UDC 666.3-13+666.762.1

A.V. Zaichuk, A.A. Amelina, Y.S. Khomenko, A.S. Baskevich, Y.R. Kalishenko

HEAT-RESISTANT CERAMICS OF β-EUCRYPTITE COMPOSITION: PECULIARITIES OF PRODUCTION, MICROSTRUCTURE AND PROPERTIES

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

Heat-resistant ceramics of β-eucryptite composition was synthesized in the current work. To this end, the method of ceramics production was combined with the principle of reactive formation of the material structure. Taking into account the calculated data about the compositions of eutectics and temperature of their melting in the specific binary systems $Li_2O{\cdot}2SiO_2-Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ and $Li_2O{\cdot}2SiO_2-Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, a comparatively low-melting glass was developed in the system $Li_2O-Al_2O_3-SiO_2$ (with a melting temperature of 1250°C). Its function in the composition consists in the intensification of the processes associated with the formation of the crystalline phase of β-eucryptite and sintering of the ceramic material as a whole. Based on the results of experimental study, we concluded that the duration and temperature of sintering of ceramics directly determine its microstructure and physicotechnical properties. In order to achieve the complex of the highest indices, the firing of eucryptite ceramics should be performed at the temperature of 1350°C with the isothermal time of 3 h. β-eucryptite phase is formed as the distinct prismatic crystals of hexagonal shape with a size of 4–7 μm. The developed composition of eucryptite ceramics allows obtaining the products or individual elements with varying complexity of shapes, which significantly reduces the amount of rejects.

Keywords: β-eucryptite, heat-resistant ceramics, phase composition, microstructure, properties.

DOI: 10.32434/0321-4095-2020-129-2-52-59

Introduction

Heat-resistant glass-ceramic materials are widely used in various technical fields. Products made of them are characterized by long service life and possibility of operation under the conditions of sharp fluctuations of temperatures. These are heat exchangers, heat-resistant pipes, fairings of radio antennas, components of rocket engines and other engines, substrates for electric heating elements, laboratory and household utensils, catalyst carriers and so on [1].

At present, quartz ceramics is commonly used as an effective heat-resistant material [2–4], along with the wide range of high-temperature glass-ceramic materials obtained primarily on the basis of aluminosilicate systems [5–9]. Expansion of the applications of products made of glass-ceramic materials requires continuous development of new materials with increased thermal resistance indices. Resistance to thermal shock is the most important factor for the choice of structural materials at the given thermomechanical modes. Materials with the crystalline phase represented by lithium aluminosilicates are traditionally treated as high-heat-resistant ones. Compositions of this type can provide low positive values as well as negative values of the thermal coefficient of linear expansion (CLTE).

Glass-ceramic materials in the modern technology follow two main trends [1]. The classical glass method of producing these materials remains to be a common one; at the same time, the powder method based on the principles of ceramic technique becomes increasingly more important.

Production of glass-ceramic materials following the conventional glass technique is an expensive and energy intensive process. First of all, it implies high melting temperatures of glass. For the glasses in the $Li_2O-Al_2O_3-SiO_2$ (LAS) system, melting temperature may reach 1650°C, depending on the composition. Xiao et al. [10] showed that the addition of P_2O_5 provides the reduction of the melting temperature of experimental LAS glasses to 1570°C, resulted from a decrease in the eutectic temperature. Furthermore, P_2O_5 leads to the intensification of

crystallization process and growth of β-spodumene crystals in the glass-ceramic material itself. At the same time, an increase in the content of phosphorus(V) oxide to 8 wt.% results in the growth of CLTE value to $12 \cdot 10^{-7}$ deg^{-1}.

A significant drawback of the glass technology is a limited possibility to vary the phase composition of materials. It is caused by the necessity of using glass-forming compositions only and strict observance of process parameters. The molding of glass billets for the production of glass-ceramic materials is also very difficult in practical terms. Many of glasses have a narrow temperature range of glass transition, which is shifted, towards higher temperatures. Another difficulty is an increased tendency of glasses to crystallization in the temperature range of billets forming [9]. For example, melting of glasses to obtain glass-ceramic materials of β-eucryptite composition is carried out at the relatively low temperature of 1450°C. However, such glasses exhibit an increased tendency to crystallize which significantly complicates their production [11].

In recent years, ceramic (powder) technology of glass ceramic materials is developed more actively. Here, glass of the given composition is crushed and molded with the use of methods of ceramic technology, and further heat-treated with the purpose of its sintering and crystallization.

The powder technique of glass-ceramic materials allows using as a parent glass an extremely wide range of compositions with low and high crystallization ability. The ceramic method can be used for producing the materials with densely sintered and adjustable porous structure. This technology, compared to the classical glass one, ensures increased stability and reproducibility of the physic-chemical properties of materials. Great advances have been made in the development of radio-transparent glass ceramic material of the grade OTM-357, which is an analog of spodumene glass ceramics AC-418. Spodumene glass ceramics contains in its structure up to 1% of closed pores that are an obstacle to propagation of micro-cracks. These peculiar features of microstructure ensure the increased resistance of the material to the thermal shock [12].

