UDC 666.7

S.G. Polozhaj, O.V. Zaichuk, A.G. Polozhaj, O.A. Amelina

GLASS-CERAMIC BINDERS IN THE EUCRYPTITE–MANGANESE CORDIERITE SYSTEM FOR HIGH-STRENGTH DISPERSION-HARDENED COMPOSITE CERAMIC MATERIALS

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

Based on the experimental results, the temperatures of melt formation in the pseudo-binary system «eucryptite–manganese cordierite» were determined, and the phase diagram was constructed. The structure and phase composition of the obtained glass-ceramic materials were investigated. The promising composition (wt.%) of 80 eucryptite and 20 manganese cordierite, corresponding to the minimum melting temperature of the experimental mixtures (1225^{0}C), was determined. It was found that the synthesis temperature required to obtain a homogeneous glass of composition $80LiAlSiO_4$–$20Mn_2Al_4Si_5O_{18}$ lies in the range of 1400–1420^{0}C, which corresponds to the melting temperatures of the most common industrial glass compositions. This glass exhibits two exothermic effects caused by crystallization at 830^{0}C and 990^{0}C, as revealed by differential thermal analysis. During heat treatment, the glass almost completely crystallizes with the formation of β-spodumene and manganese cordierite. The crystal size ranges from 0.5 to 3 μm. The coefficients of thermal expansion of the parent glass and the glass-ceramic material obtained after its crystallization are $33.7 \cdot 10^{-7}$ $^0C^{-1}$ and $27.3 \cdot 10^{-7}$ $^0C^{-1}$, respectively. The developed crystallizing glass, characterized by a low coefficient of thermal expansion both before and after crystallization, is a promising binder for low-temperature sintering of dispersion-strengthened composite ceramic materials with fillers such as SiC and Si_3N_4.

Keywords: eucryptite, manganese cordierite, melting diagram, glass, crystallization, phase composition, microstructure.

DOI: 10.32434/0321-4095-2025-163-6-196-204

Introduction

The necessity of high-temperature sintering (1800–2000^{0}C) of disperse-strengthened ceramic materials with high mechanical properties is one of the main components of their high cost. The use of low-melting glass binders makes it possible to significantly reduce the sintering temperature of such materials. At the same time, the strength and wear resistance of the resulting materials are largely determined by the properties of the glass and glass-ceramic binders used [1]. The use of sodium-calcium-aluminosilicate glasses as sintering additives allows the synthesis of wear-resistant silicon carbide ceramics at 1100^{0}C, however the compressive strength of such materials is relatively low (up to 600 MPa) [2].

A more promising approach is the use of vitreous

binders crystallize during the sintering process of ceramics is more promising. Glass-ceramic binders exhibit significantly higher strength compared to conventional glasses [3]. Crystalline fillers based on oxygen-free silicon compounds (SiC, Si_3N_4), are characterized by relatively low coefficients of thermal expansion (CTE) in the range of $(27–45)\cdot10^{-7}$ $^0C^{-1}$. This limits the search for suitable binders to silicate systems capable of forming crystalline phases with low CTE values, such as celsian ($BaAl_2Si_2O_8$) [4], strontium anorthite ($SrAl_2Si_2O_8$) [5], cordierite ($Mg_2Al_4Si_5O_{18}$) [6], spodumene ($LiAlSi_2O_6$), and eucryptite ($LiAlSiO_4$) [7]).

The use celsian-based glass binders (up to 40 wt.%) allows obtaining dispersion-strengthened SiC ceramics with a bending strength of about 450 MPa by hot pressing [8]. When Si_3N_4 is used as a filler, the bending strength of sintered composites can reach 565 MPa [9].

It is known that the sintering temperature of composite dispersion-strengthened ceramic materials is primarily determined by the melting temperature of the glass-ceramic binders used [10,11]. One of these approaches is the synthesis of glasses with compositions close to the eutectic points of the corresponding silicate systems. Its drawback is the formation of a significant amount of residual glass phase or secondary crystalline phases along with the target crystalline phase, for example, cordierite [12]. Another approach to reducing the temperature required for producing crystallizing glass binders is the introduction of low-melting components into the glasses that do not alter the composition of the target crystalline phases [13].

At the same time, a decrease in the melting temperature of the base glasses used for producing glass-ceramics and/or the sintering temperature of the corresponding glass-ceramic materials is accompanied by an increase in the amount of residual glass phase.

In some cases, this can be beneficial, as it improves the properties of the resulting materials. However, the thermomechanical properties of glass-ceramic materials are largely determined to the degree of their crystallization. Accordingly, the use of binders with a higher content of glass phase in the synthesis of dispersion-hardened ceramics may lead to a reduction in strength. A more promising approach is to search for low-melting glasses in pseudo-binary systems of such crystalline compounds, that are intended to become the main crystalline phases in the resulting glass-ceramic binders. Such glasses are characterized by a high tendency to crystallize and practically do not form secondary crystalline phases [14].

In view of the above, the aim of this work was to search for and investigate the crystallizing glasses compositions with minimum synthesis temperature in the eucryptite ($LiAlSiO_4$)–manganese cordierite ($Mn_2Al_4Si_5O_{18}$) system. The search for compositions was carried out by constructing a melting diagram, followed by their investigation in both the glassy and crystallized states.

Materials and methods

Lithium carbonate and oxides of SiO_2, Al_2O_3 and MnO with a purity of at least 99.8% were used as starting materials for glass synthesis.

