УДК 666.227.3

L.F. Papko, PhD (Engineering), assistant professor (BSTU);
I.A. Levitski, D.Sc. (Engineering), professor, head of department (BSTU);
M.V. Dyadenko, PhD (Engineering), assistant lecturer (BSTU)

HIGH-INDEX GLASS FOR THE PRODUCTS OF OPHTHALMOLOGIC OPTICS

The results of development of high-index glass for the products of ophthalmologic optics on the basis of the systems Li_2O – RO – B_2O_3 – SiO_2 and K_2O – TiO_2 – SiO_2 are presented. It is shown that the formation of complexes $[TiO_{4/2}O]^{2-}K_2^+$ in glass of the system K_2O – TiO_2 – SiO_2 interferes with the formation of the chromophore centers Fe^{2+} – O – Ti^{4+} and allows to receive colorless glass at amount of TiO_2 to 30 mol.%. The compositions of glass with a refractive index 1.65 and 1.70 at density no more than 2.91 g/cm^3 are developed. It allows to recommend them for the production of the facilitated lenses with a high optical force.

Introduction. At present various types of eyeglass lenses are presented on the world market of ophthalmologic optics. Selecting suitable lenses for corrective glass for people suffering from moderate to high myopia or hyperopia (more than 3.8 diopters) is a challenging task. The thickness of standard eyeglass lenses increases proportionally to the growth of their optical power, so these glasses are heavy, require massive frame that creates discomfort for the user. An alternative is the use of high-index glass for eyeglass lenses that allow you to increase the optical power of the lens, almost without changing its thickness. The refractive index of the high-index glass varies in a range from 1.60 to 1.80. Articles of such glass are offered by a number of foreign firms [1].

To improve the competitiveness of articles of the ophthalmologic optics produced by the domestic manufacturer (JSC "Plant "Optic"), the development of the original compositions of the high-index optical glass is required. In addition to the refractive index, which shall not be less than 1.60, high-index glass should have the least possible value of the density to reduce the weight of the spectacle lens. The technological properties of glass are also important, in particular, it is necessary to exclude the crystallization in the process of forming articles It should also be taken into account that in the development of optical glass with a high refractive index costly rare earth oxides are widely used.

The complexity of design of the high-index glass for ophthalmologic optics lies in the fact that the components effectively increasing the refractive index of glass also increase their density. These components include BaO, PbO, La_2O_3, Nb_2O_5, TiO_2 и ZrO_2.

In accordance with GOST (State Standard) 3514-94 brands of optical glass with a refractive index n_e, constituting 1.60-1.70 are known. This glass brands TC– heavy crons, F– Flint, BF – barite Flint, STK–super heavy crons.

The analysis of the properties of barite Flint shows that they have a density of not less than 3.47 g/cm^3; in this case the density increases with the growth of the refractive index.

The increased content of barium oxide in the composition of cron determines rather high density indicators at values of the refractive index being in the range 1,555-1,665.

For the manufacture of the thinner spectacle lenses flint glass is used. It has a higher refractive index constituting 1.70 at a density of up to 5.2 g/cm^3.

The refractive index of superheavy crons (SHC) is not less than 1.65, but their density is not less than 4.0 g/cm^3 due to the introduction of components such as ThO_2, ZrO_2, La_2O_3 и CdO.

Main part. In this work [2] we submit the results of studies of glass R_2O – RO – B_2O_3 – SiO_2, were R_2O – K_2O, Na_2O, RO – MgO, CaO, ZnO, SrO, BaO, if they contain 35–55 mol.% SiO_2, 30–45 mol.%. It has been found that the ratio of the oxides of magnesium, calcium, barium and zinc comprised in the composition of experimental glass which is 2 : 8 : 1 : 4, the refractive index at least 1.60 at a density of 2.79–3.10 g/cm^3 is ensured. An effective means is the introduction of the titanium oxide in an amount up to 4 mol.% which can increase the refractive index of experimental glass to values of 1.60 and higher. When using TiO_2 techno glass with a refractive index of at least 1.605 at a density of 2.8 g/cm^3 was obtained. It should be noted that by increasing the content more than 5 mol.% of TiO_2 in the glass system Na_2O – RO – B_2O_3 – SiO_2 pale yellow color appears.