However, despite the obvious advantages, the technology of producing the articles made of glass-ceramics has a number of shortcomings [12]. These shortcomings include high temperatures of parent glass melting (up to 1650°C), difficulties in regulation of the rheological properties of aqueous slips, low strength of molded billets, and complexity of their removal from the mold because of low shrinkage. One of the main process drawbacks of the ceramic technique is a difference in grain composition and density of billets (in particular, large-sized ones) made according to the method of slip casting, by height and thickness. It renders substantially difficult to produce the products with the specified level of physical and technical characteristics.

Significant reduction of energy costs and achievement of high and stable physic-technical parameters of glass-ceramic materials is possible by utilizing the ceramic technology combined with the principle of reactive formation of the structure. The phase composition of glass ceramic materials is formed in the process of their sintering due to the interaction between the components of low-melting glass with the crystalline filler. Full-scale application of the principle of reactive formation of the structure for obtaining the eucryptite ceramics is limited by the lack of known compositions of LAS system suitable for slip casting (to provide complex shapes of products).

For example, Goleus et al. [13] reported the synthesis of the eucryptite glass-ceramics from a mixture of glass of the composition $Li_2O \cdot 2SiO_2$ and crystalline filler (α-Al_2O_3) by the method of semidry pressing. Parent glass melting temperature was equal to 1300°C. The composite material synthesized at 1200°C was characterized by a low degree of sintering (water absorption (W) 24.7% and opened porosity (P) 35.6%) and positive value of CLTE $5.1 \cdot 10^{-7}$ deg^{-1}.

Therefore, the objective of the current research consisted in a further development of the physical-chemical principles of the directed formation of microstructure and phase composition of heat-resistant ceramics featuring β-spodumene composition in order to achieve the complex of high performance indices.

Materials and methods

To produce the eucryptite ceramics, LAS matrix glass E-1 developed by us, enriched kaolin of zref-1 grade and technical alumina of G0 grade were used.

The matrix glass was melted in an electric furnace in fireclay crucibles at the temperature of 1250°C during 1 h. The glass melt was subjected to dry granulation. CLTE of the glass E-1 was equal to $123.6 \cdot 10^{-7}$ deg^{-1}.

Using the initial components, ceramic slurry was prepared by joint wet grinding in the porcelain ball mill untill complete passing through the sieve No. 0063 with the subsequent ageing within 1 day. Using the prepared slurries, samples were cast into plaster molds in the form of cylinders and rods. After removal of castings from the molds, they were dried to residual moisture content of 1%. Dried specimens were firing in a furnace with silicon carbide heating

elements in the air according to specified temperature-time conditions. Maximum temperature of sintering was equal to 800–1375°C with the isothermal holding for 1–5 h.

Liquidus curves in the binary systems were calculated using the Epstein-Howland equation.

During experimental studies, standard techniques for determination of properties of obtained ceramic materials were used.

Water absorption (W), opened porosity (P) and apparent density (ρ) of the samples were determined by the saturation method with further weighing in the air and in water.

Ultimate compressive strength (σ) of specimens in the form of cylinders (d=h=10 mm) was found by using a hydraulic press.

The matrix glass and glass-ceramic samples were prepared with the dimensions of 5 mm×5 mm×50 mm (with an of accuracy of ±0.02 mm) to measure their length change ΔL with temperature and calculate the mean CLTE for the temperature range from 20°C to 400°C at the heating rate of 10°C/min.

The temperatures of softening and crystallization of the LAS matrix glass were measured by a differential scanning calorimeter (DSC, Netzsch 404PC) in the temperature interval of 20–1200°C at the heating rate of 10°C/min.

The crystal phase composition of the studied ceramics was estimated by X-ray diffraction method (XRD) by using a diffractometer Philips APD-15 in Cu-K_α radiation.

The electron microscopic investigations of the eucryptite ceramics were carried out using a scanning electron microscope REM-106I.

The thermal resistance was determined by the maximum temperature difference, which the samples withstand until their damage appears.

Dielectric constant (ε) and dielectric loss tangent (tgδ) were measured with the use of the unit comprising G4-83 generator, S4-11 spectral analyzer and bi-conical resonator. The resonator was connected in the transmission mode. Measurements were made at the frequency of 10^{10} Hz and temperature of 20°C.

Results and discussion

Production of glasses with the eucryptite composition in the system $Li_2O–Al_2O_3–SiO_2$ involves high temperatures of their melting (1450°C and above). In this regard, we considered an opportunity to develop the composition of low-melting glass in the mentioned ternary system with the use of the method of calculation of the liquidus temperatures. The phase composition of the ceramic materials containing the basic glass as an initial component was supposed to be adjusted towards the formation of β-eucryptite by introducing a clay component (kaolin). Kaolin also provides the necessary technological effectiveness of the ceramic production process.

Experimental data on the liquidus temperatures in the considered part of the $Li_2O–Al_2O_3–SiO_2$ diagram are represented in the literature only partially [13,14].

