DOI: 10.6060/ivkkt.20246707.7032

УДК: 666.113.2:666.1.037.31

ВЛИЯНИЕ КОМПОНЕНТНОГО СОСТАВА СЫРЬЕВОЙ СМЕСИ НА ПРОЦЕССЫ СПЕКАНИЯ И КРИСТАЛЛИЗАЦИИ КОРДИЕРИТОВЫХ СТЕКОЛ, ПОЛУЧЕННЫХ ПУТЕМ ПЛАВЛЕНИЯ В ТЕРМИЧЕСКОЙ ПЛАЗМЕ

Ш.М. Шарафеев, В.В. Шеховцов, Е.Е. Звягина

Шариф Мнирович Шарафеев (ORCID 0000-0002-7011-5829)*

Научно-образовательный центр Н.М. Кижнера, Инженерная школа новых производственных технологий, Национальный исследовательский Томский политехнический университет, пр. Ленина, 30, Томск, Российская Федерация, 634050
Научно-исследовательский институт строительных материалов, Томский государственный архитектурно-строительный факультет, пл. Соляная, 2, Томск, Российская Федерация, 634003
E-mail: sharafeev@tpu.ru*

Валентин Валерьевич Шеховцов (ORCID 0000-0003-4068-3347)

Научно-исследовательский институт строительных материалов, Томский государственный архитектурно-строительный факультет, пл. Соляная, 2, Томск, Российская Федерация, 634003
E-mail: shehovcov2010@yandex.ru

Елена Евгеньевна Звягина (ORCID 0009-0009-6606-5783)

Научно-образовательный центр Н.М. Кижнера, Инженерная школа новых производственных технологий, Национальный исследовательский Томский политехнический университет, пр. Ленина, 30, Томск, Российская Федерация, 634050
E-mail: eez14@tpu.ru

Настоящая статья посвящена получению стекол и стеклокристаллических материалов кордиеритового ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) состава. В работе были исследованы процессы, протекающие при кристаллизации и спекании стекол, полученных путем плазменного плавления материалов на основе природного сырья, чистых оксидов и предварительно синтезированного кордиерита. Установлено, что полученные при плазменном плавлении кордиеритовые стекла вследствие высокой скорости нагрева и охлаждения характеризуются высокой дефектностью строения. Релаксация микронапряжений в стеклах протекает в температурном диапазоне 480 – 490 °С. Стекла на основе синтезированного кордиерита характеризуются температурой кристаллизации 930 – 1020 °С в зависимости от наличия и вида нуклеатора, что примерно на 20 – 50 °С меньше по сравнению со стеклами на основе компонентных смесей. Первичным продуктом кристаллизации исследуемых стекол при температуре выше 900 °С является твердый раствор со структурой высокотемпературного кварца $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$, который при увеличении температуры выше 1000 °С образует кордиерит при разложении. Введение в состав шихт 5% ZrO_2 увеличивает вязкость размягченных стекол и температуру их кристаллизации, что увеличивает активность стеклопорошков при спекании стеклокерамики за счет большего вклада этапа жидкофазного спекания в процесс консолидации материала, что позволяет получать при температуре 1300 – 1350 °С керамику с открытой пористостью 2 – 4%. Введение в состав шихт 5% TiO_2 снижает температуру кристаллизации кордиерита на 30 – 50 °С, однако не оказывает существенного влияния на процессы спекания стеклокерамики.

Ключевые слова: кордиерит, стекло, ситаллы, тальк, плазма, плавление, кристаллизация, оксид циркония, оксид титана

Для цитирования:
Шарафеев Ш.М., Шеховцов В.В., Звягина Е.Е. Влияние компонентного состава сырьевой смеси на процессы спекания и кристаллизации кордиеритовых стекол, полученных путем плавления в термической плазме. *Изв. вузов. Химия и хим. технология*. 2024. Т. 67. Вып. 7. С. 80–87. DOI: 10.6060/ivkkt.20246707.7032.

For citation:
Sharafeev S.M., Shekhovtsov V.V., Zvyagina E.E. Batch composition influence on sintering and crystallization processes of cordierite glasses obtained by thermal plasma melting. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2024. V. 67. N 7. P. 80–87. DOI: 10.6060/ivkkt.20246707.7032.

