components of experimental glasses E-1 and E-5 with the charging components is cordierite. The formation of the cordierite phase is preceded by the process of transformation of meta kaolinite $Al_2O_3{\cdot}2SiO_2$ into mullite $3Al_2O_3{\cdot}2SiO_2$ (16) – Table 3. As a result, the mullite phase is registered in the composition of compositions C-1 and C-5, fired at a temperature of 600 °C (Fig. 2, 3, *c*). In the process of mullitization, free SiO_2 is released. In the phase composition of experimental compositions, SiO_2 is represented by a modification of β-quartz, which is formed during cooling. The source of free SiO_2 in composition C-1 is also glass E-1 due to crystallization (Table 1). In addition, at a temperature of 600 °C, a small amount of cordierite is formed. Crystallization of glasses E-1 and E-5 is observed in the temperature range of 720–990 °C. Therefore, cordierite, which is registered in the phase composition of compositions C-1 and C-5, is not a product of crystallization of experimental glasses. The formation of the cordierite phase at low temperature is obviously a consequence of reaction (26) involving MgO, SiO_2 and $3Al_2O_3{\cdot}2SiO_2$. The possibility of reaction (26) is evidenced by the absence of MgO in the phase composition of experimental compositions fired at 600 °C (Fig. 2, 3, *c*).

When the firing temperature rises to 900 °C, the cordierite phase dominates compositions C-1 and C-5. Obviously, intensive formation of cordierite occurs with the participation of magnesium silicates ($MgO{\cdot}SiO_2$, $2MgO{\cdot}SiO_2$). The cordierite phase is also formed as a result of the crystallization of experimental glasses. In addition, mullite is registered, and, in the case of composition C-1, there is a small amount of β-quartz (Fig. 2, *b*). This indicates the incompleteness of the processes of cordierite formation at 900 °C. The formation of cordierite is completely finalized at a temperature of 1300 °C, as evidenced by the results of X-ray phase studies (Fig. 2, 3, *a*).

Thus, in contrast to energy-intensive experimental studies reported in [28], our thermodynamic analysis has made it possible to determine the most optimal compositions of MAS glasses and the conditions for obtaining a cordierite phase from the components of these glasses. This becomes possible due to the establishment of features of the course of chemical reactions with the participation of glass components of eutectic compositions of MAS System. It was revealed that when the stoichiometric ratio is maintained, the only final product of the interaction of the components of eutectic glasses of the MAS system with the charging components is cordierite. The studied features of the reactions of the formation of cordierite make it possible to obtain low-temperature cordierite ceramics, to control its phase composition and properties. In this case, the volume of energy-intensive experimental studies is significantly reduced.

At the same time, the use of thermodynamic calculations and their practical implementation is limited by the fact that the results obtained determine the conditions for the formation of one crystalline phase – cordierite. To obtain a wider range of properties and, as a result, to expand the scope of heat-resistant ceramics, the conditions for the formation of the polyphase composition of cordierite-based compositions require further study. Controlling the phase composition of cordierite-based ceramics by modifying various additives will allow giving the materials that are obtained a set of special properties. The disadvantage of the research should be attributed to the fact that the results of thermodynamic calculations cannot take into account the kinetics of a process. Therefore, the results obtained require additional establishment of the time parameters of the firing process of cordierite ceramics.

Thermodynamic analysis, which has proven an effective method for assessing the likelihood of chemical reactions, can be successfully implemented in the technology of other types of ceramics. The use of thermodynamic analysis will significantly reduce the time for energy-intensive experimental research and decrease their volume.

7. Conclusions

1. Our thermodynamic calculations have determined conditions for the formation of the cordierite phase for reactions at the invariant points of the $MgO–Al_2O_3–SiO_2$ system. It has been established that cordierite is the only final product of the interaction of glass components of eutectic compositions E-1 and E-5 with charging components. The most likely is the formation of cordierite from the mullite phase, which is a product of the transformation of meta kaolinite.

2. Changes in the mineralogical composition of cordierite compositions depending on the firing temperature have been determined. The resulting mineralogical composition of the experimental compositions is represented by cordierite. The formation of the cordierite phase occurs in several stages and is finalized at a temperature of 1300 °C.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

All data are available in the main text of the manuscript.

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