Toropov et al. [14] made calculations of the liquidus curves in specific binary systems $Li_2O·2SiO_2$–$Li_2O·Al_2O_3·2SiO_2$ and $Li_2O·2SiO_2$–$Li_2O·Al_2O_3·4SiO_2$. At the same time, usage of such glasses containing lithium disilicate poses certain limitations on the complexity of shapes of the ceramic products being made. Here, semidry pressing method is effectively applicable only. Consequently, we calculated the liquidus curves in the binary systems $Li_2O·SiO_2$–$Li_2O·Al_2O_3·2SiO_2$ and $2Li_2O·SiO_2$–$Li_2O·Al_2O_3·2SiO_2$ using the Epstein-Howland equation. The initial data for calculations are given in Table.

Initial data for calculation of liquidus lines

Compounds	Number of atoms, n	Melting temperature, K
$Li_2O·SiO_2$	6	1474
$2Li_2O·SiO_2$	9	1528
$Li_2O·Al_2O_3·2SiO_2$	14	1653

The results of the calculation in the form of fusiblity curves are presented in Fig. 1.

In «pseudobinary» system $Li_2O·SiO_2$–$Li_2O·Al_2O_3·2SiO_2$, the eutectic mixture has the following composition (mol.%): 87 $Li_2O·SiO_2$ and 13 $Li_2O·Al_2O_3·2SiO_2$. The melting temperature is 1168°C.

In «pseudobinary» system $2Li_2O·SiO_2$–$Li_2O·Al_2O_3·2SiO_2$ the eutectic mixture has the following composition (mol.%): 79 $2Li_2O·SiO_2$ and 21 $Li_2O·Al_2O_3·2SiO_2$. The melting temperature is 1212°C.

Taking into account the composition of eutectic mixtutes in the considered «pseudobinary» systems and their melting temperatures, we chose the system $Li_2O·SiO_2$–$Li_2O·Al_2O_3·2SiO_2$. At the melting temperature of this eutectic mixture (1168°C), the appearance of the liquid phase in the mixture of initial components can be expected in the course of firing of ceramics.

Using the differential thermal analysis (DTA) of the developed LAS matrix glass E-1, we found that endothermic effects at the temperatures of 420 and 490°C correspond to its softening (Fig. 2).

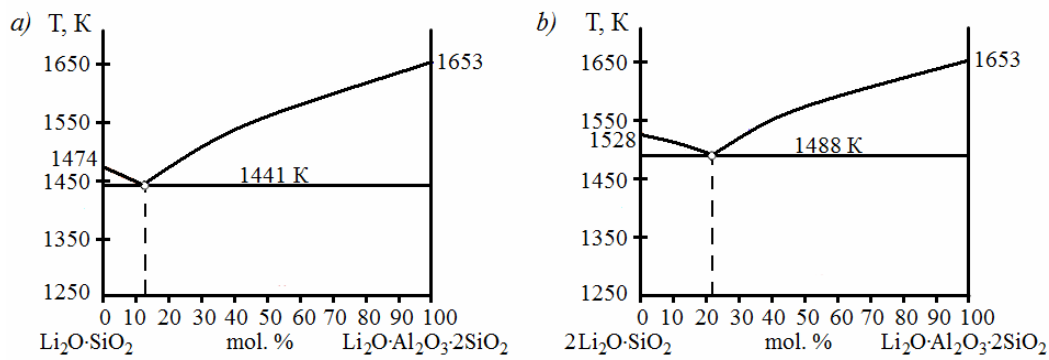

Fig. 1. Calculated liquidus lines in «pseudobinary» systems $Li_2O{\cdot}SiO_2$–$Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ (a) and $2Li_2O{\cdot}SiO_2$–$Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ (b)

Crystallization process is accompanied by intensive exo-effects on the DTA curve at the temperatures of 550 and 600°C.

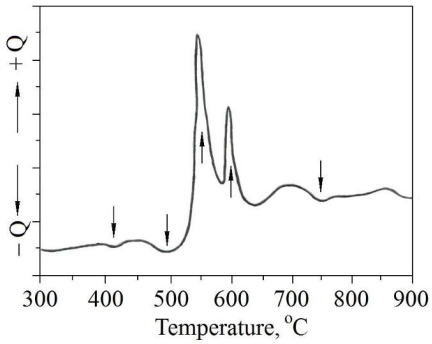

Fig. 2. Curve of differential thermal analysis of LAS matrix glass E-1

Taking into account the DTA data, the temperature and time regime of firing of eucryptite ceramics was subsequently chosen. To obtain it, lithium metasilicate ($Li_2O{\cdot}SiO_2$) was bound with the eucryptite phase according to the following equation:

$$2(Li_2O{\cdot}SiO_2)+Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O+Al_2O_3= =2(Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2)+2H_2O.$$

Therefore, LAS matrix glass E-1, enriched kaolin and technical alumina (γ-Al_2O_3) were used to produce the eucryptite ceramics.

The role of matrix glass in the experimental composition consists in the efficient mineralizing effect, as a result of which the processes connected with the formation of the crystalline phase of β-eucryptite and sintering of the ceramic material as a whole are intensified.

The presence of kaolin in the ceramic mass makes it possible to quite easily control the rheological properties of aqueous slips and obtain, after disassembling the molds, the billets of the strength sufficient for subsequent process stages. Besides, air shrinkage accompanying the process of billets drying ensures their easy extraction from the porous molds.