The introduction of ZrO_2 can significantly increase the refractive index, but with the growth of its content the density also significantly increases. This restricts the possibility of using this component. The recommended concentration of zirconium oxide comprised in experimental glass is 2–4 mol.%.

The reduction of the density of experimental glass at the refractive index of 1.608–1.650 can be achieved by the introduction of glass R_2O – RO – B_2O_3 – SiO_2 lithium oxide into the composition. The replacement of Na_2O by Li_2O determines a significant decrease in pulping temperature to 1,350°C, but with the growth of lithium oxide content up to 15 mol.% the crystallization ability of glass increases that is shown in the increase of values of the upper crystallization temperature [3]. As a result of research, technological composition of the glass with a refractive index of 1.608 and a density of 2.64 g/cm^3 was developed, which is comparable with those of the leading foreign companies.

This sets the task, aimed at obtaining glass with a refractive index of at least 1.65 at the lowest possible density values.

The development of glass with a refractive index of 1.65 and higher was carried out on the basis of the system $Li_2O – RO – B_2O_3 – SiO_2$ with additives of titanium and zirconium oxides. The content of silica is 35–45 mol.%, that of the RO group – 30 to 35 mol.%; the effect of positive influence of joint introduction of oxides CaO, ZnO, BaO and MgO on technological and physicochemical properties being used.

The temperature of the synthesis of lithium-containing glass is (1,350 ± 10)°C. The low temperature of pulping glass is associated with the ability to lower the melt viscosity of Li_2O.

The crystallization ability of experimental glass increases with the increasing of content in Li_2O. When the content of Li_2O is 10–15 mol.%, it leads to the growth of the temperature interval of crystallization, growth of the upper crystallization temperature values to 1,100–1,150°C. Besides, in the temperature range of 750–950°C damping of samples is marked which may be caused by the development of liquation processes. The sustainability of the glassy state naturally decreases with decreasing of silicon oxide content. Glass samples with a higher content of SiO_2 and B_2O_3 are characterized by a low crystallization ability, which is exhibited in the formation of a crystal film in the temperature range 700–950°C in the process of gradient thermal treatment.

With the increase of content Li_2O and B_2O_3 the refractive index of glass naturally rises to values of 1.65–1.66 at a density of 2.8–3.0 g/cm^3. Consequently, the glass of $Li_2O – RO – B_2O_3 – SiO_2$ system have a sufficiently low density with the refractive index of about 1.65.

The technological characteristics of the synthesis of lithium glass are as follows. Lithium-containing glass have a distinct yellow color when cooked in a periodic kiln flame in porcelain crucibles. This is due to the introduction of the titanium oxide into glass in an amount up to 8 mol.%. Melting of the same glass in an electric furnace in a platinum crucible eliminates coloration or reduces its degree to a light yellow tint.

It should be noted that in some cases high-index spectacle lenses of glass offered by foreign manufacturers have a color tone.

The appearance of yellow shades in titanium containing glass, in accordance with [4], is due to the formation of iron titanate complexes $Fe^{2+} – O – Ti^{4+}$ и $Fe^{3+} – O – Ti^{4+}$, thus the most intense absorption is due to chromophore complex with the ion Fe^{2+}. Such complexes are formed at presence of iron oxide impurities that are introduced into the glass with raw materials, as well as they are diffused from the material containing in a glass-melting vessel in the process of synthesis. The latter circumstance is excluded when boiled in platinum crucibles. Redox synthesis conditions also affect the formation of the chromophore complexes, due to the changes in the ratio $Fe^{2+} : Fe^{3+}$. The oxidizing atmosphere in the furnace, increasing the oxidation potential of the charge and glass provide a glass transition $Fe^{2+} \rightarrow Fe^{3+}$ and eliminate or reduce unwanted coloration.

