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LEAD-FREE HIGH-QUALITY GLASS FOR ASSORTED GLASSWARE

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Data on the synthesis of lead-free glass for assorted glassware are presented. Glasses in the system SiO_2–SnO_2–BaO–CaO–Na_2O–K_2O with 2 – 10% SnO_2 are studied. The effect of introducing BaO and SnO_2 together on the crystallizability, density, CLTE, index of refraction and microhardness of the glasses is studied. Compositions with 6 – 8% BaO and SnO_2 4 – 6% are recommended for high-quality assorted glasses. The refractive index of the glasses obtained is in the range 1.540 – 1.550, the microhardness is 3700 – 4900 MPa and the CLTE is $(95 – 98) \times 10^{-7}$ K^{-1}.

Key words: assorted glass, tin oxide, barium oxide, index of refraction, microhardness.

The problem of increasing the quality of lead-free glass for assorted articles is always topical. Giving assorted glass high transparency and increasing its refractive index makes it possible to expand considerably the range of assorted articles with new forms, demonstrating the high quality of the glass. The most striking examples of such glass are the articles manufactured by the Bohemia Company, which have proven their worth completely in the global market. The composition of Bohemian assorted glass approximately corresponds to the following oxide content (%[3]): 69.5 SiO_2, 7.8 CaO, 8.5 BaO, 10 Na_2O, 3.2 K_2O and 1 Al_2O_3. Articles made of so-called Czechoslovakian barium crystal are also well-known, though here the term "crystal" is applicable only very conditionally. Its composition is (%): 58 SiO_2, 18 BaO_2, 5 ZnO, 3 Na_2O and 16 K_2O. The index of refraction of barium crystal is close to 1.530, which corresponds to the lower limit for lead crystal [1 – 3].

In patented compositions of lead-free "crystal" glass [4 – 9] the advances proposed involve introducing into the glass the oxides of rare-earth metals or other hard to get, expensive components (e.g., Bi_2O_3). The quotation marks underscore the conditionality of the definition of the term "crystal" in application to lead-free glass. In addition, all such glass is distinguished by an elevated content of alkali-metal oxides, which adversely affect the chemical stability and CLTE of the glass.

Of great interest here is research on the development of zirconium-containing glass for high-quality assorted glassware. G. Yu. Goikhman, et al. have made a systematic study of the properties of glasses based on the system Na_2O–K_2O–CaO–ZnO–ZrO_2–SiO_2 with 1 – 15% ZrO_2. Glass with refractive index 1.530 – 1.580 and viscosity close to that of crystal and Bohemian glass have been obtained with the following compositions (%): 62.0 – 67.0 SiO_2, 3.0 – 7.0 Zr_2O, 0.1 – 0.5 B_2O_3, 1.0 – 6.0 ZnO, 8.0 – 12 CaO, 6.5 – 8.5 Na_2O and 10.0 – 12.5 K_2O. However, Zr_2O significantly "shortens" glass, even glass with a high content of alkali metals. In addition, ZrO_2 does not increase light transmission.

Higher glass transparency is largely due to cations with a large ionic radius. This is why such high-transparency glass almost always contains the oxides K_2O and BaO (the ionic radii of K and Ba are, respectively, 0.133 and 0.138 nm). In addition, a high index of refraction is very important, preferably at the level of leaded glass, i.e., not lower than 1.535, for high-quality assorted glass. In this case oxides with high partial refractive indices must be introduced into lead-free glass. They include, aside from PbO (the partial index for PbO is $n_i = 2.15 – 2.35$), quite readily available oxides, such as TiO_2 ($n_i = 2.2$), BiO ($n_i = 1.88$) and SnO_2 ($n_i = 1.94$) [10].

