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I. A. Levitskii, L. F. Papko, M. V. Dyadenko
Belarusian State Technological University

GLASS-CERAMIC CEMENT FOR VACUUM-TIGHT JOINT

Synthesis of fusible glass of ZnO – PbO – B_2O_3 system at the maintenance of components, wt %: B_2O_3 – 10–45; ZnO – 5–40; PbO – 50–85 is carried out. It was established that stability of a vitreous state is defined by a ratio of ZnO / (PbO + B_2O_3) in the glass composition.

Dependences of thermal and rheological characteristics of glass systems of ZnO – PbO – B_2O_3 from a chemical composition are studied. The increase in the maintenance of B_2O_3 superseded by PbO causes the essential growth of viscosity and decrease of its gradient. The components able to reduce viscosity are arranged in the following way: B_2O_3→ZnO→PbO.

By the results of research of glass rheological properties of ZnO – PbO – B_2O_3 system, the area of glass compositions with viscosity less than 10^5 Pa · s at a temperature not over 450°C that provides the demanded spreadability indicators is defined. Regulation of indicators of TCLE is reached by creation of compositions glass – a crystal filler. Influence of such crystal filler as zircon, spodumene, cordierite on properties of composite glass-ceramic cement is researched. The target TCLE indexes being equal to (77 ± 1) · 10^{-7} K^{-1} are achieved by the introduction of a spodumene.

The composite glass-ceramic cement, intended for vacuum-tight connections of fiber-optical elements with a metal frame was developed. TCLE indexes of the glass-ceramic cement are equal to 77.2 · 10^{-7} K^{-1}, that coordinates it with TCLE containing a fiber-optical element. Temperature of composite glass-ceramic cement soldering is 450 ± 5°C, temperature of its deformation – 520 ± 5°C.

Key words: glass-ceramic cement, fiber-optics element, low-melting glass, vacuum-tight joint, crystallization, temperature coefficient of linear expansion, viscosity, spreading, mechanical strength.

Introduction. Glass-ceramic cement is widely used to connect the various materials in electronic products. In optoelectronics, it is used as solders for connecting fiber-optics elements with metal frames. The most important properties required for glass-ceramic cement are vacuum-tightness, allowing its use in vacuum electronics; high electrical resistivity; coordination with TCLE with soldering material. Its rheological properties are also important because they must provide materials soldering at low temperatures.

Depending on the behavior of glass-ceramic cement during soldering there are three types of it: glassy, crystallizing and composite ones. Composite glass-ceramic cement includes low-melting glass and the inert filler.

The advantage of crystallizing and composite glass-ceramic cement to low-melting glass is a higher mechanical strength and heat resistance, which provides the possibility of material welding with different indices of TCLE at lower stresses in the junction.

Glass-ceramic cement based on low-melting glasses containing lead and bismuth has obtained a wide practical application as solders. The most low-melting glass solders are made on the basis of glasses of ZnO – PbO – B_2O_3 system. The temperature of the material soldering when using lead-containing glasses is 380–600°C i. e. it can be regulated in a wide range depending on the application [1–3].

Glass-ceramic cement based on low-melting glasses containing bismuth is obtained on the basis of BaO – Bi_2O_3 – B_2O_3 and ZnO – Bi_2O_3 – B_2O_3 systems [4, 5]. However, such glasses can be an alternative to lead containing ones only if it is possible to carry out soldering at temperatures of about 600°C.

Fiber optical elements are produced by sintering multi-core optical fibers, which represent the structure of “light-guiding core – reflective jacket – protection cover”. To eliminate the occurrence of stresses in the fiber optical element while its soldering with metal there must be provided its strict coordination of this indicator with a fiber-optical element, whose coefficient of linear expansion being (77 ± 1) · 10^{-7} K^{-1}. Vacuum-tight structure of the glass-ceramic cement must be formed while firing at a temperature of 450 ± 10°C.

Main part. The system ZnO – PbO – B_2O_3 containing wt %: B_2O_3 – 10–45; ZnO – 5–40;

PbO – 50–85 in a step of 5 wt % has been chosen for the development of low-melting glasses used as a base for glass ceramic cement.

Glass synthesis was carried out in a batch electric furnace at a temperature of 1,000 to 1,100°C. Glass with increased ZnO content has higher synthesis temperatures.

The crystallization ability of glass has been evaluated by gradient method which shows that he stability of the glassy state is determined by the quantitative ratio of ZnO / (PbO + B_2O_3).

