

UDC 666.266.6; 666.651.2; 623.4.08

O.V. Zaichuk ^a, K.M. Sukhyy ^a, O.A. Amelina ^a, Y.S. Hordeiev ^a, D.V. Filonenko ^a,
L.L. Rudnieva ^a, I.V. Sukha ^a, S.A. Halushka ^b

THERMODYNAMIC ANALYSIS OF THE REACTIONS OF STRONTIUM ANORTHITE FORMATION DURING THE FIRING OF THERMAL SHOCK RESISTANCE CERAMICS BASED ON THE EUTECTIC GLASSES OF THE SrO–Al₂O₃–SiO₂ SYSTEMS

^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine

^b Sumy National Agrarian University, Sumy, Ukraine

Thermal shock resistance ceramic materials must have a high degree of sintering to ensure the required mechanical strength, erosion resistance, and resistance to high-temperature oxidation. However, the search for effective ways to achieve a high degree of sintering of ceramic materials based on the SrO–Al₂O₃–SiO₂ system at low temperatures requires a large amount of experimental research. The aim of this work is to analyze thermodynamically the reactions of strontium-anorthite phase formation at the points of triple eutectics of the SrO–Al₂O₃–SiO₂ system under low-temperature firing conditions. The eutectic points were selected in the region of strontium anorthite crystallization and had a temperature not exceeding 1400°C. It has been established that in the case of compliance with the stoichiometric ratio, the final product of the interaction of the components of eutectic glasses S-1 and S-2 with the charging components is the strontium anorthite phase. The most probable is the formation of strontium anorthite in the interaction of eutectic glass components with Al₂O₃·2SiO₂, which is a product of kaolinite dehydration (Al₂O₃·2SiO₂·2H₂O). It has been found that the compounds SrO·SiO₂ and 2SrO·Al₂O₃·SiO₂ are most active in the interaction with the charging components in the direction of formation of the strontium anorthite phase than SiO₂ tridymite. As a result, the sintering of strontium-anorthite compositions at a temperature of 900°C causes a significant increase in the content of the crystalline phase of strontium anorthite. The determined patterns allow making a reasonable choice of glass in the SrO–Al₂O₃–SiO₂ system for the further manufacture of low-temperature strontium-anorthite ceramics.

Keywords: strontium-anorthite ceramics, eutectic glass, SrO–Al₂O₃–SiO₂ system, thermodynamic analysis, X-ray phase analysis.

DOI: 10.32434/0321-4095-2023-151-6-99-106

Introduction

Thermal shock-resistant glass-crystalline and ceramic materials serve as high-temperature dielectrics extensively employed across diverse industries, encompassing metallurgy, mechanical engineering, high-frequency aviation, and rocketry. To ensure high mechanical strength, erosion resistance, and resistance to high-temperature oxidation, such materials must have a high degree of sintering [1].

The range of thermal shock resistance glass-

crystalline and ceramic materials is quite wide. The most common types include quartz ceramics [1] and materials obtained based on various aluminosilicate systems [2–4].

Quartz ceramics, obtained from quartz glass, is characterized by one of the highest thermal stability indicators. At the same time, it is difficult to achieve a high degree of sintering for quartz ceramics without deterioration of thermal performance. This is due to the intense crystallization of quartz glass at temperatures above 1200°C [1,5].

© O.V. Zaichuk, K.M. Sukhyy, O.A. Amelina, Y.S. Hordeiev, D.V. Filonenko L.L. Rudnieva, I.V. Sukha, S.A. Halushka, 2023



This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Thermodynamic analysis of the reactions of strontium anorthite formation during the firing of thermal shock resistance ceramics based on the eutectic glasses of the SrO–Al₂O₃–SiO₂ systems

Utilizing glass-crystalline and ceramic materials based on various aluminosilicate systems allows achieving a high degree of sintering and bringing the density of materials closer to the theoretical one. At the same time, the effective use of lithium-aluminum-silicate materials of spodumene ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$) and eucryptite ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) compositions is limited to a temperature of 900°C [2,6], and materials of cordierite composition ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) do not exceed 1100°C [3,7].

The constant expansion of the application areas for glass-crystalline and ceramic materials leads to more stringent requirements for functional properties. To obtain high-temperature resistance (up to 1400°C) combined with low dielectric losses, high mechanical properties, and thermal stability, it is advisable to use materials of strontium-anorthite ($\text{SrO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) composition. The melting point of strontium anorthite (slavsonite) is 1654°C. This is significantly higher than the melting points of eucryptite and spodumene (1380°C), as well as cordierite (1465°C), which are used to synthesize technical sitalls and glass-ceramics for industrial use [8]. Therefore, materials based on strontium anorthite can be successfully used for the manufacture of high-temperature radio-transparent products, structural materials for mechanical engineering and energy.