A maximum temperature of ceramics firing was limited by the melting point of eucryptite (1380°C) and was stated to be in the range of 1100–1375°C. Time of holding at a given temperature was equal to 1 h.

The results of measurements of properties of obtained ceramics are shown as characteristic curves in Fig. 3.

The experiments proved that an increase in the temperature of firing of experimental ceramics to 1375°C causes a decrease in the water absorption from 10.5 to 0.4% and opened porosity from 18.7 to 0.7%. Consequently, the apparent density grows. Its maximum value is reached at the temperature of 1350°C and being equal to 1.91 g/cm^3. The dependence of index s on the firing temperature has an extremal character too. A maximum compressive strength was recorded for the samples fired at the temperature of 1350°C (170 MPa). The results of dilatometric measurements showed that the value of CLTE is gradually reduced and reaches a minimum ($2{\cdot}10^{-7}$ deg^{-1}) with an increase in temperature up to 1350°C. A further increase in firing temperature to 1375°C causes both a significant drop in the index σ (to 122 MPa) and a CLTE growth (to $11.8{\cdot}10^{-7}$ deg^{-1}). These changes in properties are accompanied by deformation of samples.

The crystalline phase composition of the obtained ceramic materials is represented only by β-eucryptite as follows from the data of X-ray phase analysis (Fig. 4). The mentioned crystalline phase is formed even at 800°C, which indicates the substantial mineralizing effect of the matrix glass in the process of ceramics firing. The size of crystalline formations gradually increases with the growth of firing temperature to 1350–1375°C. It is evidenced by growing intensity of the main diffraction maximums corresponding to β-eucryptite at $d{\cdot}10^{10}$=4.43; 3.46;

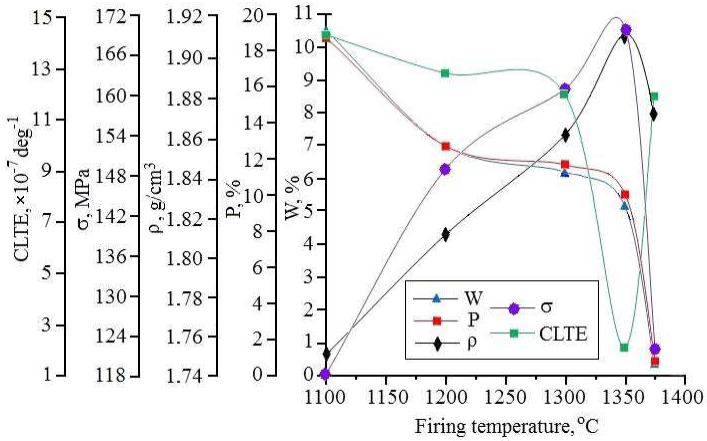

Fig. 3. Dependences of physical and technical parameters of eucryptite ceramics on the firing temperature

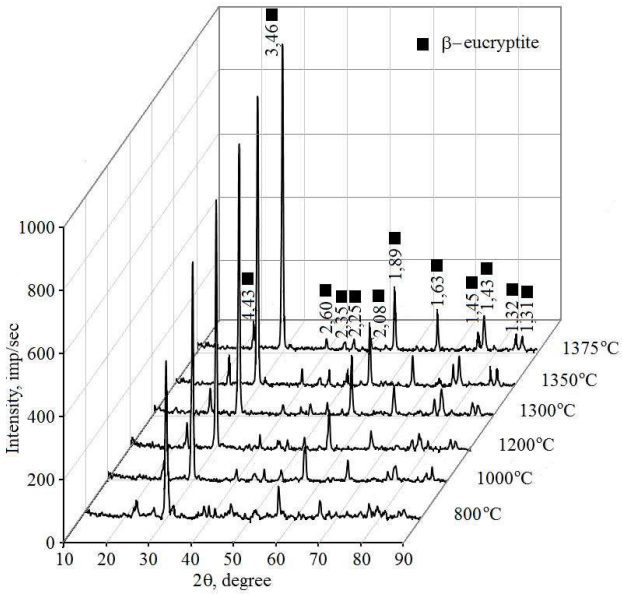

Fig. 4. X-ray diffraction patterns of eucryptite ceramics fired at different temperatures

1.89; and 1.63 m.

Thus, the firing temperature of 1350°C seems to be the most optimal one to achieve a complex of improved physical and technical parameters of the eucryptite ceramics. In connection with this, further experimental studies were aimed at identifying the effect of holding time at the given temperature on the microstructure and properties of the eucryptite ceramics. The holding time was varied in the range of 1 to 5 h.

Examination of the physicotechnical parameters of ceramic samples fired at 1350°C showed (Fig. 5) that the water absorption and opened porosity decreased with increasing holding time from 1 h to 3 h and equaled to 3.4% and 5.6%, respectively. The subsequent increase in holding time (to 5 h) is impractical because it causes a significant increase in W and P values. At the same time, a noticeable reduction is recorded for density (to 1.67 g/cm³) and compressive strength (to 120 MPa).

Change in holding time also has a significant effect on the CLTE of the experimental ceramics (Fig. 6). With an increase in duration of heat treatment at maximum temperature of 1350°C (up to 3–5 h), the CLTE coefficient shifts to the direction of negative values ($-13.1 \cdot 10^{-7}$ deg^{-1} and $-47.3 \cdot 10^{-7}$ deg^{-1}).