Crystallization is typical for glass with mentioned ratio constituting more than 0.20, the crystallization temperature being 480–650°C. Borates of lead and zinc (PbO · $2B_2O_3$ and $Zn(BO_2)_2$) are selected as crystalline phases according to X-ray diffraction. The composition range of non-crystallizing glass comprises by wt %: B_2O_3 – 10–45; ZnO – 5–10; PbO – 50–85.

TCLE data of tested glass determined by means of dilatometer DIL 402 PC "Netzsch" company, vary from $60.5 \cdot 10^{-7}$ K^{-1} to $118 \cdot 10^{-7}$ K^{-1}. Lead oxide content has the decisive effect on these indicators of the tested glasses. Replacing PbO by B_2O_3 causes a more significant decrease in the coefficient of linear expansion than the equivalent replacement of PbO by ZnO.

The use of dilatometry in the study of tested glasses allows to determine not only the TCLE indicators, but the characteristic temperatures, corresponding to specific values of viscosity, i. e. to evaluate the effect of the chemical composition of glass on the low-temperature viscosity.

Fig. 1 shows dilatometric curves of glass with a constant content of zinc oxide equal to 5 wt %. The increase in B_2O_3 content from 15 to 40 wt % used instead of PbO leads to a substantial increase in the glass formation temperature T_g (380 to 470°C). Dilatometric softening temperature of the glass also increases to 100°C.

Data analysis of glass dilatometry with different ratio of B_2O_3, ZnO and PbO reveals the complex nature of dependence of the glass transition temperature and the dilatometric softening point on the composition of the experimental glasses. A regular increase of the glass transition temperature from 318 to 420°C and softening temperature from 335 to 460°C occurs with the decrease in lead oxide content.

The glass transition temperature of tested glasses varies from 305 to 490°C, the proportion of PbO and B_2O_3 in the composition of the glasses having a decisive influence on the indicators of their low temperature viscosity.

Zinc oxide has a more pronounced fluxing effect than boron oxide.

The temperature dependences of the tested glass viscosity in the range of 10^9–10^4 Pa · s have been received with the help of viscometer PPV-1000 of Orton firm by a compression glass-cylinder method.

The increase from 15 to 40 wt % in boron oxide content used instead of PbO, causes a significant increase in viscosity, i. e. the temperature corresponding to the viscosity of 10^5 Pa · s raises from 470 to 575°C (Fig. 2).

Viscosity gradient decreases, the glass becoming "longer".

Increase in the zinc oxide content from 5 to 10 wt % used instead of lead oxide, causes a rise in viscosity index. Viscosity gradient is becoming less pronounced during plastic-liquid glass transition (Fig. 3).

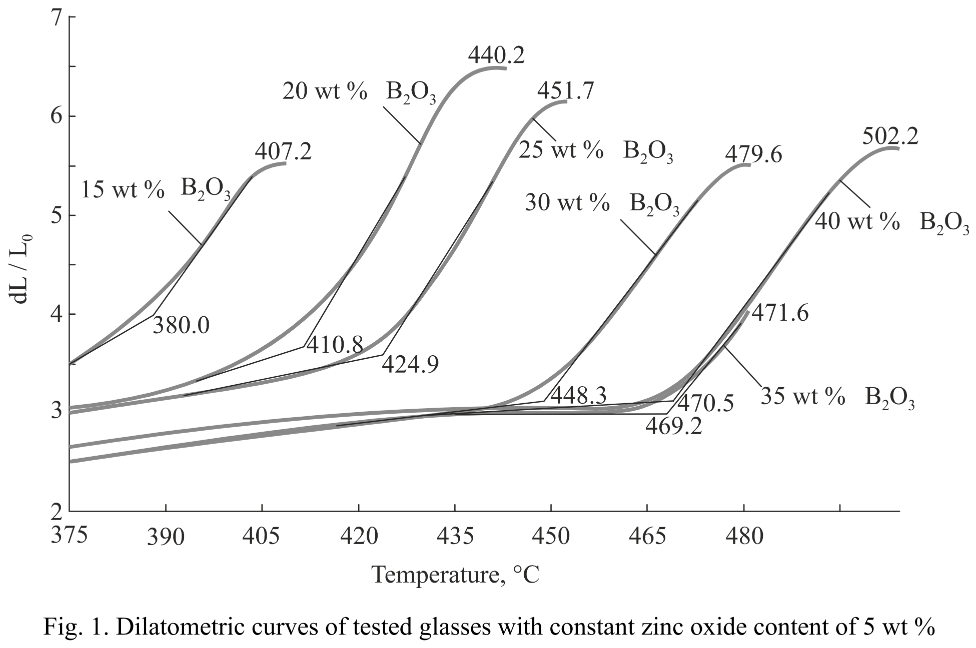


Fig. 1. Dilatometric curves of tested glasses with constant zinc oxide content of 5 wt %

