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GLASS FORMATION AND PROPERTIES OF GLASSES IN $MgO-BaO-B_2O_3$ SYSTEM

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Abstract. Glass formation in poorly boric field of $MgO-BaO-B_2O_3$ system (content of $B_2O_3 \leq 50$ mol %) has been studied. Interconnection between the properties of glasses (density, heat expansion, softening temperature, specific volume resistance) and their chemical composition has been established.

Keywords: cordierite, glassceramics, crystallization, celsian, reaction of structure formation.

1. Introduction

The glassceramic materials of cordierite composition are characterized by high dielectric characteristics due to which they are widely used for fabrication of different parts for electrotechnical purpose [1]. However, technology of their production under classical glass-ceramic technology is exceptionally power-consuming. The temperature of boiling of the basic glasses in $MgO-Al_2O_3-SiO_2$ system amounts to 1823–1923 K, the time of their crystallization reaches tens of hours.

It is possible to achieve the significant decrease of energy consumption at production of glassceramic materials containing alkaline by the use of ceramic technology in combination with the reaction of structure formation (RSF) [2].

At the same time such technology is effective for production of glassceramics of cordierite composition because the minimal temperature of liquids in $MgO-SiO_2$ binary system amounts to 1815 K due to which the temperature of boiling of the basic glass remains virtually unchanged.

A. Nosenko *et al.* [3] shows that for glassceramics of celsian composition obtaining from RSF the poorly boric glasses in $BaO-B_2O_3$ system can be used as the basic ones. The temperature of liquids in $MgO-B_2O_3$ system is much lower than in $MgO-SiO_2$ system, so we can concede that glassceramic materials can be also obtained from RSF on the basis of glasses of the specified system using the energy saving technology.

However, the field of glass formation in $MgO-B_2O_3$ system is very narrow and limited by the content of magnesium oxide that is not more than 45–50 mol % [4]. To expand the field of glass formation and decrease of crystallization ability of magnesium borate glass it is reasonable to introduce barium oxide into their composition (effect of "polycomponent structure" [5]). In addition, the glasses of such composition shows the "poly alkaline-earth effect" described in Ref. [6].

The glass formation and properties of glasses in $MgO-BaO-B_2O_3$ system are explored insufficiently [7-9]. The diagram of the specified system condition in available literature is also absent and the partial diagram of "pseudobinary" system $Mg(BO_2)_2-Ba(BO_2)_2$ condition, specified in [10], is less informative.

The aim of this work is the research of glass formation and properties of glass in poorly boric field of $MgO-BaO-B_2O_3$ system (content of $B_2O_3 \leq 50$ mol %) for the selection of the basic glasses for fabrication on their basis glassceramics of cordierite composition from RSF.

2. Experimental

The following raw materials were used at implementation of experimental research: barium carbonate and magnesium oxide (of commercial purity), and boric acid (pro analysis). The mixtures were compounded per 50 g of glass.

Boiling of glass in $MgO-BaO-B_2O_3$ system with the content of $B_2O_3 \leq 50$ mol % was carried out in corundum crucibles in a silicon carbide furnace at the maximum temperature of 1573 K, time of holding at this temperature was equal to 0.5 h. The readymade melts were made in metal moulds.

The heat expansion of materials in temperature interval of 293–573 K was determined using the automatic quartz dilatometer DKV-5A. The accuracy of measurement $\Delta\alpha = \pm 2\cdot10^{-7}$ 1/grad.

The density of glasses was determined by the method of hydrostatic weighing in toluene, the accuracy of measurement $\Delta d = \pm 0.01$ g/cm^3.

Specific volume resistance of glasses in MgO-BaO-B_2O_3 system was determined using the teraohmmeter E6-13A. The samples are defectless glass plates with electrodes made of heat-resistant graphite MPG-6.