This variation in properties of the eucryptite ceramics is defined by changes in its microstructure. The results of raster electron microscopy showed (Fig. 7, a), that ceramics fired at 800°C had no dense structure. It was represented mainly by crystals with a size of 0.5 μm or less. Such crystals form separate clusters (aggregates) having a size of about 10 μm.

Microstructure of ceramic samples for which

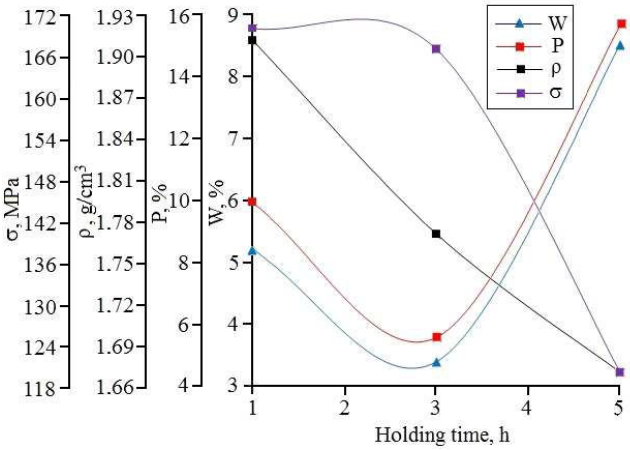

Fig. 5. Dependence of physicotechnical parameters of the eucryptite ceramics on the time of holding at the temperature of 1350°C

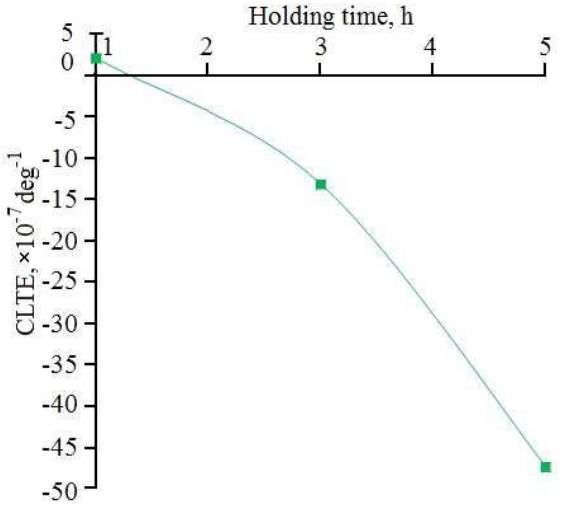

Fig. 6. Dependence of CLTE of the eucryptite ceramics on the time of holding at the temperature of 1350°C

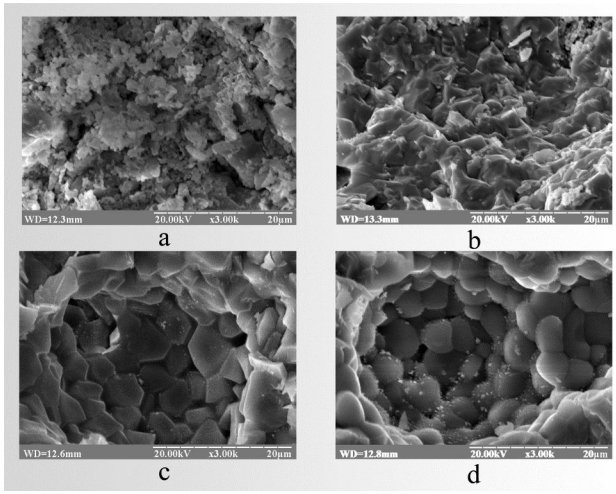

Fig. 7. Microstructure of the eucryptite ceramics fired at 800°C (a) and 1350°C during 1 h (b), 3 h (c) and 5 h (d)

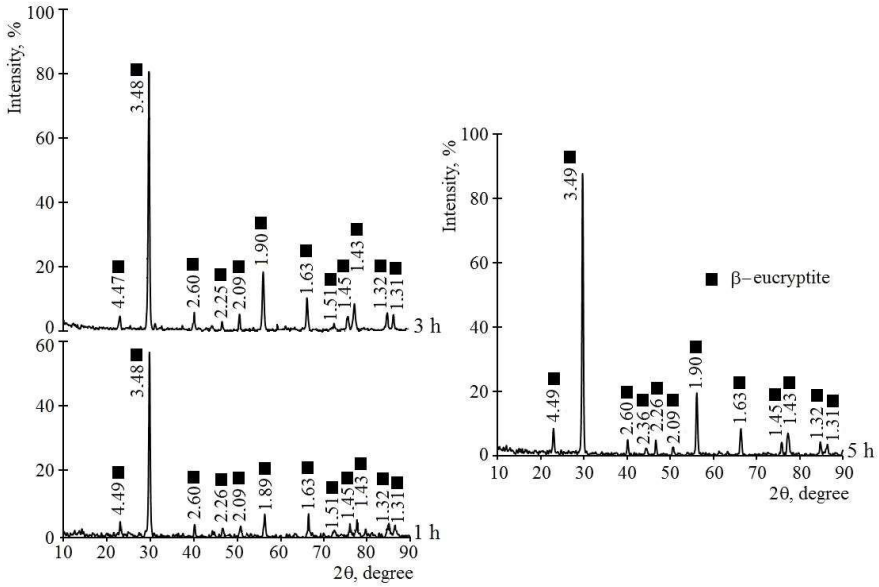

Fig. 8. X-ray diffraction patterns of eucryptite ceramics fired at the temperature of 1350°C at different holding time

