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FORMATION OF COLORING COMPLEXES IN GLASS COLORED WITH CERIUM AND TITANIUM OXIDES

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The valence state of cerium and titanium ions in barium-strontium aluminosilicate glass with a different ratio of cerium and titanium oxides was investigated and the possible composition of the cerium-titanium complexes formed in silicate glass was analyzed. It was found that an active separate reaction between cerium and titanium oxides with the appearance of complex color centers takes place in synthesis of the glass. It is hypothesized that color centers primarily form between tetravalent cerium and tetravalent titanium in glass-forming melts.

A trend toward updating the product line on the automotive light market of items used in lighting and light-signaling equipment for motor vehicles. Incandescent lights with selectively yellow or auto yellow bulbs can be considered promising. According to the UN EEC rules (Unified Regulations Concerning Official Approval of Incandescent Lights for Use in the Officially Approved Headlights of Mechanical Vehicles), the colorimetric characteristics of such glass must satisfy the following requirements with respect to the chromaticity coordinates: for selectively yellow glass, the limit toward green ($y \leq x - 0.120$), red ($y \geq 0.390$), white ($y \leq 0.790 - 0.670x$), and for auto yellow glass, the limits toward green, red, and white ($y \leq 1.29x - 0.1$, $y \geq 0.138 + 0.580x$, $y \leq 0.966 - x$, respectively). It is important to preserve the color in these articles both in direct production of the colored article and in its subsequent heat treatment and use.

At present, two fundamental directions are identified in world practice in fabrication of colored bulbs for automobile lights: direct coloring of the glass in bulk and application of a finished organic coating on the external surface of the lights. The last method has not been widely used due to rapid burn-off of the dye during use of the article. The method of coloring the glass in bulk is the most rational. A review of the compositions and properties of colored glass demonstrates the great variety of combinations of different dyes for obtaining the same color. However, most of the proposed solutions involve the use of very volatile and unstable compounds that do not guarantee stability of the color both in melting the glass and in subsequent heat treatment and use.

Sulfide glass combined with different dyes: MoO_3 and S, Sb_2O_3 and S, $\text{CdSe} + \text{CdS}$, and $\text{Se} + \text{CdS}$ (French Patent Application No. 2864531, US Patent No. 6812173), have recently become widely used [1]. Use of sulfide glasses for coloring is associated with a number of drawbacks, in particular, selective evaporation of sulfur and the necessity of constantly maintaining reducing conditions in melting the glass. It should be noted that bubbles can also appear in the glass with an excessive amount of sulfides. In these cases, the excess sulfur must be oxidized to regulate the color, and this can also unfavorably affect the final result.

The analysis of the published data showed that it is best to use rare-earth element and transition metal oxides to make colored glass for electrical applications with stable color characteristics. This coloring method is widely used for fabricating colored glass that simulates precious stones and in production of high-quality glassware. The combination of high purity of color tone and high translucence, as well as a high light refractive index are characteristic of glass colored with rare-earth element oxides. Such oxides can be used both individually and in different combinations [2].

The effect of coloring glass yellow by combined incorporation of cerium and titanium oxides has been known for a long time. However, there have been important contradictions in explaining the nature of the coloring effect and the character of the reaction of cerium and titanium oxide in silicate glass up to now. The appearance of yellow coloring in glass containing cerium and titanium compounds is due to the formation of color complexes between trivalent cerium and tetravalent titanium in the glass [3]. Formation of compounds of the $\text{Ce}(\text{TiO}_3)_2$ and $[\text{Ce}(\text{Ti}_2\text{O}_5)_2]$ type with tetravalent cerium has also been hypothesized. The increase in the intensity of coloration of cerium-containing glass with an increase in the concentration of titanium dioxide is attri-

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buted to the fact that TiO_2 , as a modifier, can decrease reduction of Ce(IV) to Ce(III) [4]. However, the latter has stimulated some objections since Ti^{4+} is easily reduced to Ti^{3+} and CeO_2 interferes in this reduction as a strong oxidant.

We investigated the valence state of cerium and titanium ions in colored glass for electrical applications with a different ratio of cerium and titanium oxides and analyzed the possible composition of the cerium-titanium complexes formed in silicate glass.

Barium-strontium aluminosilicate glass in which a constant amount of cerium oxide and a variable amount of titanium dioxide — from 7 to 15 pts. by wt. — had been incorporated in excess of 100% (i.e., keeping the ratio of all other components constant) was investigated. Optical spectroscopy in the visible wavelength range, IR spectroscopy, and electron paramagnetic resonance were the basic methods of investigating the valence and structural state of cerium and titanium ions in glass-forming melts.