3. Results and Discussion

Calculation of the liquids lines in xMgO·B_2O_3-yBaO·B_2O_3 "pseudobinary" systems (x and y from 1 to 3), carried out by the method of Epstein-Howland [11] shows that eutectics with the melting temperatures of ~ 1265 to 1548 K (Table 1, Fig. 1a) are contained in poorly boric field of MgO-BaO-B_2O_3 system. So it is possible to admit that at relatively low temperatures of synthesis in the specified field of MgO-BaO-B_2O_3 system the glasses with the low content of boric oxide can be obtained.

To check the calculated data the glass formation in a poorly boric field of MgO-BaO-B_2O_3 system was researched (content of $B_2O_3 \leq 50$ mol %). The temperature of glasses synthesis did not exceed 1573 K.

The compositions of melts creating the glasses under above conditions and the results of visual assessment of glass formation borders in the researched field of MgO-BaO-B_2O_3 system are represented in Table 2 and Fig. 1b.

The physical and chemical properties were researched for all synthesized glasses, namely, density, heat expansion, softening temperature and specific volume resistance.

Processing of the obtained experimental data using the method of multiple correlation allowed to obtain linear equations of regression of the type $Y = b_0 + \Sigma(b_i \cdot x_i)$ and $Y = \Sigma(a_i \cdot x_i)$, where $a_i = b_0 + b_i$. The equations well describe the interconnection of glasses density in the researched field of MgO-BaO-B_2O_3 system with the chemical composition of glasses in mol % ($R = 0.996$; $\Delta d = \pm 0.036$ g/cm^3):

$$d = 0.031\cdot C_{MgO} + 0.061\cdot C_{BaO} + 0.023\cdot C_{B2O3},\ \text{g/cm}^3 \quad (1)$$

$$d = 5.646 - 0.026\cdot C_{MgO} + 0.00498\cdot C_{BaO} - 0.034\cdot C_{B2O3},\ \text{g/cm}^3 \quad (2)$$

Table 1

Calculated compositions and temperature of labels melting

No.	"Pseudobinary" system	T_{melt}, K	Contents of oxides, mol %		
			MgO	BaO	B_2O_3
1	3MgO·B_2O_3-3BaOB$_2$O$_3$	1548	40.13	34.87	25.00
2	2MgO·B_2O_3-BaO·B_2O_3	1336	16.70	38.15	45.15
3	3MgO·B_2O_3-BaO·B_2O_3	1349	13.14	41.24	45.62
4	2MgO·B_2O_3-3BaO·B_2O_3	1527	35.57	34.98	29.45
5	MgO·B_2O_3-3BaO·B_2O_3	1389	39.21	16.19	44.60
6	MgO·B_2O_3-BaO·B_2O_3	1265	21.75	28.25	50.00