Glass-crystalline materials based on strontium anorthite can be produced using two technologies: classical glass and ceramic (powder). Glasses of strontium-anorthite composition are melted at high temperatures (1600–1700°C), which is a significant disadvantage of these methods [9].

As part of ceramics obtained by powder technology from traditional raw materials (strontium carbonate, aluminum, and silicon dioxide), strontium anorthite is actively formed starting from a temperature of 1150°C [10]. At the same time, high-temperature firing at 1350°C with a holding time of 5 h does not allow for achieving a high degree of sintering.

Modifying additives are introduced to reduce the sintering temperature of strontium-anorthite ceramics.

Strontium-anorthite ceramics with a high degree of sintering were obtained at a temperature of 900°C with the addition of $\text{SrO}\cdot 3\text{B}_2\text{O}_3$ as a fluxing component. However, in order to obtain $\text{SrO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ at the first stage, a long-term high-temperature firing (1400°C, 4 h) of a powder mixture of SrCO_3 and kaolin is required. In addition, the introduction of the $\text{SrO}\cdot 3\text{B}_2\text{O}_3$ compound changes the stoichiometry of strontium anorthite, which negatively affects the properties of ceramics [11].

The sintering process of strontium anorthite

ceramics is also activated by the addition of borosilicate glass [12]. Full compaction is achieved at a temperature of 1350°C with a glass content of 10 wt.%. With an increase in the glass content, a certain amount of the crystalline phase of quartz or cristobalite is formed, which negatively affects the thermal stability of the ceramic.

Earlier [13], an effective modifying effect of a glass of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system on the sintering processes of strontium-anorthite ceramics was established. However, in the process of firing such ceramics, lithium aluminosilicate of spodumene composition is formed, which reduces the temperature of their effective exploitation and increases their dielectric losses.

The current approaches to lower the sintering temperature of strontium-anorthite ceramics fall short of realizing the complete set of desired functional characteristics. The search for new ways to modify the structure of strontium-anorthite ceramics to decrease the sintering temperature usually requires a large amount of experimental research. Therefore, the use of thermodynamic studies to analyze the reactions of strontium-anorthite phase formation under low-temperature firing conditions determines the importance of these studies.

The purpose of this work is to conduct a thermodynamic analysis of the reactions of strontium-anorthite phase formation at the points of ternary eutectics of the $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (SAS) system. This will provide a reasonable choice of glasses in the SAS system with the lowest melting temperatures for the subsequent manufacture of low-temperature strontium-anorthite ceramics.

Experimental

The probability of the formation of the crystalline phase of strontium anorthite in reactions involving components of eutectic glasses of the SAS system was determined by thermodynamic analysis. The eutectic points of the SAS system, in which one of the crystalline phases is strontium anorthite, were considered. In the course of thermodynamic calculations, changes in the Gibbs energy (ΔG_T^0) were determined for possible reactions of the formation of the strontium anorthite phase with the participation of SAS glass components of the eutectic composition. One of the initial components of the reactions under consideration was metakaolinite ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), which is a product of dehydration of the mineral kaolinite ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$). Kaolinite is a clay material kaolin, which serves as a suspending additive in strontium-anorthite ceramics.

The mineralogical composition of the strontium anorthite compositions was analyzed using X-ray phase

analysis (XRD) performed on the DRON-3 diffractometer using Co-K α radiation.

Eutectic glass in the SrO–Al₂O₃–SiO₂ system, enriched kaolin (zref-1 brand), technical alumina (≥ 98 wt.%), and silicon dioxide (≥ 99.5 wt.%) were used as raw materials for obtaining of the strontium anorthite compositions. Strontium-anorthite compositions were prepared by combining wet grinding of raw materials in a ball mill. The firing was carried out in an electric furnace in an air environment at a temperature of 900°C.

Strontium carbonate (≥ 99 wt.%), technical alumina (≥ 98 wt.%), silicon dioxide (≥ 99.5 wt.%), and boric acid (≥ 99.8 wt.%) were used as raw materials for obtaining eutectic glass. Adding B₂O₃ (10 wt.% parts over 100 wt.%) to the eutectics composition of the SAS system reduces the glass melting temperature. The addition of 10 wt.% B₂O₃ is sufficient to reduce the melting temperature of glasses in the SAS system by 150–200°C. Boron oxide lowers the crystallization temperature of the initial glasses without altering the qualitative composition of the crystallization products. The melting of glass in the SrO–Al₂O₃–B₂O₃–SiO₂ (SABS) system was carried out in the electric furnace with silicon carbide heaters at 1350–1400°C for 1 h. Corundum crucibles were used for melting.