BATCH COMPOSITION INFLUENCE ON SINTERING AND CRYSTALLIZATION PROCESSES OF CORDIERITE GLASSES OBTAINED BY THERMAL PLASMA MELTING

S.M. Sharafeev, V.V. Shekhovtsov, E.E. Zvyagina

Sharif M. Sharafeev (ORCID 0000-0002-7011-5829)*

Kizhner Research Center, School of Advanced Manufacturing Technologies, National Research Tomsk Polytechnic University, Lenina ave., 30, Tomsk, 634050, Russia
Scientific Research Institute of Building Materials, Tomsk State University of Architecture and Building, Solyanaya sq., 2, Tomsk, 634003, Russia
E-mail: sharafeev@tpu.ru*

Valentin V. Shekhovtsov (ORCID 0000-0003-4068-3347)

Scientific Research Institute of Building Materials, Tomsk State University of Architecture and Building, Solyanaya sq., 2, Tomsk, 634003, Russia
E-mail: shehovcov2010@yandex.ru

Elena E. Zvyagina (ORCID 0009-0009-6606-5783)

Kizhner Research Center, School of Advanced Manufacturing Technologies, National Research Tomsk Polytechnic University, Lenina ave., 30, Tomsk, 634050, Russia
E-mail: eez14@tpu.ru

This article focuses on the production of glasses and glass-ceramic materials with a cordierite ($2MgO·2Al_2O_3·5SiO_2$) composition. The processes of crystallization and sintering of cordierite glasses, which are based on natural raw materials, pure oxides and pre-synthesized cordierite, have been investigated. It has been determined that cordierite glasses produced via plasma melting exhibit high structural defects attributed to rapid heating and cooling rates. The relaxation of microstresses in the glasses takes place within the temperature range of 480 – 490 °C. Glasses based on synthesized cordierite exhibit a crystallization temperature of 930 – 1020 °C, depending on the presence and type of nucleating agents. This is approximately 20 – 50 °C lower compared to glasses based on component mixtures. The primary crystallization product of studied glasses at 900 °C is the high-quartz solid solution with formula $MgO·Al_2O_3·3SiO_2$, which is dissociate above 1000 °C with the formation of cordierite. The addition of 5% ZrO_2 to the batch increases the viscosity of softened glasses and their crystallization temperature, resulting in increased activity of glass powders in the sintering processes due to the higher impact of liquid-phase sintering on the general densification process of glass-ceramics. This allows for the production of glass-ceramics with open porosity of 2 – 4% at 1300 – 1350 °C. The addition of 5% TiO_2 to the batch reduces the glass crystallization temperature. However it does not significantly effect on the cordierite glass-ceramics sintering processes.

Key words: cordierite, glass, glass-ceramics, talc, thermal plasma, melting, crystallization, zirconia, titanium oxide

INTRODUCTION

Cordierite is a magnesium aluminosilicate with formula $2MgO·2Al_2O_3·5SiO_2$. It has a low thermal expansion coefficient (CTE) of about 1 ppm/°C [1] and high dielectric properties [2]. This makes it widely used in science and technology as a thermal resistant and dielectric ceramic material. The most common method to obtaining cordierite and cordierite ceramics is through conventional solid state synthesis using natural talc $Mg_3Si_4O_{10}(OH)_2$, kaolin $Al_4Si_4O_{10}(OH)_4$, alumina Al_2O_3 or aluminum hydroxide $Al(OH)_3$ along with other components [3, 4]. The interactions between

these components in solid state at temperatures above 1200-1250 °C result in the formation of cordierite in accordance with reaction (1).

$$4(3MgO{\cdot}4SiO_2{\cdot}H_2O) + 7(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O) + 5Al_2O_3 = 6(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2) + 22H_2O\uparrow \quad (1)$$

The reaction also produces spinel $MgO{\cdot}Al_2O_3$, mullite $3Al_2O_3{\cdot}2SiO_2$, and clinoenstatite $MgO{\cdot}SiO_2$ as by-products. These secondary phases reduce the heat resistance of the material due to their thermophysical properties, which differ significantly from those of cordierite, including a CTE value of more than 8 ppm/°C. Additionally, cordierite ceramics has a narrow range of densely sintered state, approximately 20-30 °C, making it necessary to add different fluxes (such as B_2O_3, P_2O_5, feldspar, etc.) to the batch. These additives lower the melting formation temperature but lead to the formation of a greater quantity of the glassy phase in the material. This decreases the exploitation properties of ceramics [5], for example, the electrical breakdown strength decreases from 16-18 to 6-8 kV/mm and CTE increases to 3-4 ppm/°C, reducing the thermal shock resistance of cordierite ceramics from 600-700 to 350-400 °C.

Cordierite ceramics with exceptional properties can be obtained using advanced chemical methods such as co-precipitation or sol-gel [6-8]. However, these methods are not widely used in industry doe to the high cost of reagents, as well as the complexity of technology and equipment.

Currently, cordierite ceramics with nano- and micrograin structures and high mechanical and dielectric characteristics are produced using the crystallization of glass in the MgO-Al_2O_3-SiO_2 system [9]. The addition of different dopants to the composition of the glass makes it possible to change its technological and functional properties in wide range, as well as produce cordierite glass-ceramics based on it [2, 4, 10-12]. Melts in the MgO-Al_2O_3-SiO_2 system in the composition fields around the cordierite possess very high viscosity, which determines a high temperature of glass melting at about 1500-1600 °C. By adjusting the MgO:Al_2O_3:SiO_2 ratio or introducing additives that reduce the temperature of melt formation and its viscosity (P_2O_5, B_2O_3, K_2O, MnO, etc.) [13-15], an optimal set of technological properties of glass and functional properties of cordierite glass-ceramics can be achieved. During the crystallization of glass, secondary phases of clinoenstatite $MgO{\cdot}SiO_2$, spinel $MgO{\cdot}Al_2O_3$ and other compounds can be formed, which have a negative effect on the physical and mechanical characteristics of the material.