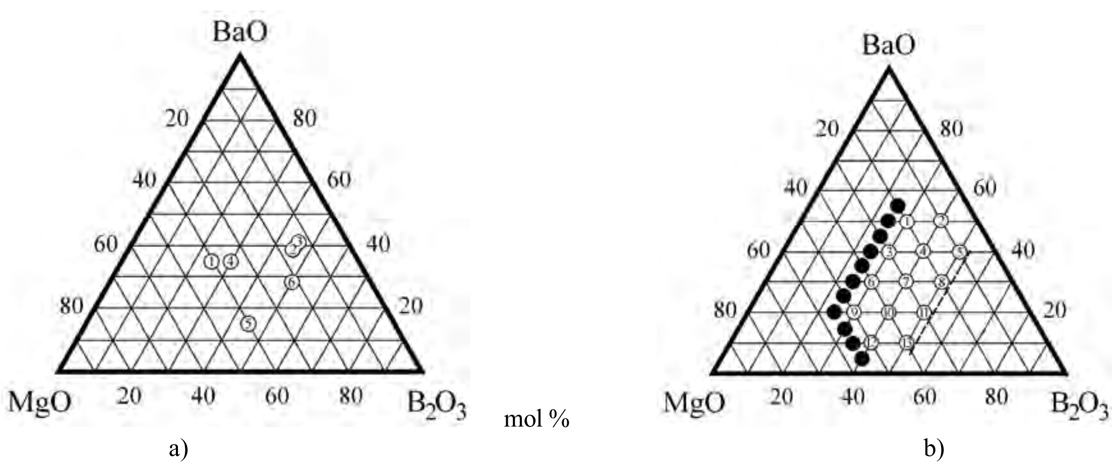

Fig. 1. Calculated compositions of eutectics obtained by the method of Epstein-Howland (a), and glass formation (1573 K, 0.5 h) in a poorly boric field of MgO-BaO-B_2O_3 system (contents $B_2O_3 \leq 50$ mol %) (b)

Table 2

Chemical composition of glass-forming melts and the properties of glasses in the researched field of MgO-BaO-B_2O_3 system

No.	Chemical composition of glass						Properties of glass			
	Mol %			Mas %			Density d, g/cm^3	TCLE, $\alpha \cdot 10^7$, 1/grad	T_s, K	lgρ_V, Ohm·cm (573 K)
	MgO	BaO	B_2O_3	MgO	BaO	B_2O_3				
1	20	50	30	7.63	72.59	19.78	4.38	127.9	493.5	9.86
2	10	50	40	3.71	70.63	25.66	4.29	117.4	521.0	11.13
3	30	40	30	12.82	65.03	22.15	3.97	119.3	501.5	9.60
4	20	40	40	8.29	63.07	28.64	3.98	108.1	543.0	11.34
5	10	40	50	4.02	61.22	34.75	3.89	97.6	570.5	12.61
6	40	30	30	19.43	55.41	25.16	3.75	111.6	525.5	10.46
7	30	30	40	14.07	53.52	32.41	3.67	96.2	571.0	11.22
8	20	30	50	9.07	51.76	39.17	3.60	88.2	597.0	12.80
9	50	20	30	28.11	42.76	29.13	3.48	103.1	574.5	10.23
10	40	20	40	21.60	41.08	37.31	3.42	86.8	598.5	12.40
11	30	20	50	15.59	39.53	44.88	3.30	77.1	616.5	12.90
12	50	10	40	31.82	24.21	43.97	3.05	80.4	611.0	11.97
13	40	10	50	24.33	23.14	52.53	2.91	66.0	641.5	12.82