Results and discussion

Earlier [7], a novel technological method was introduced to produce densely sintered cordierite ceramics at a reduced firing temperature of 1350°C. The fundamental principle of this technique involves incorporating certain constituents of cordierite ceramics by using a comparatively low-melting eutectic glass, which is synthesized within the MgO–Al₂O₃–SiO₂ pseudoternary system. As a result of the high reactivity of the glassy phase in relation to the crystalline fillers, the cordierite crystal phase is intensively formed during sintering. Furthermore, the finely dispersed crystallization of the experimental glass gives rise to the creation of cordierite, further enhancing the mechanical robustness of the ceramics. Implementing this approach in synthesizing strontium-anorthite ceramics requires a significant number of energy-intensive experimental studies. Therefore, for a reasonable selection of glasses as components of low-temperature strontium-anorthite ceramics, it is necessary to determine the thermodynamic parameters of the formation of the strontium-anorthite phase at the eutectic points of the SrO–Al₂O₃–SiO₂ system. Eutectic composition glasses exhibit the lowest melting temperatures compared to other glasses in the system, owing to their lower melt formation temperatures.

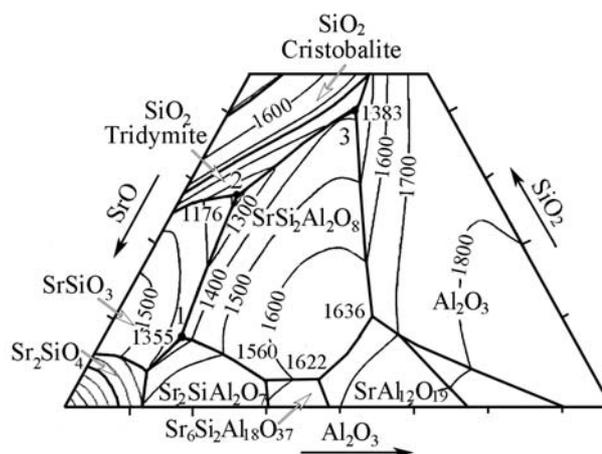


Fig. 1. Part of the SrO–Al₂O₃–SiO₂ system with eutectic points 1–3, in which one of the crystal phases is strontium anorthite

Figure 1 shows a part of the SrO–Al₂O₃–SiO₂ system with the temperatures of eutectic points in which strontium anorthite is one of the crystalline phases [14].

Since eutectic points 1–3 are located at the junction of the primary crystallization fields of different phases, there are a large number of options for the course of chemical reactions during the interaction of glass components with crystalline fillers. This circumstance establishes the potential utility of employing thermodynamic analysis as a valuable approach to evaluate the likelihood of these chemical reactions, thereby notably diminishing the need for resource-intensive experimental investigations.

The essence of thermodynamic analysis is to calculate the change in the Gibbs energy of reactions. Of the various processes that can occur in a system, the most thermodynamically probable is the one accompanied by the largest drop in the ΔG_T^0 value.

When choosing glass compositions for the subsequent low-temperature synthesis of strontium anorthite ceramics, it is necessary to determine the thermodynamic conditions for the formation of the crystalline phase of strontium anorthite at the eutectic points of the SrO–Al₂O₃–SiO₂ system. According to ref. [14], there are three eutectics in the SAS system with temperatures below 1400°C, in which one of the crystalline phases is strontium anorthite (Fig. 1). It is in these eutectic points that low-temperature glasses can be synthesized. The fine crystallization of the strontium anorthite phase from glass will provide high mechanical strength of ceramic materials. Simultaneous crystallization of three phases should occur at eutectic points 1–3. In addition to strontium anorthite and strontium metasilicate (SrO·SiO₂), strontium gelenite (2SrO·Al₂O₃·SiO₂)

crystallizes at point 1, and tridymite (SiO_2) at point 2. At eutectic point 3, along with strontium anorthite and tridymite, mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ also crystallizes.

The chemical compositions of SABS glasses are given in Table 1.

Table 1
Chemical compositions and melting temperature of SABS glasses

| Glass No. | Contents of components, wt. % | | | | Melting temperature, °C |
|-----------|-------------------------------|-------------------------|------|------------------------|-------------------------|
| | SiO_2 | Al_2O_3 | SrO | B_2O_3 | |
| S-1 | 33.0 | 9.8 | 48.1 | 9.1 | 1350 |
| S-2 | 52.2 | 6.7 | 32.0 | 9.1 | 1400 |
| S-3 | 63.6 | 14.8 | 12.5 | 9.1 | 1400 |

It should be noted that despite the lower eutectic temperature values for composition 2 (1176°C) compared to composition 1 (1355°C), according to ref. [14], the glass melting temperature of S-2 is higher and amounts to 1400°C. Eutectic composition 3, at 1400°C, does not result in glass formation (imperfect melt), indicating incomplete melting of the glass batch under current investigation conditions.

