EFFECT OF THE MELTING CONDITIONS ON THE PROPERTIES OF GLASSES IN THE SYSTEM PbO–ZnO–B₂O₃–SiO₂

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Oxide system PbO–ZnO–B₂O₃–SiO₂, with the content of lead oxide of more than 45 mol.% is the basis of non-crystallizable low-melting glasses with softening temperature of lower than 450°C. Lead-containing glasses are very aggressive, therefore they are melted in the platinum crucibles or ceramic crucibles which are resistant to the aggressive action of the lead glass melt. During the process of the melting of lead glasses in ceramic crucibles, the additives (Al₂O₃ and SiO₂) are transferred from the crucible to the glass melt. An uncontrolled amount of these additives affects the properties of the glasses. The objective of this work was to establish the effect of the temperature-time conditions of melting on the physical and chemical properties of high-lead glasses prepared in both platinum crucibles and ceramic ones. The results of the study showed significant difference in properties of glasses synthesized in crucibles fabricated from different materials. Glass synthesized in the platinum crucible under various temperature-time conditions was characterized by stable physical and chemical characteristics and low softening temperature (~380°C) without any traces of crystallization under repeated heat treatment. The melting in the alumina crucible and quartz crucible under the same temperature-time conditions resulted in both a decrease in physical and chemical characteristics of low-melting glass and an increase in the glass softening temperature to 450–470°C due to crystallization of glass during a heat treatment.

Keywords: glass, glass frits, low-melting glass, platinum crucible, softening temperature, lead glass.

DOI: 10.32434/0321-4095-2019-127-6-47-52

Introduction
Glass frits with softening temperatures below 420–450°C are currently used for sealing of semiconductor micro-electronic devices. The oxide system PbO–ZnO–B₂O₃–SiO₂ with the content of PbO of more than 45 mol.% is the basis of compositions of such low-melting glasses [1,2]. It should be noted that high-lead glasses melts are characterized by increased aggressivity towards the material of crucible where they are synthesized. Therefore, the melting of such glasses is commonly carried out in platinum, quartz or alumina crucibles, which are weekly subjected to the destructive action of high-lead glass-forming melts.

Among the above-mentioned crucibles, the crucibles made of expensive platinum are most resistant to the aggressive action of melts. Ceramic crucibles are cheaper and, accordingly, more affordable than the platinum ones. However, the use of such crucibles involves the transfer of trace components (Al₂O₃, SiO₂, etc.) to the glass-forming melt. An uncontrolled amount of these components considerably affects the properties of the glass. The amount of the above-mentioned oxides, which can be transferred to the melt, significantly depends on the glass composition and temperature-time conditions of its melting [3–5].

In connection with this, the objective of this work was to establish the effect of the temperature-time conditions of melting on the physical and chemical properties of high-lead glasses obtained in both platinum crucibles and ceramic ones.

Materials and methods
The chemical compositions of the glasses under study are shown in Table 1. For the preparation of glass mixtures, fine-grained quartz sand and chemical reagents of «chemically pure» and «analytically pure» grades (H₃BO₃, ZnO and Pb₃O₄) were used. Glass
was melted in the platinum, alumina and quartz crucibles (30–50 mL) in the electric furnace with silicon carbide heaters at the temperature of 850°C during 30 minutes.

Evaporating some properties of glasses under study are given in Table 2. This Table shows that the values of properties of glasses synthesized under the same temperature-time conditions in crucibles of different materials differ substantially.

The effect of the initial composition of glass-forming melt on the degree of its aggressivity with regard to the material of ceramic crucible can be assessed based on the data given in Fig. 1. In this case, the glass melt aggressivity (Δd) was determined by changing the density of glasses (d₁) prepared in the ceramic crucibles with regard to density of glasses (d₂) synthesized in the platinum crucible, (%): Δd=(d₁–d₂)·100/d₂.

In the process of melting in the alumina crucible, the aggressivity of glass melt grows considerably when SiO₂ is replaced by B₂O₃ (Fig. 1,a). An increase in the content of B₂O₃ from 25 to 40 mol.% leads to a decrease in the glass density from 2.6 to 4.0% owing to SiO₂ reduction. With the use of the melting in the quartz crucible, the aggressivity of glass melt increases appreciably with the replacement of SiO₂ by ZnO (Fig. 1,b). An increase in the ZnO content from 5 to 20 mol.% results in a decrease in the glass density from 3.2 to 5.0% owing to SiO₂ reduction.

