

UDC 666.175.6:666.24:546.82'665

NATURE OF COLOR CENTERS IN SILICATE GLASSES WITH ADDITIONS OF CERIUM AND TITANIUM OXIDES

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Translated from *Steklo i Keramika*, No. 7, pp. 9–13, July, 2009.

Silicate glasses with additions of cerium and titanium oxides are studied. Such glasses are of interest for manufacturing electric lights for automobile headlights and heat-stable light filters. It is established that the characteristic yellow-orange color is due to the formation chromophoric centers containing products from the interaction of cerium and titanium oxides. It is proposed on the basis of optical transmission and photoluminescence measurements as well as XPES data obtained for the composition used in light filters that titanium and cerium are present predominately as the ions Ti^{4+} , Ce^{3+} , and Ce^{4+} .

Key words: silicate glasses, additions of cerium and titanium oxides, color centers, light filters.

The topicality and importance of the problem of developing new optical materials in the glass industry are due to the possibility of controlling their colorimetric characteristics. The glasses must function reliably and keep their optical properties. Examples are glasses for electric lights in automobile headlights, light filters, and other light-engineering articles. The introduction of transition and rare-earth elements capable of coloring the glass matrix as added compounds is one method that is often used to obtain different color hues of glass [1], but such problems are mainly solved empirically. Transition and rare-earth elements introduced into glass can be in the form of ions and chromophoric centers with different composition or they can form small clusters of atoms and nanocrystalline phases (oxides, chalcogenides (provided chalcogens are introduced), and others).

All this makes it necessary to investigate in greater detail the physical–chemical aspects of the state of the form in which heavy elements — in the present work, cerium and titanium — are present in glasses.

Glasses with a combination of CeO_2 and TiO_2 additions are one promising variant of optical materials for manufacturing near-UV and visible range light filters [2, 3]. The particulars of the electronic structure of cerium and titanium ions make selective absorption possible, and when these ions are present together double oxides can form and the lowest

valence states can be stabilized, thereby expanding the optical and functional properties of the glasses.

The present work is devoted to the synthesis and investigation of the properties of silicate glasses when the additions are in the form of combinations of cerium and titanium oxides in a wide range of molar ratios in order to determine the states of these elements in the glasses and to clarify the possible nature of the chromophoric centers which are formed. This work is a continuation of previous studies [4] but with a substantially expanded range of concentrations of the added elements and using photoluminescence and x-ray photoelectron spectroscopy (XPES).

A glass matrix based on the aluminosilicate barium-strontium glass-forming system $SiO_2 - Al_2O_3 - MgO - CaO - BaO - SrO - Na_2O - K_2O - Li_2O$ was used. Two series of glasses with the TiO_2 content varying from 0 to 25%⁵ were chosen for these investigations: 1 – 1.5% CeO_2 and 2 – 10.0% CeO_2 (the CeO_2 and TiO_2 contents were calculated over and above 100% of the other components of the glass-forming system). The molar ratio $CeO_2 : TiO_2$ was used as the main parameter describing the composition of the glasses. The molar ratio $CeO_2 : TiO_2$ in the series of experimental glasses, the color of the glasses, the slope of the transmission spectrum $K_{max} = (dT/d\lambda)_{max}$ calculated for the spectra $T(\lambda)$ in Fig. 1, and the wavelengths corresponding to the maximum slope are presented in Table 1.

A sufficiently wide range of variation of the ratio $CeO_2 : TiO_2$ permits a comparative analysis of the dependence of the optical properties on the content of the oxide ad-

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⁵ Here and below — content by weight.

TABLE 1.

Glass	Molar ratio CeO ₂ : TiO ₂	Glass color	K _{max} /λ _{max}
Series 1:			
1	0.3 : 0.0	Light-yellow	3.50/350
2	0.3 : 1.0	"	3.30/356
3	0.3 : 3.0	"	2.50/361
4	0.3 : 5.0	Yellow	2.20/363
5	0.3 : 6.5	"	1.88/366
6	0.3 : 10.0	Dark-yellow	0.80/398
Series 2:			
1	2.0 : 0.0	Yellow	1.95/375
2	2.0 : 1.0	"	1.20/391
3	2.0 : 3.0	"	0.75/437
4	2.0 : 5.0	Orange	0.62/472
5	2.0 : 6.5	"	0.59/482
6	2.0 : 10.0	Dark-orange	0.58/487

ditions. At the same time the colorimetric properties of both series of experimental samples are of practical interest. The CeO₂ concentrations indicated above were chosen to obtain a series with low cerium content, for which the considerable effect of cerium on the optical properties has already been observed, and with high CeO₂ content which has an even larger effect on the change of the optical properties. The introduction of TiO₂ is limited to 25% because at high contents the glass crystallizes.