The prospective and energy-efficient method for obtaining melts and coatings based on silicates and oxides with different composition is through the use of thermal plasma [16-20]. The application of plasma thermal treatment allows for the heating and melting of materials at an average mass temperature of approximately 7000 °C, which is significantly higher than the temperature range in conventional furnaces. Many properties of silicate glasses depend on their microstructure, which is influenced not only by the chemical composition of the glass but also by the component composition, thermal history of the glass, and the heating and cooling rate of the melt. There is thermodynamically non-equilibrium melting of materials in the plasma flow under conditions of complex (conductive, convective, and radiative) heat transfer. This influences on the synthesis processes of silicates and oxides materials and chemical bonds formation during the crystallization processes of the corresponding melts and glasses.

The limited use of plasma installations for the production of ceramic materials is attributed to the challenge of predicting and modeling the properties of the final materials based on the initial component composition of the melting batch. The aim of this study is to investigate the impact of the component composition of the raw material mixture on the processes of crystallization and sintering of cordierite glasses obtained through melting in thermal plasma.

MATERIALS AND METHODS

Batches based on natural talc and kaolin (CGC-1 – Cordierite Glass-Ceramics) and pure oxides (CGC-2) were utilized as starting materials for the synthesis of cordierite glass. The CGC-1 batch contained talc TMK-28 (GOST 21234-75), kaolin KAH-1 (GOST 19607-74), brucite powder BleachMag (TU 23.99.19-002-93957848-2020), and aluminum hydroxide (analytical grade). The components were weighed in accordance with the stoichiometric of reaction (2).

$$3MgO{\cdot}4SiO_2{\cdot}H_2O + 3(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O) + Mg(OH)_2 + 2Al(OH)_3 = 2(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2) + 10H_2O\uparrow \quad (2)$$

The CGC-2 batch contained aluminum hydroxide, magnesium carbonate basic aqueous and silica (all reagents – analytical grade). The components were weighed in accordance with the stoichiometric of reaction (3).

$$MgCO_3{\cdot}Mg(OH)_2{\cdot}nH_2O + 2Al(OH)_3 + 5SiO_2 = 2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2 + (n+4)H_2O\uparrow \quad (3)$$

The components were mixed in the media of distilled water in the planetary mill Pulverisette 6 (Fritsch, Germany). A portion of the CGC-1 batch was granulated and firing at 1300 °C to preliminary synthesize the cordierite. The resulting material, which was

practically monophase cordierite, was crushed and milled to a particle size of less than 63 μm. This material was designated as CGC-1T. The formation of cordierite during thermal treatment of the CGC-2 batch is difficult due to significant structural differences between reagents, intermediate species, and products of the solid-state reaction. The phase composition of the CGC-2 batch fired at 1300-1350 °C consists of spinel, cristobalite, and cordierite. As a result, the use of firing products of the CGC-2 batch for the synthesis of cordierite glass ceramics in this study does not seem appropriate. The component composition of the studied materials is presented in Table 1.

Table 1

Component composition of batches for cordierite glass synthesis

Таблица 1. **Компонентный состав исследуемых смесей для получения кордиеритовых стекол**

Batch	Component composition, wt. %
CGC-1	Talc – 27.73 Kaolin – 56.61 Brucite – 4.26 Aluminum hydroxide – 11.40
CGC-1T	Thermal treatment of CGC-1 batch at 1300 °C
CGC-2	Magnesium hydrocarbonate – 22.58 Aluminum hydroxide – 39.44 Silica – 37.98

The nucleating agents for glass crystallization were TiO_2 and ZrO_2, which were added to the batches in a 5% concentration. The selection of the type and amount of TiO_2 and ZrO_2 was based on studies [2, 12, 21, 22]. Disks measuring 20×5 mm were pressed from powders using a binder of 5% aqueous solution of polyvinyl alcohol. The materials were melting using an electroplasma stand following the method described in [23]. A series of experiments determined that the optimal melting parameters were: current 100 A, voltage 110 V, plasma gas flow rate 1.5 g/s (nitrogen), and a melting time of 60 s. All studied cordierite glasses obtained by plasma melting were found to be amorphous materials without bulk and surface crystalline formations. The obtained glasses were crushed and milled using a vibratory mill Pulverisette 23 (Fritsch, Germany) to achieve a powder particle size of less than 63 μm. The powders of glass were pressed into discs measuring 5×1 mm and fired at temperatures ranging from 900-1350 °C. The porosity and apparent density of the materials were determined by Archimedes method using an ME 235S scales (Sartorius, Germany). The phase analysis of the materials was determined using a DRON-3M diffractometer (Burevestnik, Russia), and thermal analysis of the glasses was carried out on a synchronous thermal analyzer STA 449 F3 Jupiter (Netzsch, Germany).