The preparation of compositions was carried out in two stages. First, raw material mixtures were prepared that, after synthesis, corresponded to the chemical composition of eucryptite and manganese cordierite. They were mixed and ground in drum mills made of high-alumina porcelain until the residue on sieve No. 0063 did not exceed 1%.

The design of experiments involved studying the properties of glass and glass-ceramic materials in the range of $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$ component ratios from 10:90 to 90:10. The concentration change step was set at 10 wt.%. During final preparation, the raw material mixtures were ground to a particle size of less than 45 μm. Then, a drum mill with a liner and grinding bodies made of chalcedony was used. Coding of numbers of experimental raw mixes corresponded to 1/10 of the conventional content in them $Mn_2Al_4Si_5O_{18}$ (in wt.%). Thus, batch composition No. 1 was assigned to a mixture of components consisting of 10 wt.% $Mn_2Al_4Si_5O_{18}$ and 90 wt.% $LiAlSiO_4$. Other compositions were coded accordingly.

A chamber furnace with silicon carbide heaters was used to synthesize the experimental materials. The temperature range for heat treatment was 1200–1400^{0}C. Before heat treatment, the experimental mixtures were placed in corundum ceramics crucibles with a capacity of 5 cm^3. The heating rate of the samples in the furnace was 500^{0}C per hour. Upon reaching the maximum temperature, the samples were held for 2 hours. After that, the temperature was reduced to 600^{0}C at a rate of 100^{0}C per hour. Further cooling of the samples was not controlled. The quality of the samples after heat treatment was evaluated by visual inspection.

For extended studies, additional melting of glass composition No. 8 was carried out. The synthesis was performed in corundum ceramic crucibles with a capacity of 500 cm^3. The maximum synthesis temperature was in the range of 1400–1410^{0}C. The holding time at the maximum temperature for melt homogenization was 2 h. The prepared glass was cooled

by casting on a massive steel plate, followed by annealing in a muffle furnace from 700°C to 20°C at a cooling rate of 50–60°C/h.

The properties of synthesized glasses and glass-ceramic materials were investigated using standard methods for this class of materials. The coefficient of thermal expansion (CTE) was determined in the temperature range of 60–400°C on a vertical quartz dilatometer at a heating rate of 4–5°C/min [14].

Differential thermal analysis (DTA) was performed using a synchronous thermal analyzer (STA PT 1600, Linseis GmbH) in the temperature range of 20–1000°C at a heating rate of 10°C/min. The qualitative phase composition was determined by X-ray diffraction (XRD) using a Philips APD-15 diffractometer in Co-K_α radiation. To obtain Fourier transform infrared (FTIR) spectra of the materials under investigation, a Shimadzu IRSpirit-X with an ATR attachment (QATR-S, Specac) was used. Scanning electron microscopy was carried out on freshly fractured surfaces of glass-ceramic samples using a SEM MIRA3 TESKAN.

The elemental composition of crystalline phases was determined by energy-dispersive X-ray spectroscopy (EDS) a using a Bruker Nano XFlash Detector 610M. This method allows reliable detection of elements with atomic numbers higher than carbon. Lithium (Z=3) could not be detected; therefore, lithium-containing phases were identified indirectly based on the distribution of elements with Z≥6.

Results and discussion

The search for compositions of low-melting crystallizing glasses was performed in the pseudo-binary system «$LiAlSiO_4$–$Mn_2Al_4Si_5O_{18}$» by constructing a melting diagram. At the first stage, tendency of raw material mixtures to form a melt in the temperature range 1200–1400°C was investigated. The mixtures were studied over a wide compositional range, with $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$ ratios from 10:90 to 90:10. Based on visual evaluation after heat treatment, the samples were classified into four main groups:

The first group (soft-sintered) – weakly sintered samples with a loose structure practically not subjected to shrinkage during heat treatment.

The second group (sintered) – samples that acquired high density and strength after severe shrinkage, but have retained their original shape.

The third group (undermelt) – dense and/or low-porosity masses formed as a result of melting, showing a characteristic glassy meniscus in the crucible.

The fourth group (molten) is a foamed mass that has retained a cellular texture during heat treatment. It can be assumed that, at the initial stage of heat treatment, sufficient amount of low-melting liquid phase was or formed to induce foaming, and then dissolution of refractory charge components increased the melt viscosity and fixes the foamed texture of the mass.

A graphical representation of the obtained results is presented in the melting diagram (Fig. 1). The curve, which shows the temperature of melt existence in the pseudo-binary system «$LiAlSiO_4$–$Mn_2Al_4Si_5O_{18}$», has two temperature minima. The first minimum is observed at a $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$ ratio of 90:10 about 1300°C, whereas the second minimum is at the ratio $LiAlSiO_4$:$Mn_2Al_4Si5O_{18}$ of 20:80 (1225°C). The obtained curve is close to the temperature curve of melt formation obtained by us earlier in the study of the «$LiAlSi_2O_6$–$Mn_2Al_4Si_5O_{18}$» system [14].

All investigated compositions formed a melt at 1400°C. The melt samples obtained after cooling at a rate of 50–60°C/h exhibited a matte fracture surface, which characterizes their high tendency to crystallization. Fourier-transform infrared spectroscopy (Fig. 2) and X-ray diffraction (Fig. 3) were carried out to evaluate the structure of the samples, the degree of crystallization and to determine the composition of the released crystalline phases.