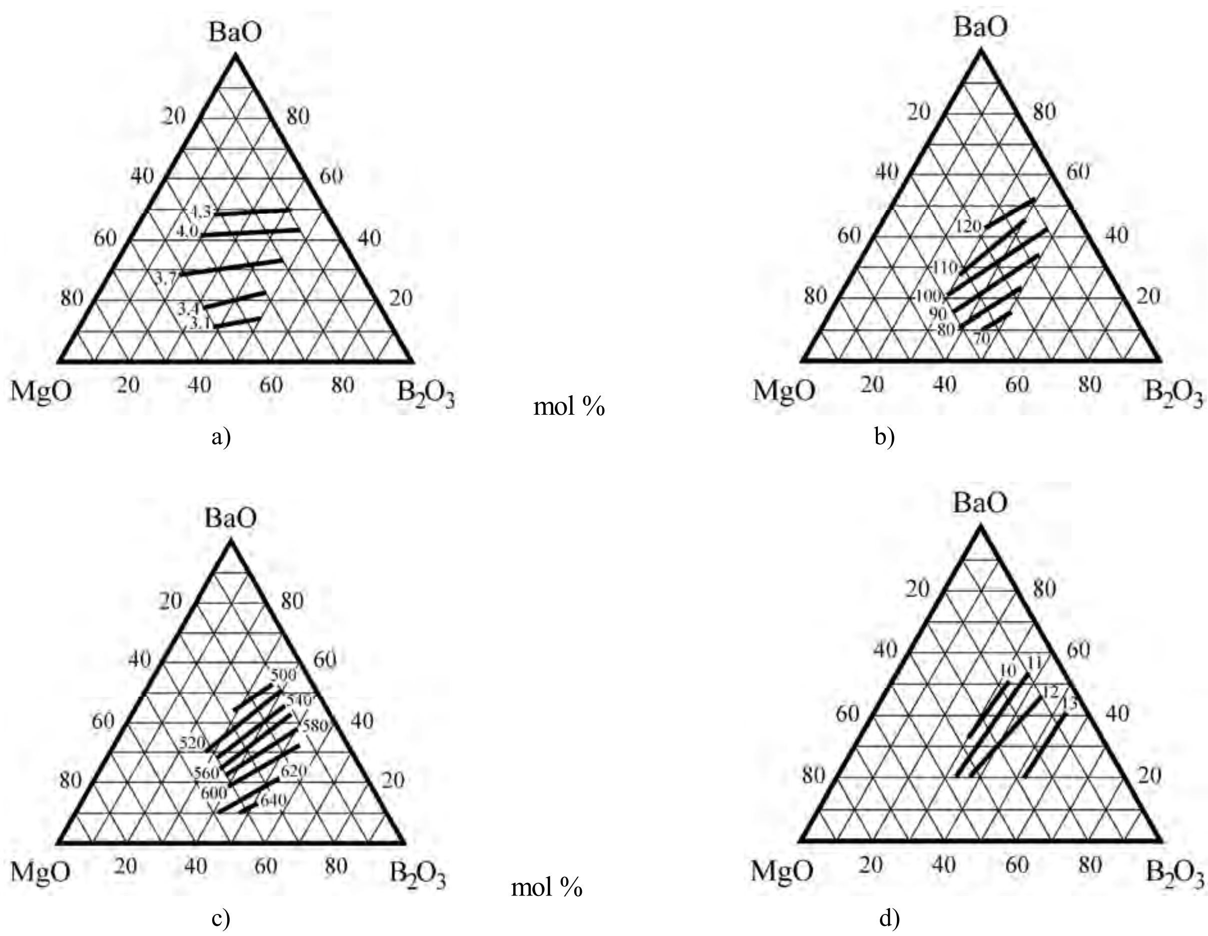

Fig. 2. Dependence of glasses properties in the researched field of MgO-BaO-B_2O_3 system (contents of $B_2O_3 \leq 50$ mol %) of their chemical composition: density d, g/cm^3 (a); TCLE $\alpha \cdot 10^7$, 1/grad (b); softening temperature T_s, °C (c) and logarithm of specific volume resistance at 573 K, Ohm·cm (d)

Analysis of Eqs. (1) and (2) shows that the glasses density in the researched field (contents of B_2O_3 is 30–50 mol %) is well surrendered to the additivity rule. Coefficients before factors in Eq. (1) can be considered as partial coefficients of density for the glass components in the researched field of compositions.

It is established experimentally that TCLE of glasses varies within $(66–128)\cdot 10^{-7}$ 1/grad in the researched field of MgO-BaO-B_2O_3 system. As a result of the obtained data processing the models of the type $Y = b_0 + \Sigma(b_i \cdot x_i)$ and $Y = \Sigma(a_i \cdot x_i)$, where $a_i = b_0 + b_i$, were developed. They excellently describe the interconnection of glasses TCLE with their chemical composition in mol % ($R = 0.997$; $\Delta\alpha = \pm 1.445\cdot 10^{-7}$, 1/degree):

$$\alpha\cdot 10^7 = 1.176\cdot C_{MgO} + 2.123\cdot C_{BaO} - 0.013 C_{B2O3}, \text{ 1/deg} \quad (3)$$

$$\alpha\cdot 10^7 = 71.356 + 0.462\cdot C_{MgO} + 1.409\cdot C_{BaO} - 0.727 C_{B2O3}, \text{ 1/deg} \quad (4)$$

It is established that heat expansion of the researched glasses is primarily determined by contents of barium oxide in their compositions and grows with the increase of content.