RESULTS AND DISCUSSION

The melting of materials in plasma flow proceeds in the following sequence in accordance with [24, 25]: melting of binary and ternary eutectics, followed by the dissolution of refractory components in the primary melt. Reactions between components in the solid state are limited due to kinetics aspects. Additionally, the very high speed of heating and cooling of materials should lead to a high degree of destruction of silicates and aluminosilicates anion groups in melts, and consequently, a high degree of disorder in the glass structure network.

The relaxation processes of microstrains in the obtained glasses are manifested as a low-temperature endothermic effect at 480-490 °C on the Differential Scanning Calorimetry (DSC) curves (Fig. 1). This is accompanied by the reorganization of the most mobile chemical bonds in the glass structure. The primary nuclei of crystallization are formed in studied glasses at 580-610 °C, as indicated by weak exothermic effects on the DSC curves. An extended endothermic effect with a weak peak at 750-850 °C is related to glass transition, and the onset of this effect corresponds to a softening temperature of about 760 °C for all studied glasses. Crystallization of the main phases is observed at temperatures above 950 °C, resulting in an intensive exothermic effect. Additionally, characteristic of the glasses under study is the formation of a melt at temperatures above 1100 °C, as evidenced by the corresponding endothermic effect.

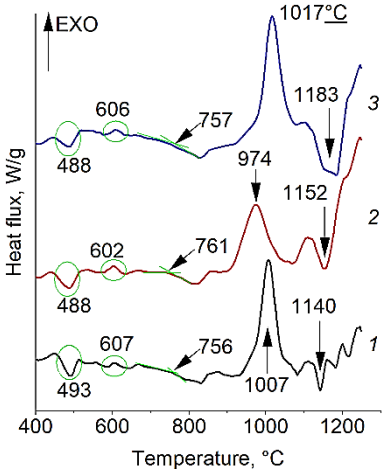

Fig. 1. DSC curves of CGC-1 glasses based on natural raw materials: 1 – without nucleating agents; 2 – 5% TiO_2; 3 – 5% ZrO_2

Рис. 1. Кривые дифференциальной сканирующей калориметрии для стекол CGC-1 на основе природного сырья: 1 – без добавок нуклеаторов; 2 – 5% TiO_2; 3 – 5% ZrO_2

The glasses exhibit significant variations in the temperature of nucleation and crystallization of the main phases (Table 2). Glasses containing TiO_2 as an

additive demonstrate lower crystallization temperature compared to those containing ZrO_2. This can be attributed to the fact that ZrO_2 increases the viscosity of the softened glasses, thereby restricting the restructuring of the glass network and its crystallization. The calculation in «SciGlass» (using the Priven-2000 method) indicates that the viscosity of ZrO_2-containing cordierite glass is 1.1 to 1.8 times higher than the viscosity of undoped cordierite glass in the temperature range of 900 to 1500 °C. Consequently, in cordierite glasses with the addition of ZrO_2, the crystallization temperature shows minimal dependence on the component composition of the starting materials and remains within the range of 1014-1017 °C.

Table 2

Temperatures of nuclei formation and main phases crystallization in cordierite glass ceramics based on glasses obtained from natural raw materials (CGC-1), pure oxides (CGC-2), and synthesized cordierite (CGC-1T)

Таблица 2. **Температуры образования зародышей кристаллизации и основных фаз кордиеритовых стекол на основе природного сырья (CGC-1), чистых оксидов (CGC-2) и синтезированного кордиерита (CGC-1T)**

Glass	Temperature of nuclei formation, °C	Temperature of main phases crystallization, °C
CGC-1	607	1007
CGC-1 + 5% TiO_2	602	974
CGC-1 + 5% ZrO_2	606	1017
CGC-2	602	1010
CGC-2 + 5% TiO_2	594	955
CGC-2 + 5% ZrO_2	584	1014
CGC-1T	569	991
CGC-1T + 5% TiO_2	589	927
CGC-1T + 5% ZrO_2	543	1014

The CGC-1T glasses, based on synthesized cordierite, without additive and with TiO_2 additive have a 30-50 °C lower crystallization temperature compared to the corresponding glasses from batches of CGC-1 and CGC-2. This is attributed to the similarity of the glass microstructure (network of atom-specific structure elements) to the cordierite structure. During plasma melting of the CGC-1 and the CGC-2 batches, anionic groups similar in composition to $[Si_5AlO_{18}]$, which are characteristic of cordierite melts, do not have time to form in the melt structure [26].

For all the glasses studied, the primary crystallization product at 900 °C is a solid solution with the composition $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ and the structure of high quartz [9]. Glasses based on pre-synthesized cordierite (CGC-1T) are characterized by the formation of cordierite already at 900 °C, which is consistent with previously obtained DSC results. As the glass firing temperature increases to 1000 °C and higher, the main crystallization product becomes cordierite $2MgO{\cdot}Al_2O_3{\cdot}5SiO_2$ (Fig. 2).