FTIR spectra of the samples recorded in the range of 300–4600 cm^{-1} (Fig. 2) showed that when the $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$ ratio of decreased to 30:70 and below, a gradual decrease in the intensity of absorption bands was observed. This change in the character of absorption bands, in our opinion, is associated with a relatively low propensity to crystallization of manganese cordierite, which is confirmed by the XRD results (Fig. 3).

All recorded FTIR spectra exhibit two absorption bands in the range of 800–1300 cm^{-1} and 400–500 cm^{-1}, which are responsible for the stretching and bending vibrations of the Si–O bond in [SiO_4] tetrahedra, respectively. Moreover, the structure of

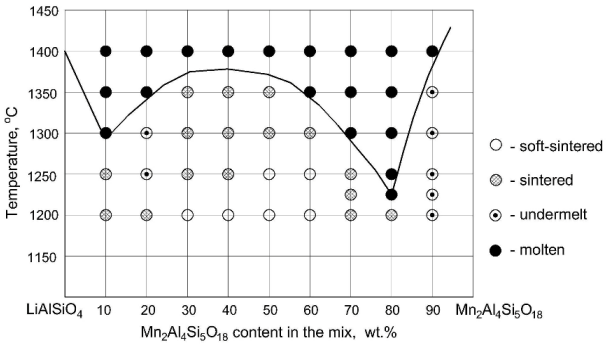

Fig. 1. Melting diagram in the pseudo-binary $LiAlSiO_4$–$Mn_2Al_4Si_5O_{18}$ system

most of the materials (compositions No. 10–50), judging by the position of the high-frequency absorption band in the range 981–986 cm^{-1}, can be attributed to orthosilicates [15]. It should be stated that the absorption band characteristic of the stretching vibrations of the Si–O bond in [SiO_4] tetrahedra is weakly expressed and appears as a small shelf at 1035 cm^{-1} in compositions No. 1–3. For the composition No. 5 this absorption band is not observed.

The main high-frequency absorption band in compositions No. 1–5 (981–986 cm^{-1}) in lithium aluminosilicates can be attributed to the stretching vibrations of the Si–O bond in isolated [SiO_4] tetrahedra. The same band is responsible for the stretching vibrations of the Al–O bond in [AlO_4] tetrahedra [14].

The absorption bands at 760 cm^{-1} and 677 cm^{-1} are also attributed to the stretching vibrations of the Si–O and Al–O binders in eucryptite. These bands are present on FTIR spectra of compositions No. 1–5, which may indicate crystallization of eucryptite phase. The absorption band at 531 cm^{-1}, well expressed in the spectrum of eucryptite [14], which is correlated with bending vibrations in the Si–O–Li binders, appears in the spectra of experimental samples in the form of a shoulder.

As the $LiAlSiO_4$ content decreases in the experimental samples, the high-frequency absorption band corresponding to the vibrations of Si–O binders becomes wider, which indicates an increase in the degree of polymerization of the silicate framework. At the transition to compositions No. 7 and No. 8 on FTIR spectra two absorption bands in the range of 500–700 cm^{-1}, which are responsible for symmetric vibrations of Si–O–Si in spodumene (pyroxene) chain, are clearly fixed. In the spodumene structure, the repetition period is two [SiO_4] tetrahedra. Therefore, in our case in the composition of No. 8 there are two intense absorption maxima with frequencies of 550 cm^{-1} and 653 cm^{-1}. According to ref. [15], this absorption character is typical for lithium-alumino-silicate ceramics during the transition from eucryptite compositions to spodumene compositions.

For composition No. 9, the spectrum obtained in the range of measurements has a smooth character without pronounced peaks, which is characteristic of

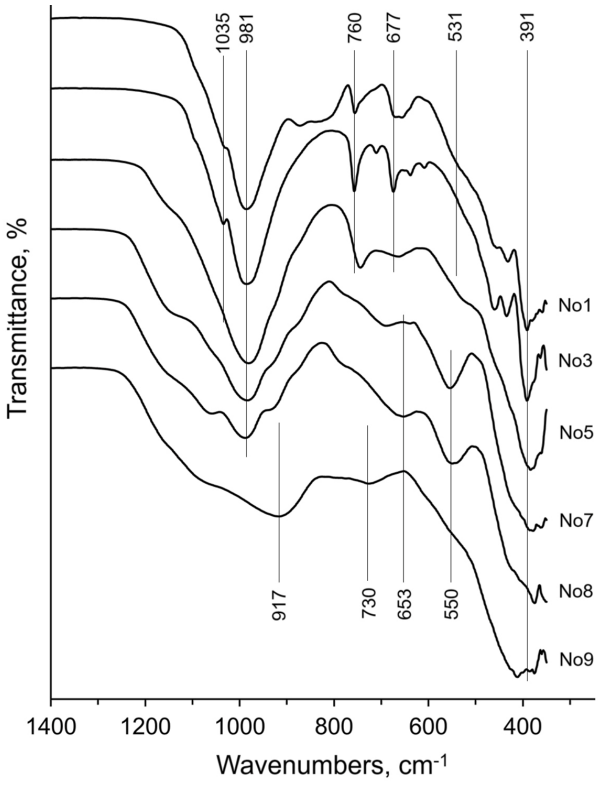

Fig. 2. FTIR spectra of material samples in the $LiAlSiO_4$–$Mn_2Al_4Si_5O_{18}$ system obtained at 1400°C