Figure 1 shows that the aggressivity of the melt

| Glass No. | Content, mol.% | Glass No. | Mg, °C | CLTE, \(\alpha \cdot 10^{-6} \cdot K^{-1}\) | Density, \(d, g/cm^3\) |
|-----------|----------------|-----------|--------|---------------------------------|-----------------|
|           | PbO | ZnO | B₂O₃ | SiO₂ | Mg, °C | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| 1         | 55  | 20  | 20   | 5    | 290  | 117 | 109 | 106 | 6.65 | 6.44 | 6.34 |
| 2         | 55  | 15  | 25   | 5    | 300  | 115 | 107 | 105 | 6.50 | 6.28 | 6.21 |
| 3         | 55  | 10  | 30   | 5    | 310  | 111 | 106 | 103 | 6.35 | 6.12 | 6.08 |
| 4         | 55  | 5   | 35   | 5    | 325  | 109 | 105 | 102 | 6.19 | 5.95 | 5.94 |
| 5         | 55  | 15  | 20   | 10   | 315  | 111 | 105 | 105 | 6.53 | 6.33 | 6.25 |
| 6         | 55  | 10  | 25   | 10   | 320  | 110 | 104 | 102 | 6.38 | 6.17 | 6.12 |
| 7         | 55  | 5   | 30   | 10   | 330  | 107 | 103 | 102 | 6.20 | 6.03 | 6.00 |
| 8         | 55  | 15  | 15   | 15   | 315  | 108 | 106 | 105 | 6.62 | 6.45 | 6.36 |
| 9         | 55  | 10  | 20   | 15   | 325  | 107 | 103 | 102 | 6.46 | 6.28 | 6.22 |
| 10        | 55  | 5   | 25   | 15   | 335  | 105 | 101 | 97  | 6.30 | 6.12 | 6.08 |
| 11        | 55  | 5   | 20   | 20   | 340  | 103 | 99  | 95  | 6.30 | 6.14 | 6.10 |

The above suggests that glass-forming melts actively interact with the surface of ceramic crucibles during the melting of experimental glasses. Because of this interaction, a substantial amount of impurities Al₂O₃ and SiO₂ are carried to the composition of glasses.

Results and discussion

Some properties of glasses under study are given in Table 2. This Table shows that the values of properties of glasses synthesized under the same temperature-time conditions in crucibles of different
Effect of the melting conditions on the properties of glasses in the system PbO–ZnO–B$_2$O$_3$–SiO$_2$

Towards the material of the ceramic crucible becomes lower with an increase in SiO$_2$ content in the glass composition, which is obviously related to an increase in the viscosity of glass melt during melting process. This is clearly seen from the dependence of Mg, characterizing the viscosity of the glass in the area of its softening, on the chemical composition of the glass (Fig. 2). An increase in the content of SiO$_2$ from 5 to 20 mol.% results in an increase in the values of Mg of the glass from 290 to 340°C.

Along with the marked impact of impurities Al$_2$O$_3$ and SiO$_2$, which can be transferred to the glass melt due to its interaction with the stuff of ceramic crucible depends not only on the chemical composition of glass, but also on the duration ($\tau$) and on temperature (t) of the melting process. In this regard, the effects of temperature and duration of melting of the glass No. 7 on its properties was determined (Tables 3 and 4).

It is known [3] that the amount of impurities Al$_2$O$_3$ and SiO$_2$, which can be transferred to the glass melt due to its interaction with the stuff of ceramic crucible depends not only on the chemical composition of glass, but also on the duration ($\tau$) and on temperature (t) of the melting process. In this regard, the effects of temperature and duration of melting of the glass No. 7 on its properties was determined (Tables 3 and 4).

Effect of the melting conditions on the properties of glasses in the system PbO–ZnO–B$_2$O$_3$–SiO$_2$
Effect of melting temperature (τ=30 min) on the physical and chemical properties of the glass No. 7 prepared in the platinum (1), alumina (2) and quartz (3) crucibles

| T, °C | Mg, °C | CLTE, α⋅10^7, K^-1 | Density, d, g/cm^3 |
|-------|--------|----------------------|-------------------|
|       | 1  2  3 | 1  2  3             | 1  2  3          |
| 850   | 330 340 360 | 107 103 102 | 6,20 6,03 6,00 |
| 900   | 330 350 370 | 107 98 98    | 6,20 5,79 5,93  |
| 950   | 330 360 375 | 107 97 96   | 6,20 5,72 5,88  |

Effect of melting duration (τ=850°C) on the physical and chemical properties of the glass No. 7 prepared in the platinum (1), alumina (2) and quartz (3) crucibles

| τ, min | Mg, °C | CLTE, α⋅10^7, K^-1 | Density, d, g/cm^3 |
|--------|--------|----------------------|-------------------|
|        | 1  2  3 | 1  2  3             | 1  2  3          |
| 30     | 330 340 360 | 107 103 102 | 6,20 6,03 6,00 |
| 60     | 330 350 360 | 107 102 101 | 6,20 5,96 5,97  |
| 90     | 330 360 365 | 107 99 99    | 6,20 5,87 5,95  |
| 120    | 330 365 370 | 107 97 95   | 6,20 5,72 5,90  |