For glasses containing TiO_2, the by-products phase magnesium dititanate $Mg_2Ti_2O_5$ crystallizes. X-Ray diffraction (XRD) patterns of the glasses after heat-treatment at 1000-1200 °C show low-intensity peaks of protoenstatite $MgO{\cdot}SiO_2$ and spinel $MgO{\cdot}Al_2O_3$. Increasing the heat-treatment temperature to 1250 °C and above result in the formation of cordierite as the main phase in the MgO-Al_2O_3-SiO_2 system. The crystallization of secondary phases in TiO_2-containing glasses is attributed to the fact that during the crystallization of $Mg_2Ti_2O_5$ in the glass, there is a deficiency of magnesium oxide relative to the cordierite stoichiometry, allowing for the crystallization of magnesium aluminate and silicate with a simpler structure [12, 22].

When ZrO_2 is present in glasses, the by-product phase tetragonal zirconium oxide *t*-ZrO_2 crystallizes after heat-treatment at 1100 °C and above, as mentioned earlier, due to their higher viscosity. Cordierite formation in these glasses is observed after heat-treatment at 1100 °C and above. The stabilization of *t*-ZrO_2 in cordierite glasses is attributed to the presence of MgO in their composition, which is capable of forming solid solutions with limited solubility in the MgO-ZrO_2 system [27].

The crystallization mechanism of plasma-melted glasses is independent of the qualitative composition of the initial batches. Crystallization nuclei form in the temperature range of 550-600 °C, and with a further increase in temperature to 900 °C, a quartz-like solid solution of $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ is formed at the initial stage of crystallization. At temperatures above 1000 °C, it dissociates to $2MgO{\cdot}Al_2O_3{\cdot}5SiO_2$ and amorphous SiO_2. Silica interacts with the residual glassy phase in glass-ceramics, leading to cordierite formation in accordance with [9, 11, 12]. This mechanism is typical for glasses of cordierite composition obtained using conventional melt-quenching technology.

The active sintering of glassy powders begins at 1300 °C. Glass-ceramics without ZrO_2 and TiO_2 additives have an open porosity of approximately 15-20% at 1300-1350 °C. The high porosity of the materials is attributed to the high content of crystalline cordierite and minimal residual glassy-phase, resulting in sintering through a diffusion solid-state mechanism.

Glass-ceramics based on the TiO_2- and ZrO_2-containing cordierite glasses exhibit higher activity in sintering processes compared to glass without additives (Fig. 3). The CGC-1 glass, which is based on natural raw materials, contains impurities such as Fe, Ti,

etc., that generally reduce the porosity of TiO_2-containing glass-ceramics (9-16%) by 2-4% in comparison to glass-ceramics based on the CGC-2 glasses (12-18%) made from pure oxides. This reduction in porosity is likely due to the slightly lower viscosity of the softened CGC-1 glass. The porosity of ZrO_2-containing glass-ceramics based on both CGC-1 and CGC-2 glasses remains nearly the same (6-9%) and shows little change with increasing sintering temperature. The higher crystallization temperature of glasses containing ZrO_2 enables active sintering of materials by liquid-phase mechanism within the temperature range of 1000-1100 °C.