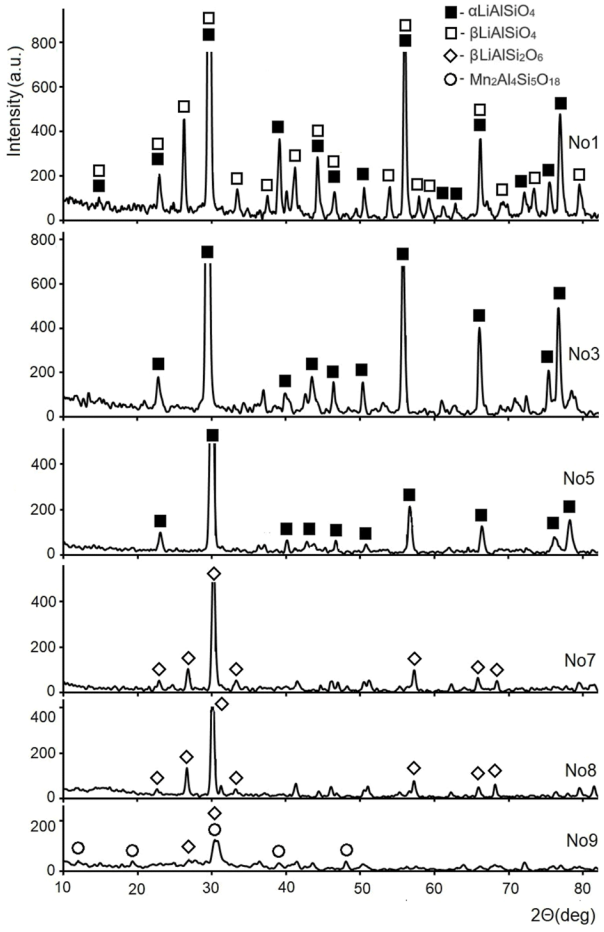

Fig. 3. XRD patterns of experimental of experimental glass-ceramic samples in pseudo-binary $LiAlSiO_4$–$Mn_2Al_4Si_5O_{18}$ system

the vitreous phase. At the same time, the main absorption band of the spectrum becomes is located in the wavenumbers range of 850–1200 cm^{-1}. This indicates a greater degree of polymerization of the silicate framework and its transition to ring structures, to which manganese cordierite belongs. Absorption bands in the range of 700–800 cm^{-1} and 570 cm^{-1}, characteristic of ring silicates, are observed as kinks on the FTIR spectrum.

The results of X-ray diffraction analysis (Fig. 3) correlate well with FTIR spectroscopy data (Fig. 2), when the compositions of the experimental melts shift towards manganese cordierite, a decrease in tendency to crystallization is observed. At the same time, the intensities of diffraction peaks in the XRD patterns of investigated glass-ceramic materials decreases. The qualitative composition of crystalline phases also undergoes changes. Decreasing the $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$ ratio from 90:10 to 50:50 wt.% in the composition of the samples corresponds to the decrease in the intensity of the main diffraction peaks of β-eucryptite ($d \cdot 10^{10}$=3.35; 1.91; 1.64; 1.46; 1.44 m) on the XRD patterns. Moreover, for the composition No. 1, the separation of eucryptite in the form of two polymorphic modifications (α- and β-forms) was noted.

In the compositions range $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$=30:70 to 10:90 wt.%, β-spodumene ($d \cdot 10^{10}$=4.61; 3.91; 3.49; 3.16 m) stands out as a lithium-bearing crystalline phase. Small amounts of manganese cordierite ($d \cdot 10^{10}$=8.65; 4.09; 3.40; 3.16 m) were noted as part of No. 9.

For further investigations, the composition No. 8 was selected due to its favorable energy and technological efficiency of glass synthesis. This was done on the assumption that the practical melting temperature of glasses correlates with their glass-forming temperature. The practical temperature of glass No. 8 synthesis was 1400±10^{0}C with holding time 2 h for melt homogenization. The CTE of the obtained glass in the range of 20–400^{0}C is 33.7·10^{-7} $^0C^{-1}$.

According to the results of differential thermal analysis (Fig. 4), an endothermic effect corresponding to the onset of softening glass No. 8 is observed at 720^{0}C. The tendency of the glass to crystallization is confirmed by the presence of exothermic peaks on the curve at temperatures of 830^{0}C and 990^{0}C.

In accordance with the DTA data, additional thermal treatment of glass samples with composition No. 8 was performed. Heating was carried out with a temperature rise rate of 5–6^{0}C/min. Isothermal holding for 1 h was applied at 720^{0}C, 830^{0}C and 990^{0}C. The CTE of the crystallized glass was 27.3·10^{-7} $^0C^{-1}$. The crystalline phases identified in the X-ray diffraction pattern of the obtained glass-ceramic material are β-spodumene ($d \cdot 10^{10}$=4.61; 3.91; 3.49; 3.16 m) and manganese cordierite, whose crystallization peaks ($d \cdot 10^{10}$=8.65; 4.09; 3.40; 3.16 m) are significantly weaker (Fig. 5a).

The microstructure observed by scanning electron microscopy (Fig. 5b) confirms the XRD results (Fig. 5a). Elongated, columnar β-spodumene crystals with well-defined facets are clearly distinguishable. Crystals of manganese cordierite are less pronounced, which is presumably due to its crystallization after β-spodumene, at the second stage of the heat treatment under constrained conditions (Fig. 5b).