One can easily see that the change of temperature-time conditions of the melting of the glass No. 7 in the platinum crucible has no effect on its properties. However, an increase in the temperature and duration of melting of the glass No. 7 promotes an active interaction of its melt with the surface of the alumina and quartz crucibles and, accordingly, a substantial change in its properties as compared with the properties of the glass melted in the platinum crucible. The reduction of temperature of the glass melting to 800°C leads to an increase in the viscosity of the glass melt and in the time of melting from 30 to 60 minutes. As a result, the melts of glasses synthesized in the alumina and quartz crucibles at the temperature of 800°C were crystallized in the process of casting.

Consequently, one can conclude that in order to prepare a glass with a minimal content of impurities (Al₂O₃ and SiO₂) the process of melting should be performed at a relatively moderate temperature (no more than 850°C) and, if possible, for the short period of time (but not less than 30 minutes).

The temperature-time conditions of melting of the experimental glass also have a strong effect on its crystallization ability (Figs. 4 and 5).

With an increase in the duration of synthesis in the quartz crucible from 30 minutes (Fig. 3,b) to 120 minutes (Fig. 4,b), the reduction of crystallization intensity at 420°C is observed that follows from a decrease in exothermic peak height. An increase in the time of melting in the alumina crucible from 30 minutes (Fig. 3,c) to 120 minutes (Fig. 4,c) causes its crystallization during the heat treatment in the temperature interval of 410–460°C, thus shifting the softening temperature of glass to 470°C.

X-ray phase analysis allowed determining the main crystalline phases, which are formed in the process of heat treatment of the glass No. 7 synthesized in the alumina crucible. X-ray patterns (Fig. 5) of the products of the glass heat treatment show that one crystalline phase, PbO (d=3.08; 2.82; 1.87) is formed in the process of crystallization of the glass at the temperature of 430°C (Fig. 5,a). When the temperature of the heat treatment is increased to 520°C, the amount of a crystalline phase of PbO grows that follows from an increase in the intensity of diffraction maximums in the X-ray patterns (Fig. 5,b).

**Conclusions**

The obtained experimental results showed the effects of the chemical composition and temperature-time conditions of the glass melting in the platinum, alumina and quartz crucibles on the physical and chemical properties of low-melting glasses in the oxide system PbO–ZnO–B₂O₃–SiO₂ with the PbO content of 55 mol.%. It was found that the glass synthesized in the platinum crucible under different temperature-time conditions featured stable physical and chemical characteristics and low softening temperature (~380°C) without any traces of crystallization after the heat treatment. It was shown that the melting in the alumina and quartz crucibles under the same conditions leads to the deterioration of the glass properties.

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ISSN 0321-4095, Voprosy khimii i khimicheskoi tekhnologii, 2019, No. 6, pp. 47-52

VПЛИВ УМОВ ВАРИННЯ НА ВЛАСНОСТІ СТЕКОЛ В СИСТЕМІ PbO–ZnO–B$_2$O$_3$–SiO$_2$

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В основі складів легкоплавких стекол, що не кристалізуються, з температурами розм'якшення нижче 450°С лежать оксидні системи PbO–ZnO–B$_2$O$_3$–SiO$_2$ із вмістом оксиду висмінін більше 45 мас.%. Прикладом легкої структури дуже агресивні, тому їх варіанти здійснюють у платинових або керамічних тиглях, які стійкі до агресивної дії розплаву свинцового скла. У процесі варіння свинцового стекла в керамічних тиглях в розплав скла з тигля переходять добавки (Al$_2$O$_3$, SiO$_2$), неконтрольовано кількість яких впливає на властивості стекол. Метою цієї роботи було встановити вплив температурно-часових умов варіння на фізико-хімічні властивості багатооксидових стекол одержаних як в платинових, так і в керамічних тиглях. Здійснені дослідження показали суттєву відмінність у властивостях стекол, синтезованих у тиглях з різних матеріалів. Скло, синтезоване в платиновому тиглі при різних температурно-часових умовах, характеризувалося стабільними фізико-хімічними характеристиками та низькою температурою розм'якшення (~380°С) без східів кристалізації при повторному термічному обробленні. Варка в керамічному тиглі в тих же температурно-часових умовах призводить до зниження фізико-хімічних характеристик легкоплавкого скла та збільшення температури розм'якшення скла до 450–470°С внаслідок іого кристалізації при термічному обробленні.

Ключові слова: скло, склоприпій, легкоплавке скло, платиновий тигель, температура розм'якшення, свинцєве скло.

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Received 04.06.2019
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