Considering the aforementioned points, the thermodynamic analysis of the formation of the strontium anorthite phase was carried out for reactions

involving tridymite, strontium metasilicate, and strontium gellenite. These compounds are products of the crystallization of glasses of eutectic compositions S-1 and S-2. The initial components of the chemical reactions were also $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, Al_2O_3 , SiO_2 and SrCO_3 (Table 2).

The temperature interval in which thermodynamic calculations of the reactions were performed was limited to the temperature of the existence of the $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ compound (873–1173 K). Metakaolinite acted as one of the main starting compounds in the reactions of strontium anorthite formation. In addition, we considered the polymorphic transformation α -quartz \rightarrow α -tridymite, which occurs at a temperature of 870°C.

The literature does not contain thermodynamic constants for minerals that are products of the crystallization of the experimental glasses in the glassy state. Considering the minimal disparity between the thermodynamic constants of various silicates in both crystalline and glassy states, we opted to utilize thermodynamic data pertaining to crystalline compounds.

The values of the thermodynamic constants of the initial compounds and products of chemical reactions at standard temperature are given in Table 3.

Table 2
Compounds that are the initial components of reactions in strontium-anorthite compositions

| Compositions number and starting components for synthesis | |
|---|--|
| SA-1 | SA-2 |
| Glass S-1 ($2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)*, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, Al_2O_3 , SiO_2 | Glass S-2 (SiO_2)*, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, Al_2O_3 , SrCO_3 |

Note: * – those phases are indicated in brackets, which, along with $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and $\text{SrO} \cdot \text{SiO}_2$, are products of the crystallization of glasses S-1 and S-2

Table 3
Initial thermodynamic constants [15]

| Compounds | $-\Delta H_{298.15}^0$, kJ/mol | $-\Delta G_{298.15}^0$, kJ/mol | $S_{298.15}^0$, J/mol | $C_p = a + b \cdot T + c \cdot T^{-2}$, J/mol·K | | |
|---------------------------------------|---------------------------------|---------------------------------|------------------------|--|----------------|-------------------|
| | | | | a | $b \cdot 10^3$ | $c \cdot 10^{-5}$ |
| SrCO_3 | 1218.96 | 1138.17 | 97.11 | 86.66 | 35.83 | -14.22 |
| SrSiO_3 | 1632.92 | 1568.24 | 94.19 | 112.02 | 19.21 | -30.31 |
| Sr_2SiO_4 | 2303.26 | 2228.58 | 150.7 | 154.04 | 28.05 | -31.48 |
| 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 |
| $\text{Al}_2\text{Si}_2\text{O}_7$ | 3316.15 | 3102.29 | 124.24 | 229.68 | 36.84 | -14.57 |
| $\text{Al}_6\text{Si}_2\text{O}_{13}$ | 6857.09 | 6462.90 | 251.16 | 485.16 | 46.88 | -154.88 |
| $\text{Sr}_2\text{Al}_2\text{SiO}_7$ | 3910.25 | 3848.37 | 207.56 | 264.33 | 41.78 | -54.9 |
| $\text{SrAl}_2\text{Si}_2\text{O}_8$ | 4235.79 | 4176.42 | 199.12 | 295.98 | 36.08 | -84.91 |
| CO_2 | 393.69 | 394.57 | 213.74 | 44.16 | 9.04 | -8.54 |

Table 4

Calculated ΔG_T^0 values for chemical reactions (1)–(10)

| Reaction number | Chemical reactions | ΔG_T^0 value for reactions (kJ/mol) at the temperature, K | | | |
|-----------------|---|---|-------|-------|-------|
| | | 873 | 973 | 1073 | 1173 |
| 1 | $\text{SrO} \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 = \text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | -508 | -560 | -612 | -668 |
| 2 | $2(\text{SrO} \cdot \text{SiO}_2) + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Al}_2\text{O}_3 = 2(\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ | -1183 | -1290 | -1396 | -1502 |
| 3 | $\text{SrO} \cdot \text{SiO}_2 + \text{SrCO}_3 = 2\text{SrO} \cdot \text{SiO}_2 + \text{CO}_2$ | -53 | -76 | -99 | -122 |
| 4 | $\text{SrO} \cdot \text{SiO}_2 + \text{SrCO}_3 + \text{Al}_2\text{O}_3 = 2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{CO}_2$ | -341 | -401 | -461 | -520 |
| 5 | $2\text{SiO}_2 + \text{SrCO}_3 + \text{Al}_2\text{O}_3 = \text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{CO}_2$ | -608 | -683 | -758 | -842 |
| 6 | $\text{SiO}_2 + 2\text{SrCO}_3 + \text{Al}_2\text{O}_3 = 2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{CO}_2$ | -442 | -525 | -607 | -693 |
| 7 | $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2 = 2(\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ | -943 | -1012 | -1081 | -1155 |
| 8 | $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{SiO}_2 = \text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SrO} \cdot \text{SiO}_2$ | -267 | -282 | -297 | -321 |
| 9 | $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 + 3\text{SiO}_2 = 2(\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ | -775 | -842 | -909 | -990 |
| 10 | $\text{SrCO}_3 + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 = \text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{CO}_2$ | -776 | -853 | -930 | -1007 |