The weak faceting of manganese cordierite crystals may be related to their lower tendency to crystallization compared to β-spodumene, as evidenced by the noticeably smaller height and area of the exothermic peak associated with its crystallization on the DTA curve. The size of β-spodumene and manganese cordierite crystals released mainly varies in the range of 0.5–3.0 μm.

The crystalline phases were identified by energy-dispersive X-ray spectroscopy performed on the fracture surface of cracked crystallized glass samples (Fig. 6). The data on the elemental composition of the identified phases are shown in Table.

The obtained compositions were recalculated in terms of atomic ratios. This made it possible to identify manganese cordierite in spectra No. 2 and 4 based on Mn:Al:Si:O ratios close to 2:4:5:18, that corresponds to its stoichiometric formula $Mn_2Al_4Si_5O_{18}$.

In spectra No. 1 and 3 (Fig. 6), manganese is practically absent, and the Al:Si:O ratio is close to 1:2:6. Taking into account that lithium cannot be detected by EDS, this elemental ratio allows these crystals to be attributed to β-spodumene with the stoichiometric formula $LiAlSi_2O_6$. Deviations of the elemental composition of the crystalline phase from the stoichiometric of composition of spodumene and manganese cordierite can be explained by the presence of a thin vitreous layer on the surface of the crystals.

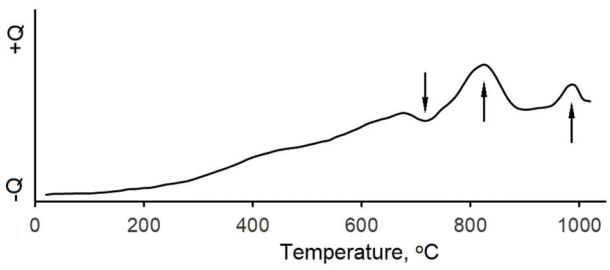

Fig. 4. Differential thermal analysis curve of glass with composition No. 8

Conclusions

Based on the experimental results, a melting diagram in the pseudo-binary system $LiAlSiO_4$:$Mn_2Al_4Si_5O_{18}$ was constructed. The ratio of eucryptite and manganese cordierite (20:80 wt.%) at which the melt formation occurs at the minimum temperature (1225^{0}C) was determined. The practical melting temperature of the glass with this composition is 1400–1420^{0}C. The synthesized glass is characterized by a CTE of $33.7 \cdot 10^{-7}$ $^0C^{-1}$, a softening temperature of 720^{0}C, and two crystallization exothermic effects at 830^{0}C and 990^{0}C. The glass crystallized according to the specified heat-treatment regime contains β-spodumene and manganese cordierite as the main crystalline phases. The size crystals is mainly range from 0.5 to 3.0 μm. The CTE of the crystallized glass is $27.3 \cdot 10^{-7}$ $^0C^{-1}$.

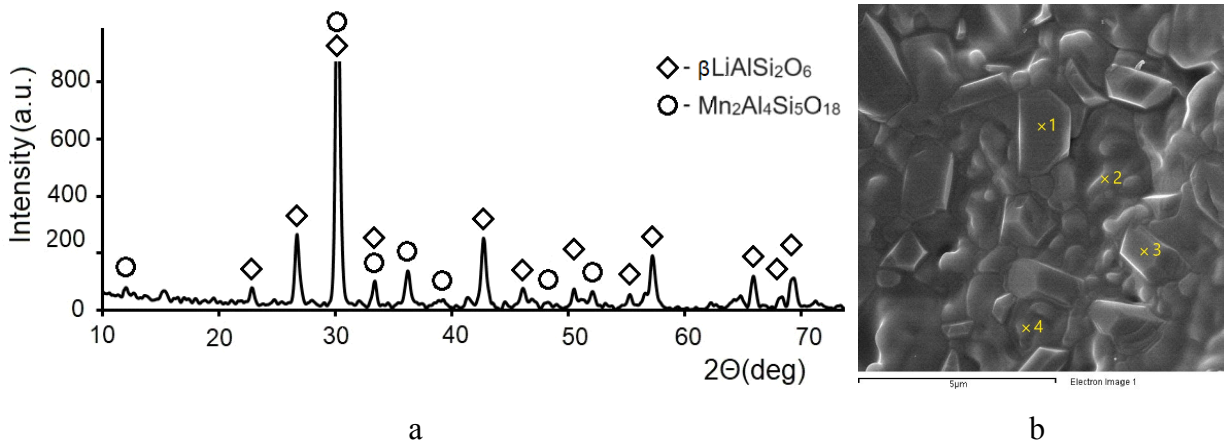

Fig. 5. XRD pattern of powder (a) and SEM image of fracture surface (b) of crystallized glass of composition No. 8