holding time at 1350°C is equal to 1 h (Fig. 7,b) is represented by the combination of grains with fragmentary morphology of about 2–4 μm in size. There are also fine-grained aggregates of β-eucryptite on the surface of the sample grains, which are obviously the crystallization products of the parent glass E-1. Samples obtained after 3-hour isothermal time (Fig. 7,c) are characterized by the presence of clearly formed and uniformly distributed prismatic crystals of β-eucryptite of predominantly hexagonal shape. In this case, the crystals increase in size to 4–7 μm, but are not densely placed relative to each other. This feature of the microstructure of experimental ceramics leads to a decrease in its density to 1.77 g/cm^3 (Fig. 5).

The data of electron microscope investigations also agrees with X-ray diffraction analysis results (Fig. 8). With an increase in isothermal time at the temperature of 1350°C from 1 h to 3–5 h, a significant growth of the intensity of main diffraction maximums was observed, these being responsible for β-eucryptite (d·10^{10}=4.49; 3.49; 1.90; and 1.63 m).

The micrograph of the ceramic sample obtained after 5 h holding show (Fig. 7,d) that the shape of crystals of the eucryptite phase is approaches to a spherical one. However, this fact does not provide the formation of dense microstructure of the material. Formation of rather large channels of tunnel type with the lateral size of 15–30 μm is detected, as

shown in Fig. 9.

Therefore, to achieve the complex of enhanced physicotechnical parameters, it is appropriate to increase the isothermal time of the eucryptite ceramics fired at 1350°C up to 3 h. For these ceramics, the dielectric constant ε and the dielectric loss tangent tgδ were determined, which at the frequency of 10^{10} Hz and temperature of 20°C were equal to 7.8 and 0.01, respectively. Low values of ε and tgδ indicate that the developed ceramic can be used as a dielectric material. It is also characterized by a high thermal resistance (1050°C).

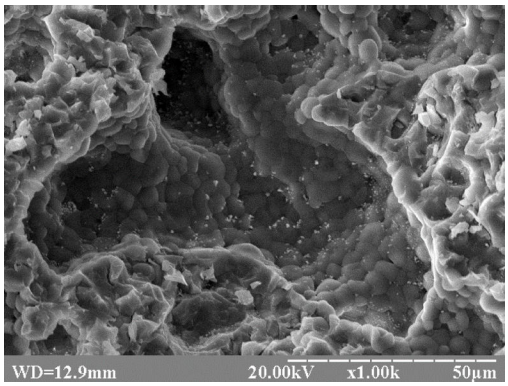

Fig. 9. Microstructure of the eucryptite ceramic fired at the temperature of 1350°C during 5 h

Conclusions

Heat-resistant ceramics of β-eucryptite composition was synthesized as a result of theoretical and experimental studies. Taking into account the calculated data about eutectics composition and temperature of their melting, comparatively low-melting glass was developed in the system $Li_2O–Al_2O_3–SiO_2$ (with the melting temperature of 1250°C). Its role consists in the intensification of processes connected with formation of the crystalline phase of β-eucryptite and sintering of the ceramic material as a whole. Based on the results of experimental studies, we concluded that the time and temperature of sintering of ceramics directly determine its microstructure and physicotechnical properties. As a consequence, at the temperature of 1350°C for 3 h isothermal time, the eucryptite ceramics with the complex of high physicotechnical parameters (σ=167 MPa, $CLTE_{20-400^0C}$ = $=-13.1\cdot10^{-7}$ deg^{-1}, heat resistance of 1050°C, ε=7.8 and tgδ=0.01) were obtained. Furthermore, β-eucryptite phase is formed as distinct prismatic crystals of hexagonal shape of 4–7 μm in size.

REFERENCES

1. *Zanotto E.D.* A bright future for glass-ceramics // Am. Ceram. Soc. Bull. – 2010. – Vol.89. – No. 8. – P.19-27.

2. *Pivinsky Yu.E., Suzdaltsev E.I.* Kvartsevaya keramika i ogneupory. – M.: Teploenergetik, 2008. – 458 p.

3. *Zaychuk A.V., Amelina A.A.* Doslidzhennya shlyakhiv pidvyshchennya fizyko-tekhnichnykh pokaznykiv kvartsovoyi keramiky // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2017. – No. 6. – P.63-67.

4. *Quartz* ceramics modified by nanodispersed silica additive / *Khomenko E.S., Zaichuk A.V., Karasik E.V., Kunitsa A.A.* // Funct. Mater. – 2018. – Vol.25. – No. 3. – P.613-618.

5. *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.