Thus, on the basis of $Li_2O – RO – B_2O_3 – SiO_2$ system with TiO_2 additives glass with a refractive index of 1.6523 and a density of 2.92 g/cm^3 were obtained. However, the increase of the refractive index to a value of 1.70, based on lithium-containing glass, is not achieved. This is due to the fact that the increase in the values of the refractive index of glass of $Li_2O – RO – B_2O_3 – SiO_2$ to 1.67 – 1.70 is ensured by increasing the content of Li_2O to 15 mol.%, TiO_2 up to 10–12 mol.%. This increases the tendency of the glass to phase separation – the upper crystallization temperature increases, which may cause the crystallization of glass in the process of industrial production. Besides, the increase in the content of lithium titanium oxide glass leads to a stable yellow-brown color even when melted in an electric furnace in a platinum crucible.

In this connection, a subsequent step was to carry out the synthesis with a refractive index of glass on the basis of $K_2O – TiO_2 – SiO_2$ systems at a content of components, mol.%: TiO_2 – 20–30, K_2O – 15–35, SiO_2 – 35–65. The experimental glass compositions are shown in Fig. 1.

The synthesis of glass was carried out in an electric glass furnace of a periodic action in a platinum crucible at a maximum temperature of (1,400 ± 10)°C. The peculiarity of the synthesis mentioned above is to provide oxidizing conditions in the process of cooking by using potassium nitrate as the raw material.

As stated above, the color of the titanium-containing glass is mainly due to the formation of the chromophore complexes $Fe^{2+} – O – Ti^{4+}$. With the high oxidation potential of the charge, firstly, the transition $Fe^{2+} \rightarrow Fe^{3+}$ (complexes $Fe^{3+} – O – Ti^{4+}$ are characterized by low absorption intensity), and secondly, Ti^{4+} does not go into a coloring form of Ti^{3+}. As a result, even when the content of titanium oxide is 20–30%, most glass samples of $K_2O – TiO_2 – SiO_2$ system are colorless. Glass with a lower content of K_2O are yellow-brown, while the ratio K_2O : TiO_2 is below 0.8.

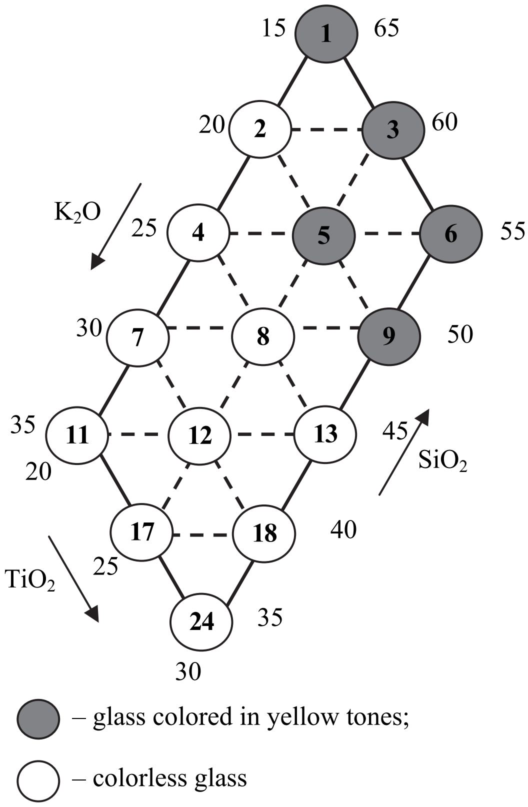

Fig.1. Area of glass compositions of $K_2O – TiO_2 – SiO_2$ system

As shown in the work [4], the formation of complexes of coloring depends on the basicity of glass, in particular, on the content of the oxides of R_2O group and the form of these oxides. Thus, when the ratio Na_2O : TiO_2 is greater than one, complexes $[TiO_{4/2}O]^{2-}Na_2^+$ are formed, while coloring complexes $Fe^{2+} – O – Ti^{4+}$ are destroyed. This causes a decrease in the intensity of color or its elimination.