The results of ΔG_T^0 calculations for chemical reactions (1)–(10) in the temperature range of 873–1173 K are given in Table 4.

The results of thermodynamic calculations (Table 4) indicate that the likelihood of the strontium-anorthite phase forming from the constituents of eutectic glasses in the SAS system is highest during direct interaction with $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The ΔG_T^0 values of reactions (2), (5), (7), and (10) indicate that strontium anorthite is the only end product of the interaction of the initial components. The lowest values (–1183...–1502 kJ/mol) in the temperature range of 873–1173 K are characteristic of the formation of strontium anorthite from the $\text{SrO}-\text{SiO}_2$ compound by reaction (2). Further, the formation of strontium anorthite with the participation of strontium gellenite $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (reaction 7) is possible. For the composition S-2, which contains SrCO_3 as a charge component, along with reaction (2), the formation of strontium anorthite can occur according to reaction (10). After that, the formation of strontium anorthite with the participation of SiO_2 tridymite according to reaction (5) is possible.

In order to verify the data of thermodynamic calculations, strontium-anorthite compositions were prepared based on glasses of eutectic compositions S-1 and S-2.

The weight percentages of glass in the strontium-anorthite compositions are as follows: SA-1 59.9%; and SA-2 48.7%. The initial glass compositions were chosen to ensure the complete conversion of their components into stoichiometric strontium-anorthite, achieved by introducing crystalline fillers as outlined in Table 2. The compositions were fired at a temperature of 900°C,

followed by X-ray phase analysis of the products obtained (Fig. 2).

The results of XRD studies are in full agreement with the thermodynamic calculations. It has been established that the final mineralogical composition of both SA-1 and SA-2 compositions consists of a singular crystalline phase, namely, strontium anorthite. Strontium-anorthite composition SA-1 is characterized by the maximum content of strontium anorthite, which is confirmed by the highest intensity of the main diffraction maxima of this compound

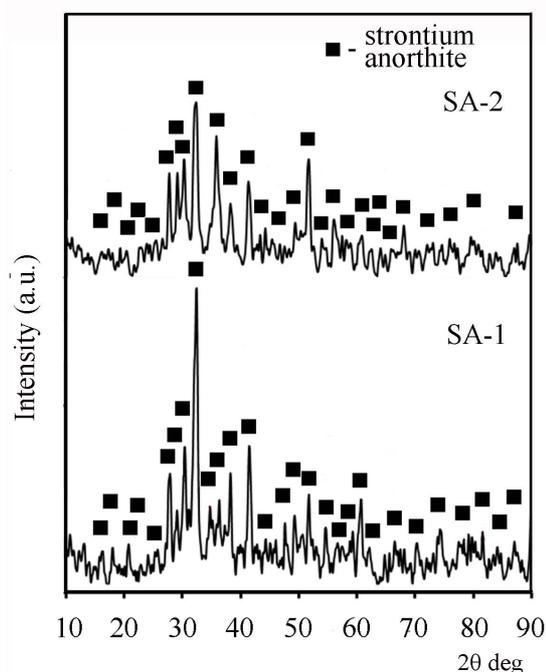


Fig. 2. X-ray patterns of strontium-anorthite compositions fired at 900°C

($d \cdot 10^{10} = 3.70; 3.41; 3.19; 2.72; 2.51$ and 1.77 m) on the corresponding X-ray diffraction pattern (Fig. 2). It is worth noting that the SA-1 composition was obtained from eutectic glass S-1, and its crystallization products encompass not only strontium anorthite but also strontium metasilicate and strontium gellenite. The formation of strontium anorthite from strontium metasilicate and strontium gellenite due to their interaction with crystalline fillers is the most energy-efficient (Table 4). Tridymite, which is a product of the crystallization of S-2 glass, is less active in relation to crystalline fillers (Table 4). This is apparently the reason for the less intense diffraction pattern of the strontium-anorthite composition SA-2 sintered at 900°C .

Considering the above, using eutectic glass S-1 is most appropriate for obtaining low-temperature strontium-anorthite ceramics with a high degree of sintering. The crystallization of such glass occurs with the formation of the strontium-anorthite phase, as well as strontium metasilicate and strontium gellenite.