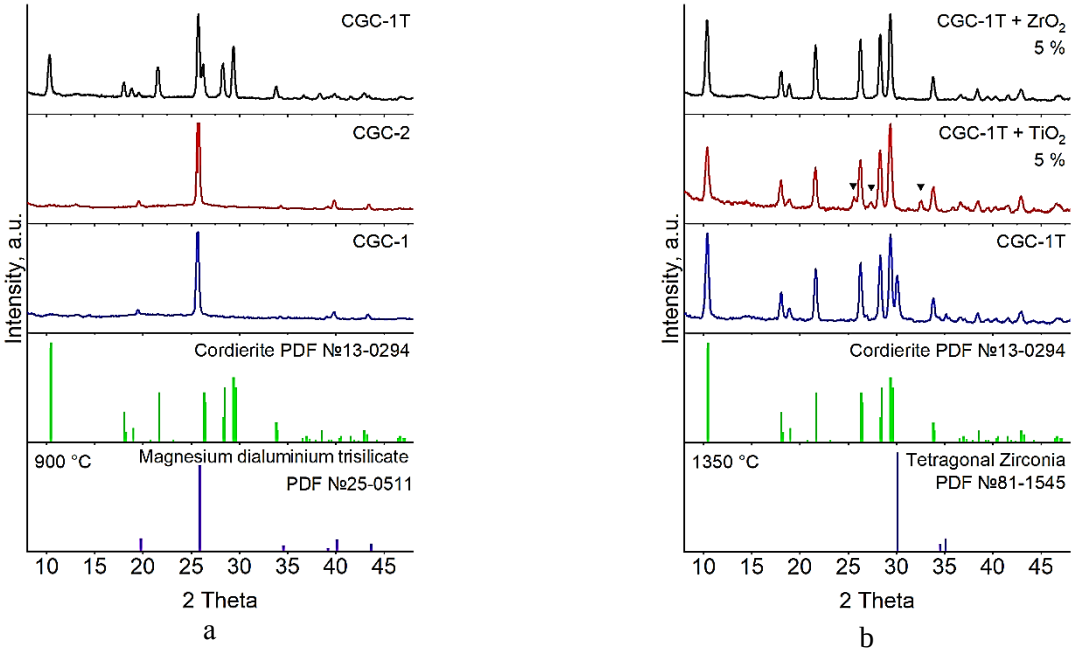

Fig. 2. XRD patterns of cordierite glasses after sintering at 900 °C (a) and 1350 °C (b) and reference patterns of cordierite $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (PDF # 13-0294), solid solution with structure of high temperature quartz $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ (PDF N 25-0511), tetragonal zirconium oxide t-ZrO_2 (PDF N 51-1545)
▽ - $MgTi_2O_5$ PDF N 79-0832

Рис. 2. Рентгеновские дифрактограммы кордиеритовых стекол после обжига при температуре 900 °C (a) и 1350 °C (b) и эталонные штрих-дифрактограммы кордиерита $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (PDF № 13-0294), твердого раствора на основе высокотемпературного кварца $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ (PDF № 25-0511) и тетрагонального оксида циркония t-ZrO_2 (PDF № 51-1545)
▽ - $MgTi_2O_5$ PDF № 79-0832

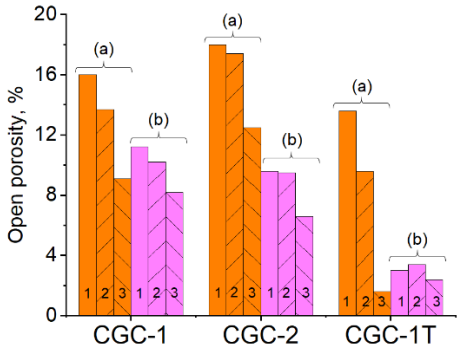

Fig. 3. Open porosity of cordierite glass-ceramics based on glass obtained from natural raw materials (CGC-1), pure oxides (CGC-2) and synthesized cordierite (CGC-1T) with TiO_2 (a) and ZrO_2 (b) additives with sintering temperatures: 1 - 1300 °C, 2 - 1325 °C, 3 - 1350 °C

Рис. 3. Зависимость открытой пористости кордиеритовой стеклокерамики на основе стекол с добавкой TiO_2 (a) и ZrO_2 (b), полученных на основе природного сырья (CGC-1), чистых оксидов (CGC-2) и синтезированного кордиерита (CGC-1T), после обжига при температуре: 1 - 1300 °C, 2 - 1325 °C, 3 - 1350 °C

Ceramics based on pre-synthesized cordierite glasses exhibit lower porosity (2-4% for glass with the addition of ZrO_2) compared to materials made from CGC-1 and CGC-2 glasses. The results described above suggest that softened glasses derived from pre-synthesized cordierite have lower viscosity than glasses obtained from mixtures of natural and synthetic raw materials, likely due to microstructural differences in their composition.

CONCLUSION

Glasses based on pre-synthesized cordierite exhibit crystallization temperatures approximately 20-50 °C lower than glasses based on mixes of natural raw materials or pure oxide. This may be attributed to the similarity of the microstructure of the silicate melt network of atom-specific units to the cordierite structure.

The addition of ZrO_2 to cordierite glasses slightly increases their viscosity and crystallization

temperature, while TiO_2 reduces the crystallization temperature compared to undoped glasses by approximately 30-50 °C. Powders of ZrO_2-containing glasses sinter more actively due to the delayed crystallization of cordierite and the increased contribution of the liquid-phase sintering stage, because of the softened glass during the compaction process of glass-ceramics. Glass-ceramics based on pre-synthesized cordierite are sintered at temperatures of 1300-1350 °C to achieve an open porosity of 2-4%.

The technology for producing silicate glasses in the MgO-Al_2O_3-SiO_2 system by melting in thermal plasma seems promising for the production of cordierite ceramic and glass-ceramic materials.