From this perspective it is possible to explain the removal of unwanted color in the glass with a higher ratio K_2O: TiO_2. We should note the fundamental difference in the effect of the color of the titanium oxide in lithium and potassium-containing glass. The formation of potassium titanate complexes $[TiO_{4/2}O]^{2-}K_2^+$ is no doubt, while the possibility of the formation of such complexes with lithium ion is not possible due to the high field strength of the lithium cation.

The formation of complexes $[TiO_{4/2}O]^{2-}K_2^+$ affects not only the color of the glass. Due to the formation of such complexes, tendency to phase separation (liquation, crystallization), characteristic of titanosilicate glass, is suppressed.

According to the results of the gradient thermal treatment in the temperature range 600–1,100°C, it was determined that the crystallization ability of glass containing 20–25 mol.% TiO_2 and 15–25 mol.% K_2O is manifested in the formation of the crystalline crust, the upper temperature of crystallization is 1,080°C.

The results of investigation of the density and the refractive index of experimental glass are shown in Fig. 2.

The increasing of potassium oxide content from 15 to 35 mol.%, introduced instead of SiO_2, causes a monotonic increase in the refractive index by 0.020–0.025. Naturally, the greatest contribution to the refractive index is made by TiO_2, and the values of the given quantity within 1.65–1.70 are achieved when the titanium oxide content is 30–35 mol.%.

Experimental glass is characterized by rather low rates of density not exceeding 2.95 g/cm^3 (Fig. 2*b*). According to the combination of technological and optical properties, the following glass comprising, mol.`%: SiO_2 – 45, TiO_2 – 20–30, K_2O – 25–35, the refractive index of which is 1,6425–1,7002 density of 2.69–2.89 g/cm^3, the dispersion coefficient 31–35, are distinguished.

The transmission spectra of glass with different content of TiO_2 introduced instead of K_2O at constant SiO_2 of 45 mol.% are shown in Fig. 3.

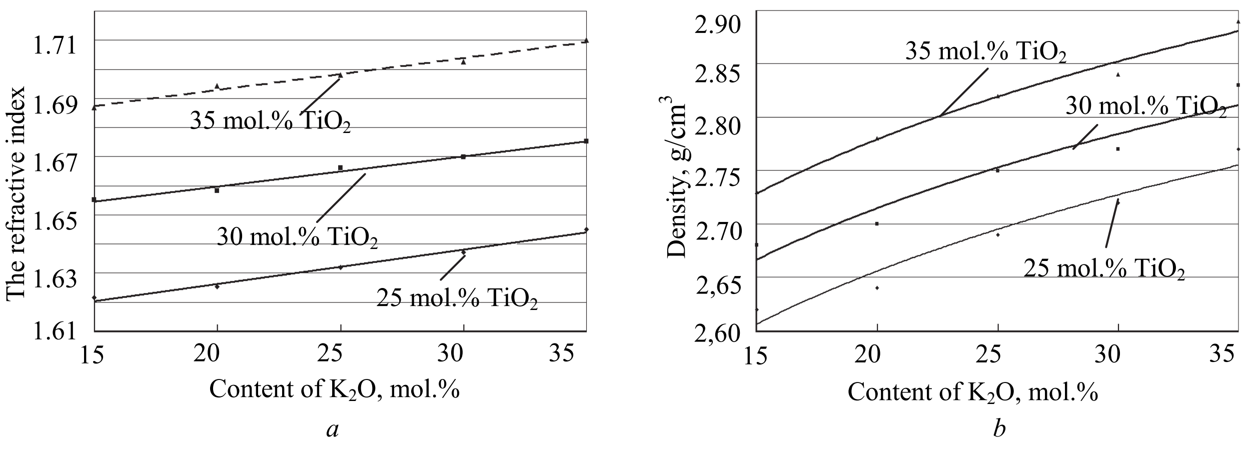

Fig. 2. Influence of K_2O and TiO_2 on the refractive index *(a)* and density *(b)* of the experimental glass