The light transmission spectral curves were made in the wavelength range from 380 to 760 nm for a series of samples. The transmission spectra obtained are shown in Fig. 1. The absorption band edge is gradually shifted to higher wavelengths with an increase in the TiO_2 content, intensifying absorption in the purple and blue parts of the spectrum. This shift to the long-wave region of the spectrum basically characterizes formation of a cerium-titanium complex similar to what is formed in solutions [4].

A pronounced absorption peak in the 500 nm wavelength region is characteristic of Ti^{3+} ions [5]. In our case, such absorption was not observed in the spectra. This suggests that either all of the titanium is in the tetravalent state or a very insignificant amount of Ti^{3+} ions is formed and does not significantly affect the coloring mechanism. The transmission spectra of the glass containing Ce^{3+} and Ce^{4+} ions have an absorption band in the 350–400 nm region [5]. In our case, such absorption is observed and indicates the probable presence of both of these ions in the glass. It should be hypothesized that structural groups formed by tri- and tetravalent cerium and tetravalent titanium ions are formed in this glass in combined incorporation of cerium and titanium oxides. The pronounced change in the slope of the curves of cerium-titanium glass in comparison to glass containing no TiO_2 is because the contribution to formation of optical absorption when both ions (cerium and titanium) are present significantly exceeds the contribution in the presence of cerium ion alone.

The basic colorimetric characteristics of cerium-titanium glass with a constant cerium oxide content and variable titanium dioxide content were determined using the International Lighting Commission's (CIE) three-color coordinates (see Table 1).

It follows from these data that the dominant wavelength is shifted to the long-wave part of the spectrum (574–584 nm), accompanied by an increase in the purity of tone and intensification of the color from light yellow to orange

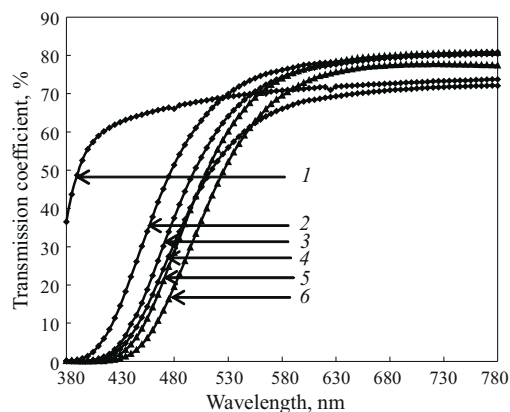


Fig. 1. Transmission coefficient of cerium-titanium glass with a constant content of cerium oxide and variable amount of titanium oxide. TiO_2 content (pts. by wt.): 1) 0; 2) 7; 3) 9; 4) 11; 5) 13; 6) 15.

when the TiO_2 content increases from 7 to 15 pts. by wt. This behavior can be attributed to the high field strength of Ti^{4+} and Ce^{4+} ions. These ions can polarize the surrounding oxygen ions. After polarization of the oxygen ions by the trivalent titanium ions, the electric field of the titanium ions is weakened and as a consequence, the absorption bands are shifted to the longer-wave region. For Ce^{4+} , polarization of the oxygen ions will also shift the absorption band to the long-wave part of the spectrum. As a consequence, the effect of these two ions on the spectral characteristics of the glass in both cases will shift the absorption bands, accompanied by intensification of the color.

The IR spectra were made for glass with a constant CeO_2 constant and variable TiO_2 content (from 7 to 15 pts. by wt.) to reveal any possible structural changes in the structure of the silicon-oxygen structural network in incorporation of a different amount of TiO_2 in the presence of CeO_2 . $[\text{TiO}_4]$ groups can be incorporated in the silicon-oxygen network, replacing $[\text{SiO}_4]$ tetrahedrons, and perceptible distortions should be observed in the structure of the silicon-oxygen network, since the $[\text{TiO}_4]$ tetrahedrons are much larger than the $[\text{SiO}_4]$ tetrahedrons. The ion radii of Si and Ti cations are 0.039 and 0.064 nm. For this reason, the possible amount of titanium ions incorporated in the silicon-oxygen network is limited. Separation with formation of regions rich in SiO_2 or TiO_2 is observed in silicate glass with a significant TiO_2 con-

TABLE 1

TiO_2 content, pts. by wt.	Chromaticity coordinates		Purity of tone, %	Dominant wave-length, nm	Color
	x	y			
7	0.4061	0.4223	50	574	Yellow
9	0.4334	0.4476	65	576	"
11	0.4395	0.4519	70	578	"
13	0.4523	0.4601	85	580	Yellow-orange
15	0.5078	0.4658	93	584	Orange