GRATITUDE AND FUNDING

The work was supported by the state assignment of the Ministry of Science and Higher Education of the Russian Federation FEMN-2022-0001. The research was carried out using the equipment of the CSU NMNT TPU, supported by the RF MES project #075-15-2021-710.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Работа выполнена при поддержке государственного задания Министерства науки и высшего образования РФ FEMN-2022-0001. В работе применялось оборудование ЦКП НОИЦ НМНТ ТПУ, поддержанного проектом Минобрнауки России № 075-15-2021-710.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

REFERENCES
ЛИТЕРАТУРА

1. **Kuscer D., Ines B., Hrovat M., Malic B.** The microstructure, coefficient of thermal expansion and flexural strength of cordierite ceramics prepared from alumina with different particle sizes. *J. Eur. Ceram. Soc.* 2017. V. 37. N 2. P. 739-746. DOI: 10.1016/j.jeurceramsoc.2016.08.032.
2. **Vandray S.N., Zaychuk T.V., Ustinova Yu.S., Orlov A.A., Lemeshev D.O.** Cordierite Glass-Ceramic for Radioengineering Articles. *Glass Ceram.* 2020. V. 76. N 9-10. P. 334-339. DOI: 10.1007/s10717-020-00195-7.
3. **Smail L., Redaoui D., Sahnoune F., Saheb N.** Microstructure, thermal expansion, hardness and thermodynamic parameters of cordierite materials synthesized from Algerian natural clay minerals and magnesia. *Bol. Soc. Esp. Cer. Vidr.* 2021. V. 60. N 5. P. 291-306. DOI: 10.1016/j.bsecv.2020.03.008.
4. **Yahya A.M, El-Kalioubi B.A., Soltan A.M.M., Esmat M.A. Hamzawy., Kenawy S.H.** Cordierite ceramic through glass and ceramic routes from kaolin and talc. *Egypt. J. Chem.* 2021. V. 64. N 4. P. 1751-1758. DOI: 10.21608/EJCHEM.2021.53853.3115.
5. **Толкачева А.С., Павлова И.А.** Технология керамики для материалов электронной промышленности. Екатеринбург: Изд-во УрФУ. 2019. 124 с. **Tolkacheva A.S., Pavlova I.A.** Technology of ceramics for electronic industry materials. Yekaterinburg: Izd. UrFU. 2019. V. 1. 124 p. (in Russian).
6. **Tabit K., Waqif M., Saâdi L.** Crystallization behavior and properties of cordierite synthesized by sol-gel technique and hydrothermal treatment. *J. Aust. Ceram. Soc.* 2019. V. 55. N 2. P. 469-477. DOI: 10.1007/s41779-018-0253-9.
7. **Menchi A.M., Scian A.N.** Mechanism of cordierite formation obtained by the sol–gel technique. *Mater. Lett.* 2005. V. 59. N 21. P. 2664-2667. DOI: 10.1016/j.matlet.2005.04.014
8. **Janković-Častvan I., Lazarević S., Tanasković D., Orlović A., Petrović R., Janaćković Dj.** Phase transformation in cordierite gel synthesized by non-hydrolytic sol–gel route. *Ceram. Int.* 2007. V. 33. N 7. P. 1263-1268. DOI: 10.1016/j.ceramint.2006.05.003.
9. **Xu X., Lao X.** Effect of MgO/SiO_2 ratio and Al_2O_3 content on crystallization behavior and properties of cordierite-based glass–ceramics. *J. Eur. Ceram. Soc.* 2021. V. 41. N 2. P. 1593-1602. DOI: 10.1016/j.mtcomm.2022.103316.
10. **Wang L., Ma B., Ren X., Yu C., Tian J., Liu C., Deng C., Hu C., Liu Z., Yu J., Jiang Z.** Phase-engineering strategy of ZrO_2 for enhancing the mechanical properties of porous cordierite ceramics. *Mater. Today Commun.* 2022. V. 30. P. 103032. DOI: 10.1016/j.mtcomm.2021.103032.
11. **Sun Y., Yang Z., Delong C., Zhang Z., Liu Q., Fang S., Feng L., Shi L., Wang Y., Jia D.** Crystallization Kinetics, Properties of α-cordierite Based Glass-ceramics Prepared by Glass Powder Sintering. *J. Inorg. Mater.* 2022. V. 37. N 12. P. 1351. DOI: 10.15541/jim20220179.
12. **Yu W., Cao S., Wang J., Zhang Z., Han J., Liu C., Ruan J.** Crystallization mechanisms of cordierite glass-ceramics with «surface-center» crystallization behavior. *J. Eur. Ceram. Soc.* 2021. V. 41. N 13. P. 6708-6721. DOI: 10.1016/j.jeurceramsoc.2021.05.061.
13. **Song L., Wu J.-F., Li Z., Hao X., Yu Y.** Crystallization mechanisms and properties of α-cordierite glass–ceramics from K_2O–MgO–Al_2O_3–SiO_2 glasses. *J. Non-Cryst. Solids.* 2015. V. 419. P. 16-26. DOI: 10.1016/j.jnoncrysol.2015.03.023.
14. **Li B., Xia Q., Wang Z.** Effect of MnO on the crystallization, microstructure, and properties of MgO-Al_2O_3-SiO_2 glass-ceramics. *J. Aust. Ceram. Soc.* 2021. V. 57. N 3. P. 927-932. DOI: 10.1007/s41779-021-00588-z.
15. **Dechandt I.C.J., Soares P., Pascual M.J., Serbena F.C.** Sinterability and mechanical properties of glass-ceramics in the system SiO_2-Al_2O_3-MgO/ZnO. *J. Eur. Ceram. Soc.* 2020. V. 40. N 15. P. 6002-6013. DOI: 10.1016/j.jeurceramsoc.2020.07.032.
16. **Volokitin O.G., Shekhovtsov V.V.** Prospects of Application of Low-Temperature Plasma in Construction and Architecture. *Glass Phys. Chem.* 2018. V. 44. N 3. P. 251-253. DOI: 10.1134/S1087659618030185.
17. **Boissonnet G., Chalk C., Nicholls J.R., Bonnet G., Pedraza F.** Thermal insulation of CMAS (Calcium-Magnesium-Alumino-Silicates) attacked plasma-sprayed thermal barrier coatings. *J. Eur. Ceram. Soc.* 2020. V. 40. N 5. P. 2042-2049. DOI: 10.1016/j.jeurceramsoc.2019.12.040.
18. **Samal S.** Thermal plasma technology: The prospective future in material processing. *J. Clean. Prod.* 2017. V. 142. P. 3131-3150. DOI: 10.1016/j.jclepro.2016.10.154.
19. **Смирнова К.В., Извекова А.А., Шутов Д.А., Иванов А.Н., Манукян А.С., Рыбкин В.В.** Плазменно-растворный синтез никельсодержащих порошков под действием тлеющего разряда постоянного тока. *Изв. вузов. Химия и хим. технология.* 2022. Т. 65. Вып. 12. С. 112-118. DOI: 10.6060/ivkkt.20226512.6743.