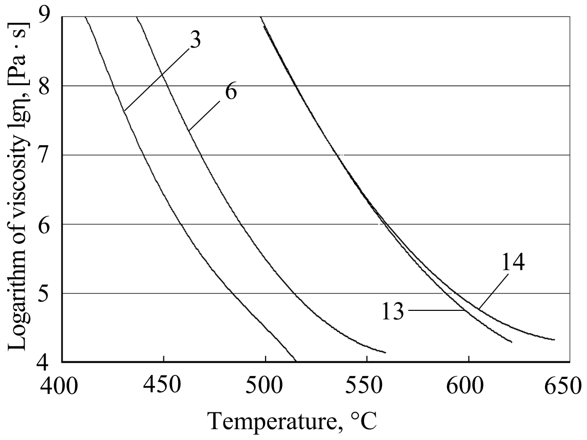
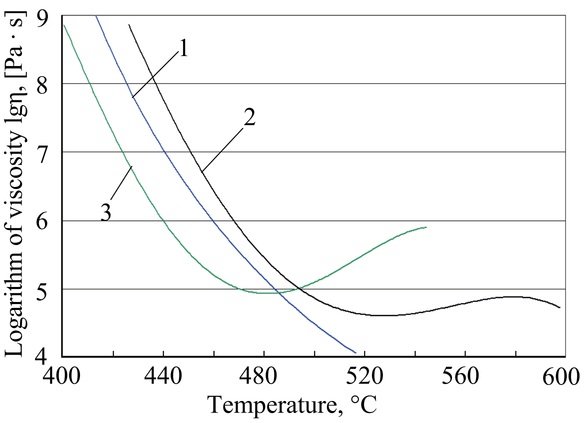


Fig. 2. Temperature dependence of the glass viscosity at constant 5 wt %



The content of ZnO, wt %: 1–5; 2–10; 3–15

Fig. 3. Temperature dependence of the glass viscosity at constant content of B_2O_3, equal to 10 wt %

The peculiarity of the temperature dependence of tested glass viscosity is an increase in this indicator in the samples containing 10 and 15 wt % of ZnO at temperatures above 480°C due to their crystallization.

Substitution B_2O_3 for ZnO leads to an increase in the viscosity in the range of 10^9–10^5 Pa · s in single order.

Crystallization of glass with a zinc oxide content of 10 wt % or more at a temperature above 520°C makes viscosity indices to grow. The viscosity indices of less than 10^5 Pa · s, for the glass studied are achieved at temperature above 490°C.

Thus, the study of the rheological properties of glass in the range of dynamic viscosity coefficient of 10^{12}–10^5 Pa · s has revealed that the forming components are arranged in the following way: $B_2O_3 \rightarrow ZnO \rightarrow PbO$ according to the ability to reduce viscosity. Boron oxide is known as a flux of silicate glasses, i. e. a component actively reducing their viscosity. In the case of the studied lead borate glasses zinc oxide has more pronounced fluxing action. Obviously, it is due to the influence of B_2O_3 on the structure of these glasses.

Lead borate glass was studied by infrared spectroscopy using Fourier IR spectrometer NEXUS to find out the peculiarities of its structure (Fig. 4).

Three main absorption bands at 1,200–1,300, 900–1,050 and 695–700 cm^{-1} appear in all spectra. The absorption band at 1,300 cm^{-1} can be attributed to $[BO_3]$ groups in the plane grids. The presence of absorption peaks at 1,200 cm^{-1} is obviously related to valence vibrations of atoms in bonds between the two groups $[BO_3]$ and $[BO_4]$, i. e. in the links of B^{III}–O–B^{IV}. A weak absorption band at 695–700 cm^{-1} also corresponds to the deformation vibrations of the atoms in the groups $[BO_3]$. Absorption band with maxima at 900–1,030 cm^{-1} in borate glass is associated with the stretching vibrations of the atoms in the groups $[BO_4]$ [6, 7].