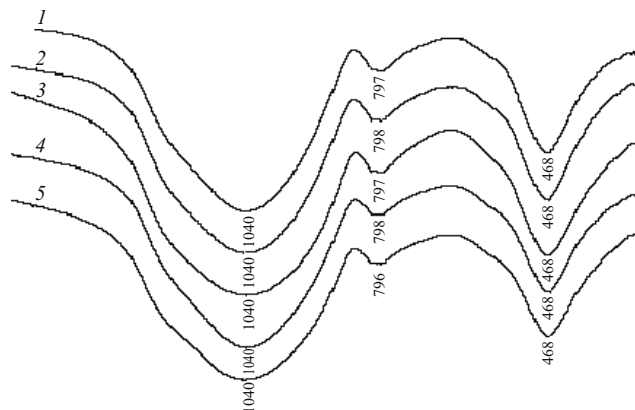


Fig. 2. IR spectra of experimental glass. TiO₂ content (pts. by wt.): 1) 7; 2) 9; 3) 11; 4) 13; 5) 15.

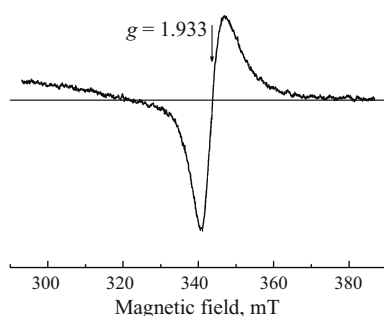


Fig. 3. EPR signal of trivalent titanium.

tent (usually greater than 10 pts. by wt.) the crystallizability of this glass increases sharply, which is widely used in synthesis of glass ceramics.

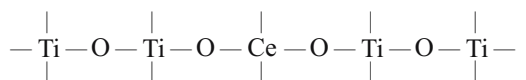
However, all of the experimental cerium-titanium glass exhibited elevated resistance to crystallization even for a 15 pts. by wt. TiO₂ content, which was not characteristic of titanium-containing, cerium-free silicate glass. The IR spectra of cerium-titanium glass with a different TiO₂ content are shown in Fig. 2. Note the total identity of the spectra regardless of the amount of TiO₂ incorporated. These values of the absorption bands correspond to the fundamental bands of the silicon-oxygen skeleton. Titanium dioxide probably is either not incorporated in the silicon-oxygen network in general in the presence of cerium oxide or its presence in the silicate structure is restricted by a defined limit which is constant in all of the glass. No absorption bands were found in general for Ti–O bonds, probably due to the weak activity of these bonds in the IR spectra.

The change in the color of this glass from yellow to orange indicates that in the presence of CeO₂, titanium remains in the tetravalent state, since trivalent titanium colors glass dark blue or even black.

The titanium ion is probably kept in the tetravalent state due to the very pronounced oxidizing effect of CeO₂ and perhaps its partial reduction to the trivalent state. The EPR spectra of a series of glasses containing titanium dioxide alone, cerium oxide alone, and both together were made to reveal

the presence of trivalent cerium and titanium ions. The appearance of an EPR signal which can be assigned to the Ti³⁺ ion (Fig. 3) is observed in glass containing titanium dioxide alone (g factor of 1.933), which is in good agreement with the well-known finding for titanium-containing glasses [6]. Titanium is thus easily reduced to Ti³⁺ in the absence of CeO₂ in the experimental conditions of synthesis. In cerium and cerium-titanium glass, Ti³⁺ and Ce³⁺ ions were not detected, which suggests that tetravalent cerium and titanium ions are the basic structural state of cerium and titanium in color centers. This indicates that tetravalent cerium and titanium ions are the basic structural state of cerium and titanium in color centers. However, this suggests the formation of an insignificant number of tetravalent cerium ions, which does not significantly affect the coloring mechanism.

Based on our study, we can hypothesize that in combined incorporation of cerium and titanium oxides, only a limited part of the titanium, in the form of [TiO₄] tetrahedrons, can be incorporated in the silicon-oxygen structural network with which the tetravalent cerium ion can be bound. The existence of stable compounds in the form of cerium titanates, for example, Ce(TiO₃)₂, [Ce(Ti₂O₅)₂], etc., confirms this role of cerium. As a consequence, formation of the following complex group between cerium and titanium ions is possible in glass when the concentration of tetravalent titanium ions increases in the presence of Ce⁴⁺:



The experimental data obtained in studying the structural state of cerium and titanium in barium-strontium aluminosilicate glass thus allow concluding that active separate reaction between cerium and titanium oxides in their insignificant reaction with the silicate matrix with formation of complex color centers containing both elements takes place in synthesis of the glass. We hypothesize that the color centers between tetravalent cerium and tetravalent titanium primarily appear in the reaction of cerium and titanium in a glass-forming melt.

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