Conclusions

Possible reaction pathways for the formation of strontium anorthite phase at the triple eutectic points in the $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have been determined through thermodynamic calculations. The eutectic points were selected in the region of strontium anorthite crystallization and had a temperature not exceeding 1400°C . The formation of strontium anorthite is most likely in the interaction of eutectic glass components ($\text{SrO} \cdot \text{SiO}_2$ and $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) with $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which is a product of kaolinite dehydration. At the same time, strontium anorthite is the only final product of the interaction of the components of glasses of eutectic compositions S-1 and S-2 with crystalline fillers. The determined regularities make it possible to make a reasonable choice of glass in the $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system with the lowest melting temperature for the further manufacture of low-temperature strontium-anorthite ceramics.

REFERENCES

1. *Pilate P., Delobel F.* Low thermal expansion ceramic and glass-ceramic materials // Encyclopedia of materials: technical ceramics and glasses. – 2021. – Vol.2. – P.47-58.
2. *Effect of sintering treatment time on the sintering behaviour and thermal shock resistance of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramics / Lutpi H.A., Mohamad H., Abdullah T.K., Ismail H.* // J. Asian Ceram. Soc. – 2021. – Vol.9. – P.507-518.
3. *Characterisation of thermo-mechanical properties of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramic with different heat treatment temperatures / Shamsudin Z., Hodzic A., Soutis C., Hand R.J., Hayes S.A., Bond I.P.* // J. Mater. Sci. – 2011. – Vol.46. – No. 17. – P.5822-5829.
4. *Synthesis and characteristic of celsian ceramics with the use of glass in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ / Zaichuk A.V., Amelina A.A., Hordieiev Yu.S., Kalishenko Y.R., Sribniak N.N.* // Funct. Mater. – 2020. – Vol.27. – P.827-835.
5. *Zaychuk A.V., Amelina A.A.* Search for the ways to improve the physical and technical parameters of quartz ceramics // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2017. – No. 6. – P.63-67.
6. *Heat-resistant ceramics of β -eucryptite composition: peculiarities of production, microstructure and properties / Zaichuk A.V., Amelina A.A., Khomenko Y.S., Baskevich A.S., Kalishenko Y.R.* // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2020. – No. 2. – P.52-59.
7. *Aspects of development and properties of densely sintered of ultra-high-frequency radio-transparent ceramics of cordierite composition / Zaichuk A., Amelina A., Kalishenko Y., Hordieiev Y., Saltykov D., Sribniak N., et al.* // J. Korean Ceram. Soc. – 2021. – Vol.58. – P.483-494.
8. *Beall G.H.* Refractory glass-ceramics based on alkaline earth aluminosilicates // J. Eur. Ceram. Soc. – 2009. – Vol.29. – No. 7. – P.1211-1219.
9. *Sung Y.M., Kim S.* Sintering and crystallization of off-stoichiometric $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glasses // J. Mater. Sci. – 2000. – Vol.35. – No. 17. – P.4293-4299.
10. *The formation of feldspar strontian ($\text{SrAl}_2\text{Si}_2\text{O}_8$) via ceramic route: reaction mechanism, kinetics and thermodynamics of the process / Ptacek P., Soukal F., Opravil T., Bartonickova E., Wasserbauer J.* // Ceram Int. – 2016. – Vol.42. – No. 7. – P.8170-8178.
11. *Chen S., Zhu D.G., Cai X.S.* Low-temperature densification sintering and properties of monoclinic- $\text{SrAl}_2\text{Si}_2\text{O}_8$ ceramics // Metall. Mater. Trans. A. Phys. Metall. Mater. Sci. – 2014. – Vol.45. – No. 9. – P.3995-4001.
12. *El-Kheshen A.A., Zawrah M.F., Hamzawy E.M.* Development of low thermal expansion mono crystalline Sr-feldspar phase via Sr-cordierite ceramic/borosilicate glass composite // Ceram. Int. – 2018. – Vol.44. – No. 12. – P.13720-13726.
13. *Patterns in the synthesis processes, the microstructure and properties of strontium-anorthite ceramics modified by glass of spodumene composition / Zaichuk O., Amelina A., Hordieiev Y., Kalishenko Y., Sribniak N., Halushka S.* // East.-Eur. J. Enterprise Technol. – 2020. – Vol.106. – No. 6. – P.15-26.
14. *Shukla A.* Development of a critically evaluated thermodynamic database for the systems containing alkaline-earth oxides. – Montreal: Ecole Polytechnique, 2012. – 350 p.
15. *Binnewies M., Milke E.* Thermochemical data of elements and compounds, 2nd edition. – Weinheim: Wiley-VCH Verlag GmbH, 2002. – 928 p.