The role of glass-former forming the framework structure of the glass is increasing while reducing lead oxide and increasing the content of boron oxide B_2O_3. The emergence of stronger links with the four-coordinated boron in comparison with the strength of the connections in the structural network formed by tetrahedrons $[PbO_4]$ in multi-lead glass causes the growth of viscosity index of glass with a high content of B_2O_3.

Substitution of B_2O_3 for ZnO causes the shift of the maximum absorption in the 1,200–1,300 cm^{-1} in the higher frequency region and the increase in absorption intensity in the region of 900–1,030 cm^{-1}. It can be assumed that an increase in the content of B_2O_3 is differentiated by the type of boron-oxygen groups to form separate structures of the groups $[BO_3]$ and $[BO_4]$. Increasing the share of $[BO_4]$ groups greatly raises a degree of the structure connectivity of borate glass.

The study of thermal and rheological properties of glass of ZnO – PbO – B_2O_3 system has established that glass with lead oxide content of 60–70 wt % and ZnO 20–30 wt % have the closest TCLE indicators to the given ($(77 \pm 1) \cdot 10^{-7}$ K^{-1}). However, with the increase in B_2O_3 and ZnO content glass viscosity significantly increases, which does not allow to take them as the basis for tight solders at the firing temperature of 450°C. Obtaining a composite material based on the test fusible glass is the solution of the problem on the development of glass-ceramic cement with a given TCLE index to connect fiber-optical elements with a metal frame. Therefore, for further research we have chosen the region of compositions of non-crystallizing glass comprising, by wt %: B_2O_3 – 10–15; ZnO – 5–12.5; PbO – 75–85. Glass viscosity indicators in the temperature range of 450–500°C constitute not less than 10^5–10^6 Pa · s, while for tight junction formation viscosity at the firing temperature should be 10^4–10^5 Pa · s.

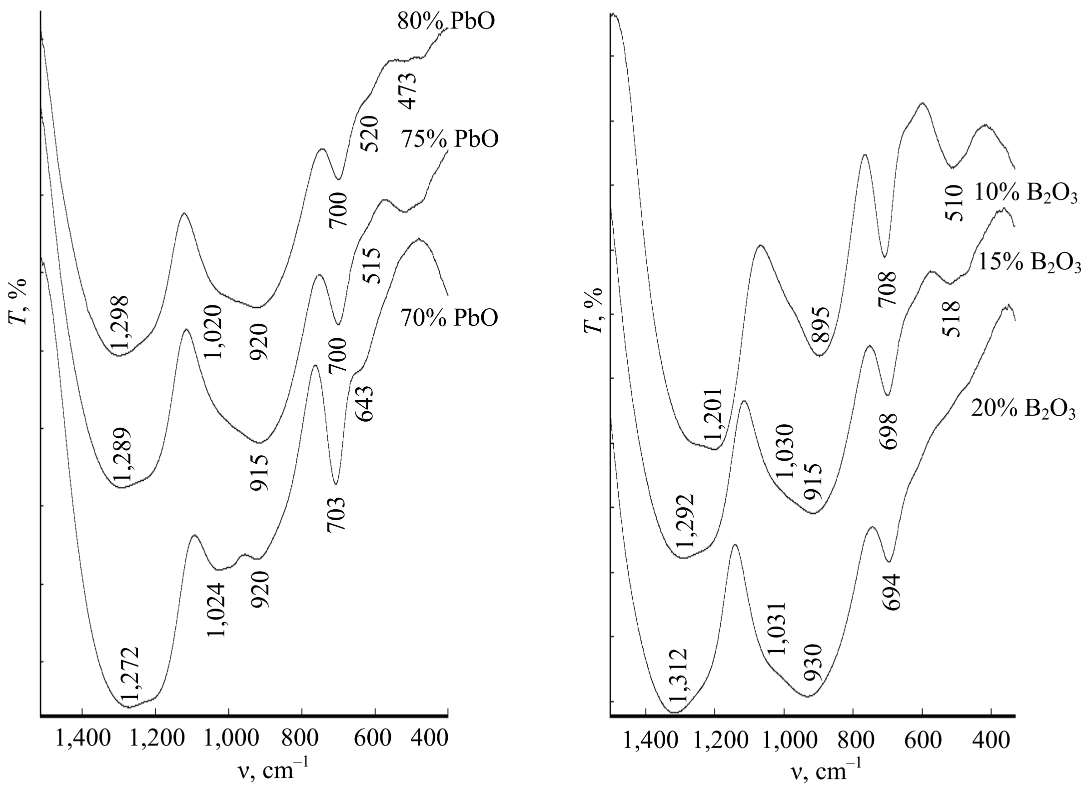


Fig. 4. IR spectra of experienced glasses

Therefore, tested glass compositions have been modified by partial replacement of zinc oxide by CaO and BaO oxides in the amount of from 1.5 to 5.5 wt with step 2%. The glass composition in a mass ratio B_2O_3:ZnO, i. e. 5:3 has been selected as a basic structure for the modification according to combined rheological and thermal properties.