6. *Radio-transparent* ceramic materials of spodumene-cordierite composition / Zaichuk A.V., Amelina A.A., Karasik Y.V., Khomenko Y.S., Lementareva V.A., Saltykov D.Yu. // Funct. Mater. – 2019. – Vol.26. – No. 1. – P.174-181.

7. *Particulars* of a reactive interaction in the composite mixture of glass $0.5MgO\cdot0.2BaO\cdot0.3B_2O_3$ – kaolin / Fomenko G.V., Nosenko A.V., Goleus V.I., Il'chenko N.Yu., Amelina A.A. // Glass Ceram. – 2018. – Vol.74. – P.316-318.

8. *Sebastian M.T., Ubic R., Jantunen H.* Low-loss dielectric ceramic materials and their properties // Int. Mater. Rev. – 2015. – Vol.60. – No. 7. – P.392-412.

9. *Optimization* of the compositions area of radiotransparent ceramic in the $SrO–Al_2O_3–SiO_2$ system / Lisachuk G.V., Kryvobok R.V., Dajneko K.B., et al. // Przeglad Elektrotechniczny. – 2017. – Vol.93. – No. 3. – P.79-82.

10. *Microstructure* and properties of $Li_2O–Al_2O_3–SiO_2–P_2O_5$ glass-ceramics / Xiao Z., Zhou J., Wang Y., Luo M. // Open Mater. Sci. J. – 2011. – No. 5. – P.45-50.

11 *Smal K.V., Spiridonov Yu.A., Chakvetadze D.K.* Issledovanie vliyaniya tekhnologicheskikh parametrov i rezhimov na sintez β-evkriptita // Adv. Chem. Chem. Technol. – 2016. – Vol.30. – No. 7. – P.107-109.

12. *Khamitsaev A.S.* Teplofizicheskie kharakteristiki i zavisimost' svoistv konstruktsionnoi keramiki ot temperatury // Aerosp. Eng. Technol. –2004. – Vol.5. – No. 13. – P.42-53.

13 *O kristallofazovom* sostave litievo-alyumosilikatnoi steklokeramiki s reaktsionno-formiruemoi strukturoi / Goleus V.I., Nosenko A.V., Ilchenko N.Yu. // Bulletin of the Kharkov State Polytechnic University. – 1999. – No. 34. – P.61-64.

14. *Diagrammy* sostoyaniya silikatnykh sistem: spravochnik / Toropov N.A., Barzakovsky V.P., Lapin V.V., Kutseva N.N., Boykova A.I. – L.: Nauka, 1972.

Received 06.01.2020

ТЕРМОСТІЙКА КЕРАМІКА β-ЕВКРИПТИТОВОГО СКЛАДУ: ОСОБЛИВОСТІ ОДЕРЖАННЯ, МІКРОСТРУКТУРА ТА ВЛАСТИВОСТІ

О.В. Зайчук, О.А. Амеліна, О.В. Хоменко, О.С. Баскевич, Ю.Р. Калішенко

В даній роботі була синтезована термостійка кераміка β-евкриптитового складу. При цьому комбінували метод керамічної технології з принципом реакційного формування структури матеріалу. З урахуванням розрахункових даних про склад евтектики і температуру її плавлення в подвійних системах $Li_2O{\cdot}2SiO_2{-}Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ і $Li_2O{\cdot}2SiO_2{-}Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ розроблено відносно легкоплавке скло в системі $Li_2O{-}Al_2O_3{-}SiO_2$ (температура варіння 1250°С). Його роль в складі композиції полягає в інтенсифікації процесів, які пов'язані з формуванням кристалічної фази β-евкриптиту і зі спіканням керамічного матеріалу в цілому. На підставі результатів експериментальних досліджень зроблено висновок про те, що тривалість і температура спікання кераміки безпосередньо визначають її мікроструктуру і фізико-технічні властивості. Для досягнення комплексу найбільш високих показників випал евкриптитової кераміки необхідно проводити при температурі 1350°С з ізотермічним витримуванням протягом 3 год. При цьому β-евкриптитова фаза формується у вигляді чітких призматичних кристалів гексагональної форми розміром 4–7 мкм. Розроблений склад евкриптитової кераміки дозволяє одержувати вироби або окремі елементи різної складності форм, значно знижуючи при цьому кількість браку.

Ключові слова: β-евкриптит, термостійка кераміка, фазовий склад, мікроструктура, властивості.

HEAT-RESISTANT CERAMICS OF β-EUCRYPTITE COMPOSITION: PECULIARITIES OF PRODUCTION, MICROSTRUCTURE AND PROPERTIES

A.V. Zaichuk *, A.A. Amelina, Y.S. Khomenko, A.S. Baskevich, Y.R. Kalishenko

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

* **e-mail: zaychuk_av@ukr.net**

Heat-resistant ceramics of β-eucryptite composition was synthesized in the current work. To this end, the method of ceramics production was combined with the principle of reactive formation of the material structure. Taking into account the calculated data about the compositions of eutectics and temperature of their melting in the specific binary systems $Li_2O{\cdot}2SiO_2{-}Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ and $Li_2O{\cdot}2SiO_2{-}Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, a comparatively low-melting glass was developed in the system $Li_2O{-}Al_2O_3{-}SiO_2$ (with a melting temperature of 1250°C). Its function in the composition consists in the intensification of the processes associated with the formation of the crystalline phase of β-eucryptite and sintering of the ceramic material as a whole. Based on the results of experimental study, we concluded that the duration and temperature of sintering of ceramics directly determine its microstructure and physicotechnical properties. In order to achieve the complex of the highest indices, the firing of eucryptite ceramics should be performed at the temperature of 1350°C with the isothermal time of 3 h. β-eucryptite phase is formed as the distinct prismatic crystals of hexagonal shape with a size of 4–7 μm. The developed composition of eucryptite ceramics allows obtaining the products or individual elements with varying complexity of shapes, which significantly reduces the amount of rejects.