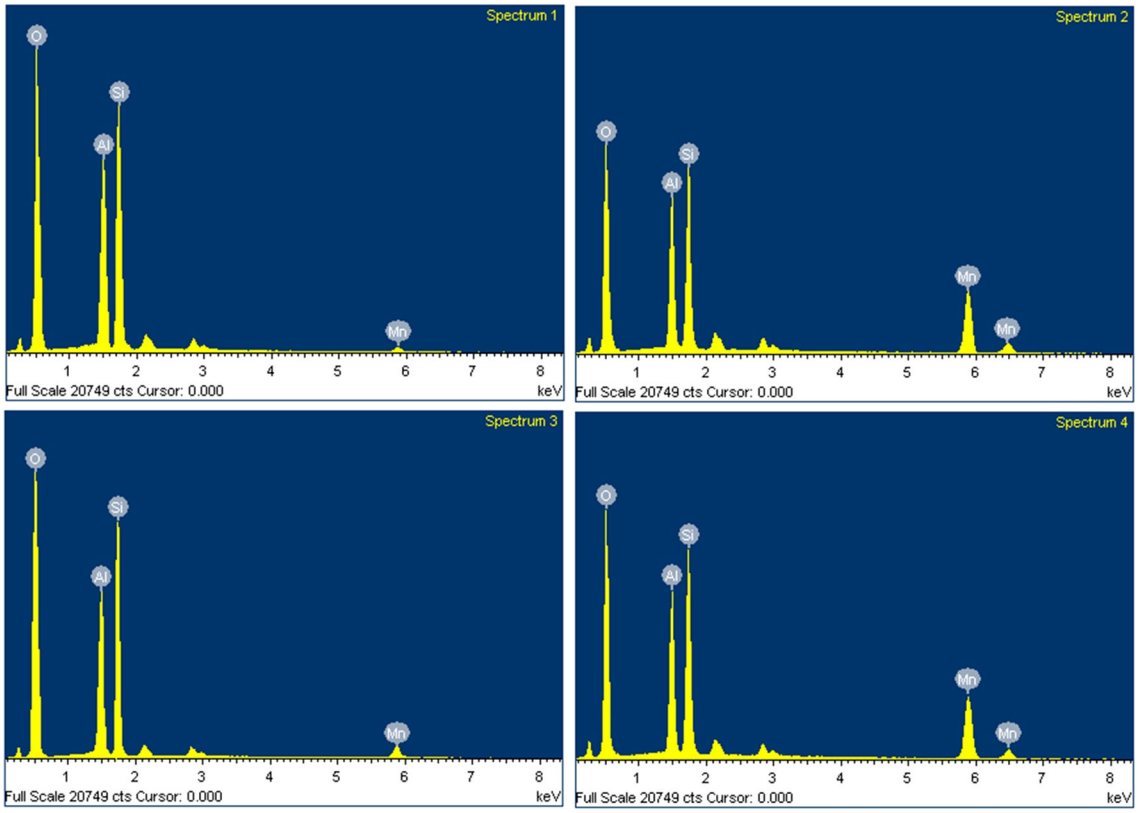

Fig. 6. Energy dispersive X-ray spectral analysis of the crystalline phase in crystallized glass No. 8

Results of energy-dispersive X-ray spectroscopy for crystallized glass eucryptite–(Mn) cordierite composition

Spectrum No.	Elemental content, at.%					Element ratio			
	O	Al	Si	Mn	Total	O	Al	Si	Mn
1	64.61	11.57	23.41	0.41	100	5.59	1.00	2.02	0.04
2	62.21	12.72	18.04	7.03	100	17.70	3.62	5.13	2.00
3	64.61	11.33	23.48	0.58	100	5.70	1.00	2.07	0.05
4	62.16	13.25	17.67	6.92	100	17.97	3.83	5.11	2.00

Due to its low melting temperature and pronounced tendency to crystallization, the developed material is a promising candidate for use as a glass-ceramic matrix for dispersion-strengthened ceramic materials with SiC and Si_3N_4 fillers at reduced sintering temperatures.

Funding

This research received funding from the Ministry of Education and Science of Ukraine under Scientific and Technical Program No 0124U000199.

REFERENCES

1. *Dispersnouprochnennye* kompozity na osnove steklo/steklokristallicheskih matric: svojstva i oblasti primenenija (obzor) / Chainikova A.S., Orlova L.A., Popovich N.V., Lebedeva Yu.E., Solntsev S.St. // Aviat. Mater. Technol. – 2014. – No. 3. – P.45-54.

2. *Polozhaj S.G., Shmatko T.Yu.* Vliyanie soderzhaniya steklosvyazki na spekanie karbidokremnievoj keramiki // Ogneupory i tehnicheskaya keramika. – 2006. – No. 11. – P.6-7.

3. *Effect* of B_2O_3 on the crystallization, structure and properties of $MgO–Al_2O_3–SiO_2$ glass-ceramics / Luo W., Bao Z., Jiang W., Liu J., Feng G., Xu Y., Tang H., Wang T. // Ceram. Int. – 2019. – Vol.45. – P.24750-24756.

4. *Synthesis* and characteristic of celsian ceramics with the use of glass in the system $Li_2O–Al_2O_3–B_2O_3–SiO_2$ / Zaichuk A.V., Amelina A.A., Hordieiev Yu.S., Kalishenko Y.R., Sribniak N.N. // Funct. Mater. – 2020. – Vol.27. – P.827-835.

5. *Patterns* in the synthesis processes, the microstructure and properties of strontium-anorthite ceramics modified by glass of spodumene composition / Zaichuk O., Amelina A., Hordieiev Yu., Kalishenko Y., Sribniak N., Halushka S., Borodai D., Borodai A. // East. Eur. J. Enterprise Technol. – 2020. – Vol.6. – P.15-26.

6. *Characterisation* of thermo-mechanical properties of $MgO–Al_2O_3–SiO_2$ 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.