Smirnova K.V., Izvekova A.A., Shutov D.A., Ivanov A.N., Manukyan A.S., Rybkin V.V. Plasma-solution synthesis of nickel-containing powders under the action of a glow discharge of direct current. *ChemChemTech [Izv. Vyssh.Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2022. V. 65. N 12. P. 112-118 (in Russian). DOI: 10.60/ivkkt.20226512.6743.

20. **Смирнова К.В., Шутов Д.А., Иванов А.Н., Манукян А.С., Рыбкин В.В.** Плазменно-растворный синтез оксида железа (III). *Изв. вузов. Химия и хим. технология.* 2021. Т. 64. Вып. 7. С. 83-88. DOI: 10.6060/ivkkt.20216407.6409.
Smirnova K.V., Shutov D.A., Ivanov A.N., Manukyan A.S., Rybkin V.V. Plasma-solution synthesis of iron oxide (III). *ChemChemTech [Izv. Vyssh.Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2021. V. 64. N 7. P. 83-88 (in Russian). DOI: 10.60/ivkkt.20216407.6409.
21. **Ohsato H., Kim J.S., Cheon C., Kagomiya L.** Crystallization of indialite/cordierite glass ceramics for millimeter-wave dielectrics. *Ceram. Int.* 2015. V. 41. P. S588-S593. DOI: 10.1016/j.ceramint.2015.03.140.
22. **Barry T.I., Cox J.M., Morrell R.** Cordierite glass-ceramics - effect of TiO_2 and ZrO_2 content on phase sequence during heat treatment. *J. Mater. Sci.* 1978. N 13. P. 594-610. DOI: 10.1007/BF00541810.
23. **Shekhovtsov V.V, Abzaev Yu.A., Volokitin O.G., Skripnikova N.K., Klopotov A.A.** Structure and Phase Composition of Natural Magnesite in 1173–6500 K Temperature Range. *Russ. Phys. J.* 2022. V. 65. N 7. P. 1142-1148. DOI: 10.1007/s11182-022-02743-w.
24. **Matvienko O.V., Volokitin O.G., Shekhovtsov V.V.** Investigation of the Melting of Silicate Materials as a Result of Exposure to Low-Temperature Plasma. *J. Eng. Phys. Thermophys.* 2023. V. 96. N 1. P. 150-159. DOI: 10.1007/s10891-023-02671-7.
25. **Skripnikova, N.K., Otmakhov V.I., Volokitin O.G.** Processes occurring during plasma-chemical synthesis of refractory silicate materials. *Glass Ceram.* 2010. V. 67. N 1-2. P. 19-21. DOI: 10.1007/s10717-010-9221-8.
26. **Savova O.V., Fesenko O.I., Voronov G.K., Tymofieiev V.D., Babich P.V.** Investigation of the structure glass-ceramic materials according to data of IR spectroscopy. *Vopr. Khim.Khim. Tekhnol.* 2021. N 6. P. 71-78. DOI: 10.32434/0321-4095-2021-139-6-71-78.
27. **Cheng Y., Thompson D.P.** The transformability of tetragonal ZrO_2 in some glass systems. *J. Mater. Sci. Lett.* 1990. N 9. P. 24–27. DOI: 10.1007/BF00722858.

Поступила в редакцию 07.12.2023
Принята к опубликованию 26.12.2023

Received 07.12.2023
Accepted 26.12.2023