Received 14.08.2023

**ТЕРМОДИНАМІЧНИЙ АНАЛІЗ РЕАКЦІЙ
УТВОРЕННЯ СТРОНЦІЄВОГО АНОРТИТУ ПРИ
ВИПАЛІ ТЕРМОСТІЙКОЇ КЕРАМІКИ НА ОСНОВІ
ЕВТЕКТИЧНИХ СТЕКОЛ СИСТЕМИ SrO–Al₂O₃–SiO₂**

Зайчук О.В., Сухий К.М., Амеліна О.А., Гордєєв Ю.С.,
Філоненко Д.В., Руднєва Л.Л., Суха І.В., Галушка С.А.

Термостійкі керамічні матеріали для забезпечення необхідних показників механічної міцності, ерозійної стійкості і стійкості до високотемпературного окиснення повинні володіти високим ступенем спікання. Проте пошук ефективних шляхів досягнення високого ступеня спікання керамічних матеріалів на основі системи SrO–Al₂O₃–SiO₂ при знижених температурах потребує великого об'єму експериментальних досліджень. Метою даної роботи є термодинамічний аналіз реакцій утворення стронцій-анортитової фази в точках потрійних евтектик системи SrO–Al₂O₃–SiO₂ в умовах низькотемпературного випалу. Евтектичні точки були обрані на ділянці кристалізації стронцієвого анортиту і мали температуру, яка не перевищувала 1400°C. Встановлено, що у випадку дотримання стехіометричного співвідношення кінцевим продуктом взаємодії компонентів евтектичних стекол S-1 і S-2 з підшихтовними компонентами є стронцій-анортитова фаза. Найбільш ймовірним є утворення стронцієвого анортиту при взаємодії компонентів евтектичних стекол з Al₂O₃·2SiO₂, який є продуктом дегідратації каолініту (Al₂O₃·2SiO₂·2H₂O). Встановлено, що сполуки SrO·SiO₂ і 2SrO·Al₂O₃·SiO₂ у порівнянні з тридимітом SiO₂ проявляють найбільшу активність при взаємодії з підшихтовними компонентами в напрямі утворення фази стронцієвого анортиту. Як результат спікання композицій стронцій-анортитового складу при температурі 900°C обумовлює суттєве збільшення вмісту кристалічної фази стронцієвого анортиту. Визначені закономірності дають змогу здійснити обґрунтований вибір скла в системі SrO–Al₂O₃–SiO₂ для подальшого виготовлення низькотемпературної стронцій-анортитової кераміки.

Ключові слова: стронцій-анортитова кераміка, евтектичне скло, система SrO–Al₂O₃–SiO₂, термодинамічний аналіз, рентгенофазовий аналіз.

**THERMODYNAMIC ANALYSIS OF THE REACTIONS OF
STRONTIUM ANORTHITE FORMATION DURING THE
FIRING OF THERMAL SHOCK RESISTANCE CERAMICS
BASED ON THE EUTECTIC GLASSES OF THE
SrO–Al₂O₃–SiO₂ SYSTEMS**

O.V. Zaichuk ^{a,*}, K.M. Sukhyi ^a, O.A. Amelina ^a,
Y.S. Hordeiev ^a, D.V. Filonenko ^a, L.L. Rudnieva ^a,
I.V. Sukha ^a, S.A. Halushka ^b

^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine

^b Sumy National Agrarian University, Sumy, Ukraine

* e-mail: zaychuk_av@ukr.net

Thermal shock resistance ceramic materials must have a high degree of sintering to ensure the required mechanical strength, erosion resistance, and resistance to high-temperature oxidation. However, the search for effective ways to achieve a high degree of sintering of ceramic materials based on the SrO–Al₂O₃–SiO₂ system at low temperatures requires a large amount of experimental research. The aim of this work is to analyze thermodynamically the reactions of strontium-anorthite phase formation at the points of triple eutectics of the SrO–Al₂O₃–SiO₂ system under low-temperature firing conditions. The eutectic points were selected in the region of strontium anorthite crystallization and had a temperature not exceeding 1400°C. It has been established that in the case of compliance with the stoichiometric ratio, the final product of the interaction of the components of eutectic glasses S-1 and S-2 with the charging components is the strontium anorthite phase. The most probable is the formation of strontium anorthite in the interaction of eutectic glass components with Al₂O₃·2SiO₂, which is a product of kaolinite dehydration (Al₂O₃·2SiO₂·2H₂O). It has been found that the compounds SrO·SiO₂ and 2SrO·Al₂O₃·SiO₂ are most active in the interaction with the charging components in the direction of formation of the strontium anorthite phase than SiO₂ tridymite. As a result, the sintering of strontium-anorthite compositions at a temperature of 900°C causes a significant increase in the content of the crystalline phase of strontium anorthite. The determined patterns allow making a reasonable choice of glass in the SrO–Al₂O₃–SiO₂ system for the further manufacture of low-temperature strontium-anorthite ceramics.