7. *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.

8. *Microstructure* compatibility and its effect on the mechanical properties of the α-SiC/β-Si_3N_4 co-reinforced barium aluminosilicate glass ceramic matrix composites / Liu L., Ye F., Zhou Y., Zhang Z. // Scr. Mater. – 2010. – Vol.63. – P.166-169.

9. *Synthesis* of silicon nitride-barium aluminosilicate self-reinforced ceramic composite by a two-step pressureless sintering / Ye F., Liu L., Zhang J., Iwasa M., Su C.-L. // Compos. Sci. Technol. – 2005. – Vol.65. – P.2233-2239.

10. *Banjuraizah J., Mohamad H., Ahmad Z.A.* Effect of impurities content from minerals on phase transformation, densification and crystallization of α-cordierite glass-ceramic // J. Alloys Compd. – 2011. – Vol.509. – No. 28. – P.7645-7651.

11. *Drummond III C.H.* Glass formation and crystallization in high-temperature glass-ceramics and Si_3N_4 // J. Non-Cryst. Solids. – 1990. – Vol.123. – No. 1-3. – P.114-128.

12. *Densely* sintered carbide-silicon ceramics on a glass-crystal binder of cordierite composition / Polozhaj S.G., Zaichuk O.V., Sukhyy K.M., Polozhaj A.G. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2023. – No. 5. – P.98-105.

13. *Crystallization* behavior and thermal properties of B_2O_3–containing $MgO-Al_2O_3-SiO_2-Li_2O$ glass-ceramic and its wettability on Si_3N_4 ceramic / Sun L., Liu C., Fang J., Zhang J., Lu C. // J. Eur. Ceram. Soc. – 2019. – Vol.39. – No. 4. – P.1532-1539.

14. *Polozhaj S.G., Zaichuk O.V., Polozhaj A.G.* Fusible glass-crystalline binder in the spodumene–manganese cordierite system // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2024. – No. 6. – P.117-122.

15. *Vibrational* spectroscopy of beta-eucryptite ($LiAlSiO_4$): optical phonons and phase transition(s) / Zhang M., Xu H., Salje E., Heaney P.J. // Phys. Chem. Minerals. – 2003. – Vol.30. – P.457-462.

Received 30.07.2025

СКЛОКРИСТАЛІЧНІ ЗВ'ЯЗКИ В СИСТЕМІ ЕВКРИПТИТ–МАРГАНЦЕВИЙ КОРДІЄРИТ ДЛЯ ВИСОКОМІЦНИХ ДИСПЕРСІЙНО ЗМІЦНЕНИХ КОМПОЗИТНИХ КЕРАМІЧНИХ МАТЕРІАЛІВ

С.Г. Положай, О.В. Зайчук, А.Г. Положай, О.А. Ameліна

На підставі результатів здійснених досліджень встановлено температури утворення розплаву в псевдодвокомпонентній системі «евкриптит–марганцевий кордієрит». Побудовано відповідну діаграму плавлення. Досліджено структуру та фазовий склад дослідних склокристалічних матеріалів. Визначено перспективний склад (мас.%) евкриптиту – 80 та марганцевого кордієриту – 20, що відповідає мінімальній температурі плавлення експериментальних сумішей 1225^{0}C. Виявлено, що температура синтезу для одержання однорідного скла складу $80LiAlSiO_4–20Mn_2Al_4Si_5O_{18}$ знаходиться в діапазоні 1400–1420^{0}C, що відповідає температурам плавлення найпоширеніших складів промислових стекол. Цей склад скла має два екзотермічні ефекти, зумовлені кристалізацією при температурах 830^{0}C та 990^{0}C, що показано за допомогою диференціального термічного аналізу. Таке скло майже повністю кристалізується в процесі термічного оброблення з виділенням β-сподумену та марганцевого кордієриту. Розмір кристалів коливається від 0,5 до 3 мікрометрів. Коефіцієнти теплового розширення скла та склокристалічного матеріалу, одержаного після його кристалізації, становлять $33{,}7\cdot10^{-7}$ $^0C^{-1}$ та $27{,}3\cdot10^{-7}$ $^0C^{-1}$, відповідно. Розроблене скло з низьким коефіцієнтом теплового розширення як до, так і після кристалізації є перспективним зв'язуючим матеріалом для низькотемпературного спікання дисперсійно зміцнених композитних керамічних матеріалів з наповнювачами, такими як SiC (Si_3N_4).

Ключові слова: евкриптит, марганцевий кордієрит, діаграма плавлення, скло, кристалізація, фазовий склад, мікроструктура.

GLASS-CERAMIC BINDERS IN THE EUCRYPTITE–MANGANESE CORDIERITE SYSTEM FOR HIGH-STRENGTH DISPERSION-HARDENED COMPOSITE CERAMIC MATERIALS