The softening temperature (T_s) of the researched glasses is within 767–915 K and increases linearly with the increase of glasses TCLE. Equation T_s = 813.7 – 2.507TCLE describes the interconnection between glasses TCLE and their softening temperature (R = -0.986).

Dependence of T_s of glasses on their chemical composition in mol % is described well enough by linear Eqs. (5) and (6) ($R = 0.989$; $\Delta T_s = \pm 6.74$ K):

$$T_s = 5.226\cdot C_{MgO} + 2.80\cdot C_{BaO} + 8.144\cdot C_{B2O3}, \text{ K} \quad (5)$$

$$T_s = 562.212 - 0.034\cdot C_{MgO} + 2.461\cdot C_{BaO} + 2.879\cdot C_{B2O3}, \text{ K} \quad (6)$$

The researched glasses are characterized by very high dielectric characteristics, their specific volume resistance at 573 K varies within $10^{9.6}–10^{12.9}$ Ohm·cm. The interconnection between logarithm of specific volume resistance of glasses (573 K) and their chemical composition is described by linear dependences (7) and (8) well enough ($R = 0.97$; $\Delta \lg\rho_V = \pm 0.276$ Ohm·cm):

$$\lg\rho_V = 0.071\cdot C_{MgO} + 0.05\cdot C_{BaO} + 0.198\cdot C_{B2O3}, \text{ Ohm·cm} \quad (7)$$

$$\lg\rho_V = 7.937 - 0.008683\cdot C_{MgO} - 0.029\cdot C_{BaO} + 0.118\cdot C_{B2O3}, \text{ Ohm·cm} \quad (8)$$

It is established that specific volume resistance of glasses increases with the increase of boron oxide contents. At the constant contents of B_2O_3 the replacement of magnesium oxide with barium oxide in compositions of glasses has a little influence on the change of their specific volume resistance.

The results of determination of glasses properties are represented in the form of isolines applied on concentration triangles (Fig. 2).

Crystallization capacity of the obtained glasses was researched by the methods of mass crystallization and differential thermal analysis (DTA). It is established that virtually all glasses containing less than 50 mol % of boric oxide are characterized by increased crystallization capacity. The thermogram of glass composition $0.5Mg\cdot 0.2BaO\cdot 0.3B_2O_3$ (9) containing maximum amount of magnesium oxide and minimal amount of boric anhydride is represented in Fig. 3.

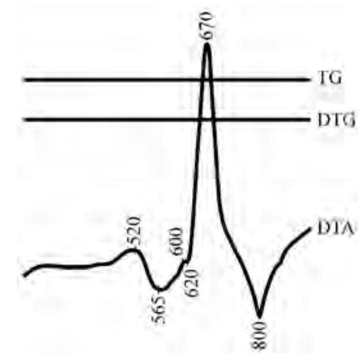

Fig. 3. Thermogram of the glass powder of composition $0.5MgO\cdot 0.2BaO\cdot 0.3B_2O_3$ (Table 2, No. 9)

4. Conclusions

As a result of complex research of the glasses properties in a poorly boric field of MgO-BaO-B_2O_3 system for the following research the recommended composition $0.5Mg\cdot 0.2BaO\cdot 0.3B_2O_3$ is suitable for use as the basic at production of glassceramics of cordierite composition from RSF.

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СКЛОУТВОРЕННЯ Й ВЛАСТИВОСТІ СТЕКОЛ У СИСТЕМІ MgO-BaO-B_2O_3

Анотація. *Досліджено склоутворення в малоборній області системи MgO-BaO-B_2O_3 (вміст $B_2O_3 \leq 50$ мол. %). Встановлено взаємозв'язок між властивостями стекол (щільність, теплове розширення, температура початку розм'якшення, питомий об'ємний опір) та їх хімічним складом.*

Ключові слова: *кордієрит, склокераміка, кристалізація, цельзиан, реакційне формування структури.*