The injection of calcium and barium oxides causes the viscosity reduction practically in the entire temperature range. The most significant influence of the oxide-modifier nature is shown in the temperature range below the temperature of Littleton corresponding to viscosity indicators – $10^{6.6}$ Pa · s. The viscosity indicators below 10^5 Pa · s at a temperature of 450 ± 10°C are achieved by injection of calcium oxide in an amount of 3.5 wt %.

Low-melting glass of modified composition has a TCLE index of $115 \cdot 10^{-7}$ K^{-1} and deformation temperature of 360 ± 5°C.

Compositions of fusible glass – crystal filler have been tested to ensure the specified TCLE index which is $(77 \pm 1) \cdot 10^{-7}$ K^{-1}, and to increase the thermo-mechanical strength of the composite glass-ceramic cement. The choice of crystal fillers is based on the following requirements:

– their inertness to the low-melting glass for the stability of the ratio of vitreous and crystalline phases;

– crystalline filler should not melt and have a conversion of modification in the temperature range of the firing;

– filler must have a lower coefficient of linear expansion than the low-melting glass.

TCLE indicators of crystalline compounds vary widely, but of most interest are cordierite (coefficient of linear expansion in the range of 25–700°C is $26 \cdot 10^{-7}$ K^{-1}), spodumene (coefficient of linear expansion in the range of 20–1,000°C is $9 \cdot 10^{-7}$ K^{-1}), zircon (coefficient of linear expansion in the range of 20–700°C is $42 \cdot 10^{-7}$ K^{-1}). Therefore, these compounds have been used as fillers in the compositions of low-melting glass.

The basis of the composition of the glass – the crystal filler consists of glass powder of modified composition with a specific surface of 1.5–2.0 m^2/g. Laser dispersion method performed by using the device "Analysette 22" has shown that the predominant fraction comprises particles of 5–10 μm; particles larger than 12 μm – less than 5%.

Crystalline fillers (zircon, cordierite and spodumene) with a specific surface of 1.7–2.1 m^2/g were introduced into the compositions in the amount of 10–30 pts. wt for 100 pts. wt of the glass powder. On the basis of compositions we have formed samples, which were baked at a temperature of 450 ± 5°C to determine the coefficient of linear expansion and spreadability.

Introduction of crystalline fillers makes it possible to adjust the TCLE of glass-ceramic cement in a rather wide range – from $77.8 \cdot 10^{-7}$ to $116.8 \times \times 10^{-7}$ K^{-1}.

The specified TCLE index of $(77 \pm 1) \cdot 10^{-7}$ K^{-1} is achieved during the synthesis of glass-ceramic cement on the basis of composition of low-melting glass – spodumene at a mass ratio of 5:1. In the composite glass-ceramic cement spodumene is present as the main crystal phase and eucryptite is a co-crystalline phase.

Conclusion. Thus, the developed glass-ceramic cement fully meets the following requirements: in terms of TCLE index it is agreed with fiber-optical elements; it has a low firing temperature,which is 50 ± 5°C; deformation temperature is above 520 ± ± 5°C; TC_{100} indicators – temperature corresponding to the specific electro-resistance of 10^6 ohm · m is 320°C. Composite glass-ceramic cement provides thermomechanical strength and vacuum tightness of vitreous fiber optical element with a metal frame during firing and cyclic thermal loads in operation.

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Information about the authors

Levitskii Ivan Adamovich – D. Sc. Engineering, professor, head of the Department of Glass and Ceramics Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: levitskii@belstu.by

Papko Ludmila Fedorovna − Ph. D. Engineering, assistant professor, Department of Glass and Ceramics Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: papko@belstu.by

Dyadenko Mikhail Vasil'evich – Ph. D. Engineering, senior lecturer, Department of Glass and Ceramics Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: dyadenko@belstu.by

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