S.G. Polozhaj, O.V. Zaichuk, A.G. Polozhaj, O.A. Amelina *

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

* **e-mail: amelinaalex1@gmail.com**

Based on the experimental results, the temperatures of melt formation in the pseudo-binary system «eucryptite–manganese cordierite» were determined, and the phase diagram was constructed. The structure and phase composition of the obtained glass-ceramic materials were investigated. The promising composition (wt.%) of 80 eucryptite and 20 manganese cordierite, corresponding to the minimum melting temperature of the experimental mixtures (1225^{0}C), was determined. It was found that the synthesis temperature required to obtain a homogeneous glass of composition $80LiAlSiO_4–20Mn_2Al_4Si_5O_{18}$ lies in the range of 1400–1420^{0}C, which corresponds to the melting temperatures of the most common industrial glass compositions. This glass exhibits two exothermic effects caused by crystallization at 830^{0}C and 990^{0}C, as revealed by differential thermal analysis. During heat treatment, the glass almost completely crystallizes with the formation of β-spodumene and manganese cordierite. The crystal size ranges from 0.5 to 3 μm. The coefficients of thermal expansion of the parent glass and the glass-ceramic material obtained after its crystallization are $33.7\cdot10^{-7}$ $^0C^{-1}$ and $27.3\cdot10^{-7}$ $^0C^{-1}$, respectively. The developed crystallizing glass, characterized by a low coefficient of thermal expansion both before and after crystallization, is a promising binder for low-temperature sintering of dispersion-strengthened composite ceramic materials with fillers such as SiC and Si_3N_4.

Keywords: eucryptite; manganese cordierite; melting diagram; glass; crystallization; phase composition; microstructure.

REFERENCES

1. Chainikova AS, Orlova LA, Popovich NV, Lebedeva YuE, Solntsev SSt. Dispersnouprochnennye kompozity na osnove steklo/steklokristallicheskih matric: svojstva i oblasti primenenija (obzor) [Dispersion reinforced composites based on glass/glass-ceramics matrixes: properties and possible applications (review)]. *Aviat Mater Technol.* 2014; (3): 45-54. (*in Russian*). doi: 10.18577/2071-9140-2014-0-3-45-54.

2. Polozhaj SG, Shmatko TYu. Vliyanie soderzhaniya steklosvyazki na spekanie karbidokremnievoi keramiki [The influence of glass binder content on the sintering of silicon carbide ceramics]. *Ogneupory i Tehnicheskaya Keramika.* 2006; 11: 6-7.

3. Luo W, Bao Z, Jiang W, Liu J, Feng G, Xu Y, et al. Effect of B_2O_3 on the crystallization, structure and properties of $MgO–Al_2O_3–SiO_2$ glass-ceramics. *Ceram Int.* 2019; 45: 24750-24756. doi: 10.1016/j.ceramint.2019.08.215.

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 $Li_2O–Al_2O_3–B_2O_3–SiO_2$. *Funct Mater.* 2020; 27: 827-835. doi: 10.15407/fm27.04.827.

5. Zaichuk O, Amelina A, Hordieiev Yu, Kalishenko Y, Sribniak N, Halushka S, et al. 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; 6: 15-26. doi: 10.15587/1729-4061.2020.216754.

6. Shamsudin Z, Hodzic A, Soutis C, Hand RJ, Hayes SA, Bond IP. Characterisation of thermo-mechanical properties of $MgO-Al_2O_3-SiO_2$ glass ceramic with different heat treatment temperatures. *J Mater Sci*. 2011; 46: 5822-5829. doi: 10.1007/s10853-011-5538-0.

7. 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.

8. Liu L, Ye F, Zhou Y, Zhang Z. Microstructure compatibility and its effect on the mechanical properties of the α-SiC/β-Si_3N_4 co-reinforced barium aluminosilicate glass ceramic matrix composites. *Scr Mater*. 2010; 63: 166-169. doi: 10.1016/j.scriptamat.2010.03.040.

9. Ye F, Liu L, Zhang J, Iwasa M, Su CL. Synthesis of silicon nitride-barium aluminosilicate self-reinforced ceramic composite by a two-step pressureless sintering. *Compos Sci Technol*. 2005; 65: 2233-2239. doi: 10.1016/j.compscitech.2005.04.015.

10. Banjuraizah J, Mohamad H, Ahmad ZA. Effect of impurities content from minerals on phase transformation, densification and crystallization of α-cordierite glass-ceramic. *J Alloys Compd*. 2011; 509: 7645-7651. doi: 10.1016/j.jallcom.2011.04.129.

11. Drummond III CH. Glass formation and crystallization in high-temperature glass-ceramics and Si_3N_4. *J Non-Cryst Solids*. 1990; 123: 114-128. doi: 10.1016/0022-3093(90)90778-K.

12. Polozhaj S, Zaichuk O, Sukhyy K, Polozhaj A. Densely sintered carbide-silicon ceramics on a glass-crystal binder of cordierite composition *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2023; (5): 98-105. doi: 10.32434/0321-4095-2023-150-5-98-105.

13. Sun L, Liu C, Fang J, Zhang J, Lu C. Crystallization behavior and thermal properties of B_2O_3–containing $MgO-Al_2O_3-SiO_2-Li_2O$ glass-ceramic and its wettability on Si_3N_4 ceramic. *J Eur Ceram Soc*. 2019; 39: 1532-1539. doi: 10.1016/j.jeurceramsoc.2018.12.002.

14. Polozhaj SG, Zaichuk OV, Polozhaj AG. Fusible glass-crystalline binder in the spodumene–manganese cordierite system. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2024; (6): 117-122. doi: 10.32434/0321-4095-2024-157-6-117-122.

15. Zhang M, Xu H, Salje E, Heaney PJ. Vibrational spectroscopy of beta-eucryptite ($LiAlSiO_4$): optical phonons and phase transition(s). *Phys Chem Minerals*. 2003; 30: 457-462. doi: 10.1007/s00269-003-0337-z.