Keywords: strontium-anorthite ceramics; eutectic glass; SrO–Al₂O₃–SiO₂ system; thermodynamic analysis; X-ray phase analysis.

REFERENCES

1. Pilate P, Delobel F. Low thermal expansion ceramic and glass-ceramic materials. *Encyclopedia of Materials: Technical Ceramics and Glasses*. 2021; 2: 47-58. doi: 10.1016/B978-0-12-818542-1.00048-5.
2. Lutpi HA, Mohamad H, Abdullah TK, Ismail H. Effect of sintering treatment time on the sintering behaviour and thermal shock resistance of Li₂O–Al₂O₃–SiO₂ glass-ceramics. *J Asian Ceram Soc*. 2021; 9: 507-518. doi: 10.1080/21870764.2021.1896094.
3. Shamsudin Z, Hodzic A, Soutis C, Hand RJ, Hayes SA, Bond IP. Characterisation of thermo-mechanical properties of MgO–Al₂O₃–SiO₂ glass-ceramic with different heat treatment temperatures. *J Mater Sci*. 2011; 46: 5822-5829. doi: 10.1007/s10853-011-5538-0.

4. Zaichuk AV, Amelina AA, Hordieiev YuS, Kalishenko YR, Sribniak NN. Synthesis and characteristic of celsian ceramics with the use of glass in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$. *Funct Mater*. 2020; 27(4): 827-835. doi: 10.15407/fm27.04.827.
5. Zaychuk AV, Amelina AA. Search for the ways to improve the physical and technical parameters of quartz ceramics. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2017; (6): 63-67.
6. Zaichuk AV, Amelina AA, Khomenko YS, Baskevich AS, Kalishenko YR. Heat-resistant ceramics of β -eucryptite composition: peculiarities of production, microstructure and properties. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2020; (2): 52-59. doi: 10.32434/0321-4095-2020-129-2-52-59.
7. Zaichuk A, Amelina A, Kalishenko Y, Hordieiev Y, Saltykov D, Sribniak N, et al. Aspects of development and properties of densely sintered of ultra-high-frequency radio-transparent ceramics of cordierite composition. *J Korean Ceram Soc*. 2021; 58: 483-494. doi: 10.1007/s43207-021-00125-5.
8. Beall GH. Refractory glass-ceramics based on alkaline earth aluminosilicates. *J Eur Ceram Soc*. 2009; 29: 1211-1219. doi: 10.1016/j.jeurceramsoc.2008.08.010.
9. Sung YM, Kim S. Sintering and crystallization of off-stoichiometric $\text{SrO}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ glasses. *J Mater Sci*. 2000; 35: 4293-4299. doi: 10.1023/A:1004880201847.
10. Ptacek P, Soukal F, Opravil T, Bartonickova E, Wasserbauer J. The formation of feldspar strontian ($\text{SrAl}_2\text{Si}_2\text{O}_8$) via ceramic route: reaction mechanism, kinetics and thermodynamics of the process. *Ceram Int*. 2016; 42: 8170-8178. doi: 10.1016/j.ceramint.2016.02.024.
11. Chen S, Zhu DG, Cai XS. Low-temperature densification sintering and properties of monoclinic- $\text{SrAl}_2\text{Si}_2\text{O}_8$ ceramics. *Metall Mater Trans A Phys Metall Mater Sci*. 2014; 45: 3995-4001. doi: 10.1007/s11661-014-2344-8.
12. El-Kheshen AA, Zawrah MF, Hamzawy EM. Development of low thermal expansion mono crystalline Sr-feldspar phase via Sr-cordierite ceramic/borosilicate glass composite. *Ceram Int*. 2018; 44: 13720-13726. doi: 10.1016/j.ceramint.2018.04.213.
13. Zaichuk O, Amelina A, Hordieiev Y, Kalishenko Y, Sribniak N, Halushka S. Patterns in the synthesis processes, the microstructure and properties of strontium-anorthite ceramics modified by glass of spodumene composition. *East Eur J Enterprise Technol*. 2020; 106(6): 15-26. doi: 10.15587/1729-4061.2020.216754.
14. Shukla A. *Development of a critically evaluated thermodynamic database for the systems containing alkaline-earth oxides* [dissertation]. Montreal (Canada): Ecole Polytechnique; 2012. 350 p.
15. Binnewies M, Milke E. *Thermochemical data of elements and compounds*. Weinheim: Wiley-VCH Verlag GmbH; 2002. 928 p. doi: 10.1002/9783527618347.