With respect to partial refractive indices titanium dioxide is closest to PbO, but titanium dioxide not only strongly "shortens" glass but it also decreases light transmission because coloring iron-titanium complexes tend to form even with a very low content of iron oxide impurities. For this reason, we became interested in developing compositions for

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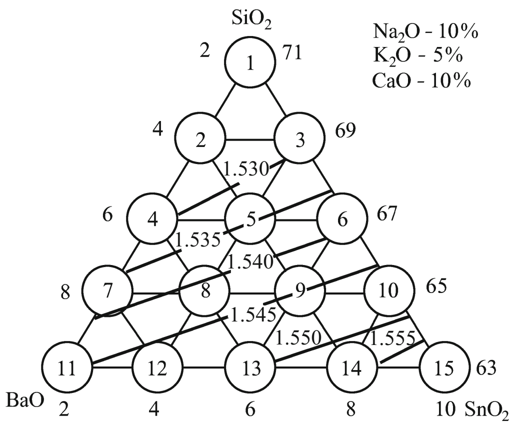

Fig. 1. The index of refraction of glasses versus the composition (wt.%).

high-quality assorted glass with BaO and SnO_2 introduced together. The studies were performed for the system SiO_2–SnO_2–BaO–CaO–Na_2O–K_2O with 63 – 71% SiO_2, 2 – 10% BaO and 2 – 10% SnO_2. The sum of the oxides Na_2O, K_2O and CaO remained constant and equal to 25% in all glasses. The glasses were synthesized in a gas furnace with porcelain crucibles and maximum melting temperature 1450°C.

A study of the crystallizability of glasses showed that the experimental glasses are not prone toward crystallization at temperatures 600 – 1050°C with 1-h soaking. The softening temperature, CLTE, density and microhardness of the synthesized glasses were studied and the refractive index was calculated. Special attention was devoted to the effect of replacing BaO with SnO_2 on the properties of the glasses.

The density of the glasses in the experimental composition range varies in the range 2520 – 2750 kg/m^3 and increases considerably with increasing total BaO and SnO_2 content. However, the effect of replacing BaO with SnO_2 on the glass density is very small. Thus, the density of glass containing 10% BaO and 2% SnO_2 is 2720 kg/m^2, and for the opposite ratio of BaO and SnO_2, i.e., 2% BaO and 10% SnO_2, the density increases to 2750 kg/m^3. A much larger change occurs in the refractive index when BaO is replaced with SnO_2. For the ratio BaO : SnO_2 = 10 : 2 the refractive index with the minimum SiO_2 content of 63% equals 1.535, while for the ratio BaO : SnO_2 = 1 : 10 the index increases to 1.560, i.e., in this case the index of refraction even exceeds its value for ordinary crystal glass (see Fig. 1). The experimental glasses have moderate values of CLTE — $(89.5 – 98.9) \times 10^{-7}\ K^{-1}$. Characteristically, the microhardness of the experimental glasses is relatively low (3700 – 4400 MPa), only negligibly higher that the microhardness of lead-containing crystal glasses (3600 MPa).

The latter can be explained by the particularities of the incorporation of the tin ions in the silicon-oxygen structural network. The ionic radius of Sn^{4+} is 0.064 nm, which suggests oxygen coordination numbers 4 and 6. In a tetrahedral environment the tin ions can replace silicon and embed into the silicon-oxygen structural network. The presence of cations — BaO and K — stabilized the groups $[SnO_4]$. Since the total molar content of BaO and K_2O in the experimental glasses exceeds that of SnO_2, the tin in the glass matrix is probably mainly in the four-fold coordination state. But, since the $[SnO_4]$ tetrahedron is much larger than the $[SiO_4]$ tetrahedron (ionic radii of Sn^{4+} and Si^{4+} are, respectively, 0.067 and 0.039 nm), embedding of $[SnO_4]$ groups into the silicon-oxygen structural network results in significant deformational distortions and, in consequence, strength reduction of the glass.

In terms of the combination of glass properties for the production of high-quality assorted glass, the best compositions are those with 6 – 8% BaO and 4 – 6% SnO_2 and SiO_2 content not exceeding 67%. The positive effect of SnO_2 on the density, refractive index, CLTE (decrease), chemical stability and light transmission (92 – 94% in the visible part of the spectrum) is confirmed.

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