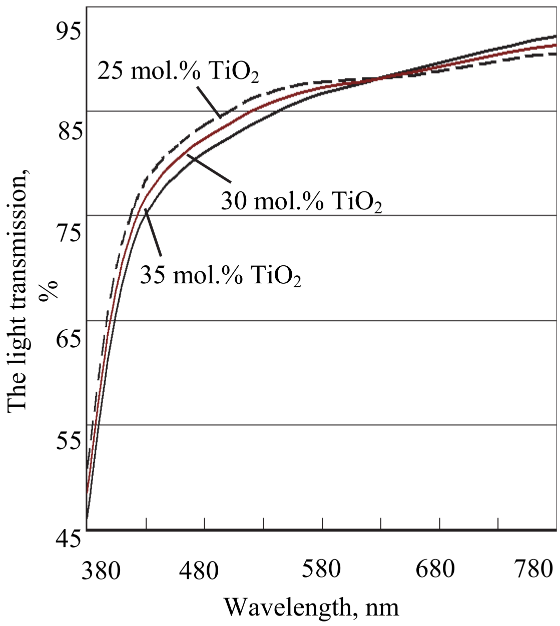

Fig. 3. Transmission spectra of glass of $K_2O – TiO_2 – SiO_2$ system

The absorption edge of experimental glass is shifted toward longer wavelength with the increasing of titanium oxide content. It is characteristic of Ti^{4+} to be able to absorb with a high intensity at the range of 370 nm, which causes a sharp decrease in the transmittance of the titanium-containing glass in the ultraviolet spectrum. This is a positive factor because glass for ophthalmologic optics must protect the eyes from ultraviolet radiation.

Conclusion. Thus, the compositions of glass with a refractive index of 1.65 and 1.70 and a density of 2.73 g/cm^3 and 2.91 were worked out on the basis of $Li_2O – RO – B_2O_3 – SiO_2$ and $K_2O – TiO_2 – SiO_2$ systems. By a combination of optical and of technological properties, glass can be recommended for the manufacture of lightweight eyeglass lenses with a high optical power. Their synthesis should be carried out in an electric furnace at a high oxidation potential of the charge and glass in connection with the possible appearance of yellowish brown color tones due to the formation of the chromophore complexes $Fe^{2+} – O – Ti^{4+}$.

References

1. Хацевич, Т. Н. Медицинские оптические приборы: в 2 ч. Ч. 2. Очковая оптика / Т. Н. Хацевич. – Новосибирск: СГГА, 2002. – 241 с.

2. Левицкий, И. А. Стекла для офтальмологической оптики / И. А. Левицкий, Л. Ф. Папко, М. В. Дяденко // Междунар. науч.-техн. конф., Минск, 22–23 нояб. 2012 г.: в 2 ч. / Белорус. гос. технол. ун-т. – Минск, 2012. – Ч. 1. – С. 52–56.

3. Левицкий, И. А. Высокоиндексные стекла для очковой оптики / И. А. Левицкий, Л. Ф. Папко, М. В. Дяденко // IV Междунар. конф. Рос. хим. о-ва им. Д. И. Менделеева, Москва, 24–25 окт. 2012 г. / Рос. хим.-технол. ун-т им. Д. И. Менделеева. – М., 2012. – Т. 1. – С. 220–221.

4. Ходаковская, Р. Я. Химия титансодержащих стекол и ситаллов / Р. Я. Ходаковская. – М.: Химия, 1978. – 288 с.

Received 22.02.2013