Keywords: β-eucryptite; heat-resistant ceramics; phase composition; microstructure; properties.

REFERENCES

1. Zanotto E.D. A bright future for glass-ceramics. *American Ceramic Society Bulletin*, 2010, vol. 89, no. 8, pp. 19-27.

2. Pivinsky Yu.E., Suzdaltsev E.I. *Kvartsevaya keramika i ogneupory.* [Quartz ceramics and refractories]. Teploenergetik Publishers, Moscow, 2008. 458 p. (*in Russian*).

3. Zaychuk A.V., Amelina A.A. Doslidzhennya shlyakhiv pidvyshchennya fizyko-tekhnichnykh pokaznykiv kvartsovoyi keramiky [Search for the ways to improve the physical and technical parameters of quartz ceramics]. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2017, no. 6, pp. 63-67. (*in Ukrainian*).

4. *Khomenko E.S., Zaichuk A.V., Karasik E.V., Kunitsa A.A.* Quartz ceramics modified by nanodispersed silica additive. *Functional Materials*, 2018, vol. 25, no. 3, pp. 613-618.

5. Shamsudin Z., Hodzic A., Soutis C., Hand R.J., Hayes S.A., Bond I.P. Characterisation of thermo-mechanical properties of $MgO{-}Al_2O_3{-}SiO_2$ glass ceramic with different heat treatment temperatures. *Journal of Materials Science*, 2011, vol. 46, pp. 5822-5829.

6. Zaichuk A.V., Amelina A.A., Karasik Y.V., Khomenko Y.S., Lementareva V.A., Saltykov D.Yu. Radio-transparent ceramic materials of spodumene-cordierite composition. *Functional Materials*, 2019, vol. 26, no. 1, pp. 174-181.

7. Fomenko G.V., Nosenko A.V., Goleus V.I., Il'chenko N.Yu., Amelina A.A. Particulars of a reactive interaction in the composite mixture of glass $0.5MgO{\cdot}0.2BaO{\cdot}0.3B_2O_3$ – kaolin. *Glass and Ceramics*, 2018, vol. 74, pp. 316-318.

8. Sebastian M.T., Ubic R., Jantunen H. Low-loss dielectric ceramic materials and their properties. *International Materials Reviews*, 2015, vol. 60, pp. 392-412.

9. Lisachuk G.V., Kryvobok R.V., Dajneko K.B., Zakharov A.V., Fedorenko E.Y., Prytkina M.S., Chefranov Y.V., Annabaev A., Kisala P., Mussabekov K., Romaniuk R. Optimization of the compositions area of radiotransparent ceramic in the $SrO{-}Al_2O_3{-}SiO_2$ system. *Przeglad Elektrotechniczny*, 2017, vol. 93, no. 3, pp. 79-82.

10. Xiao Z., Zhou J., Wang Y., Luo M. Microstructure and properties of $Li_2O{-}Al_2O_3{-}SiO_2{-}P_2O_5$ glass-ceramics. *The Open Materials Science Journal*, 2011, vol. 5, pp. 45-50.

11. Smal K.V., Spiridonov Yu.A., Chakvetadze D.K. Issledovanie vliyaniya tekhnologicheskikh parametrov i rezhimov na sintez β-evkriptita [Investigation of the influence of technological parameters and modes on the synthesis of β-eucriptite]. *Advances in Chemistry and Chemical Technology,* 2016, vol. 30, no. 7, pp. 107-109. (*in Russian*).

12. Khamitsaev A.S. Teplofizicheskie kharakteristiki i zavisimost' svoistv konstruktsionnoi keramiki ot temperatury [Thermophysical characteristics and the dependence of the properties of structural ceramics on temperature]. *Aerospace Engineering and Technology*, 2004, vol. 5, no. 13, pp. 42-53. (*in Russian*).

13. Goleus V.I., Nosenko A.V., Ilchenko N.Yu. O kristallofazovom sostave litievo-alyumosilikatnoi steklokeramiki s reaktsionno-formiruemoi strukturoi [On the crystal phase composition of lithium aluminosilicate glass ceramics with a reaction-formed structure]. *Bulletin of the Kharkov State Polytechnic University*, 1999, no. 34, pp. 61-64. (*in Russian*).

14. Toropov N.A., Barzakovsky V.P., Lapin V.V., Kutseva N.N., Boykova A.I., Diagrammy sostoyaniya silikatnykh sistem: spravochnik [*Diagrams of the state of silicate systems: a reference book*]. Nauka, Leningrad, 1972. (*in Russian*).