The glasses were synthesized in porcelain crucibles placed in a gas furnace at temperature 1450–1500°C with 2 h soaking at the maximum temperature. This gave uniformly colored glasses, whose physical–technical properties (CLTE $87 \times 10^7 - 92 \times 10^7 \text{ K}^{-1}$ and resistivity at 350°C $> 10^6 \Omega \cdot \text{m}$) correspond to the colored glasses used to manufacture color filters and bulbs for incandescent automobile headlights.

The optical light transmission was measured on an MS 122 spectrophotometer in the wavelength range 300–780 nm and the photoluminescence spectra were measured on a Fluoromax-2 fluorimeter ($\lambda_{\text{exc}} = 325 \text{ nm}$). Plane-parallel polished samples of 0.4 mm thick glass were used for optical studies. The luminescence spectra were normalized to 1 with the maximum intensity as the reference value. A correction for the spectrum of the radiation detector was made only by the means in the fluorimeter itself. The XPES spectra were obtained with an ÉS 2401 electron spectrometer (MgK_α radiation, 1253.6 eV) directly for the glass samples without damaging them; ionic cleaning of the surface in vacuum was performed before the spectra were obtained. The positions of the peaks in the XPES spectra were calibrated according to the C 1s 284.6 eV line [5].

Optical Spectroscopy. The transmission spectra for the series of glasses indicated above are displayed in Fig. 1. In

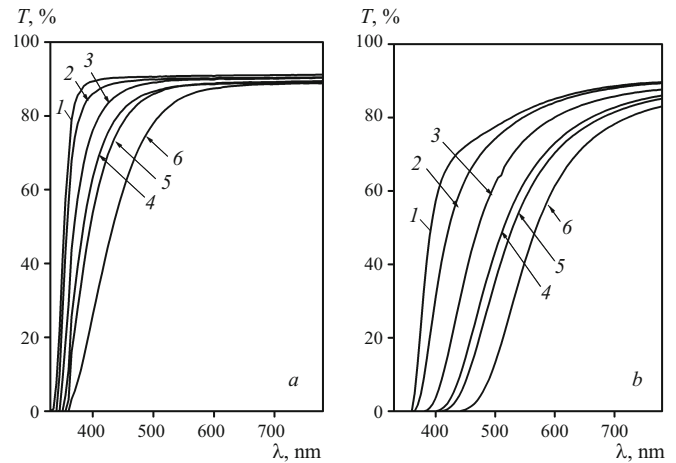


Fig. 1. Optical transmission spectra of glasses with different molar ratio CeO₂ : TiO₂: a and b) series 1 and 2, respectively; the numbering of the curves corresponds to the numbering of the glasses in Table 1.

general, their shape is close to stepped with different slopes; this is due to the presence of an absorption (transmission) edge of the glasses without distinct bands in the experimental region of the spectrum. The glass matrix itself strongly absorbs radiation with wavelength $< 350 \text{ nm}$, so that it is impossible to observe the absorption bands at shorter wavelengths. The addition of up to 10% CeO₂ (see Fig. 1a and b, curves 1) shifts the absorption edge from 330 to 380 nm. The transmission in the long wavelength part of the spectrum reaches 90% but it decreases somewhat when TiO₂ is introduced (see Fig. 1a and b, curves 2–6). The series-1 (1.5% CeO₂) spectrum is characterized by a large slope — 3.5 nm^{-1} , which decreases appreciably as the TiO₂ content decreases. However, the spectrum of glasses containing only CeO₂ (see Fig. 1a, curve 1) does not differ much from the spectrum with TiO₂ additions — 2.5% (see Fig. 1a, curve 2). TiO₂ additions in amounts above 1.5% (see Fig. 1a, curves 3–6) decrease the slope to 0.8 nm^{-1} .

For series-2 glasses with 10% CeO₂ the absorption edge for glass 1 (no TiO₂) lies at 360 nm; the spectrum is flatter (the slope is 1.95 nm^{-1}) than with low CeO₂ content. This attests that as the CeO₂ content increases, a long wavelength shift of the spectrum occurs even without TiO₂. Adding TiO₂ results in an appreciable shift of the absorption edge to 450 nm and decreases the slope to 0.58 nm^{-1} . In general, increasing the TiO₂ or CeO₂ content in cerium- and titanium-containing glasses results in a long-wavelength shift of the spectra and appreciably decreases their slope.

The transmission spectra of glasses containing only TiO₂ [6] are substantially different. This is due to light absorption by Ti³⁺ in the range 500–600 nm. Thus, the contribution of titanium to the optical properties of the experimental glasses cannot be attributed to Ti³⁺, and the state of titanium changes considerably, if titanium is present in the glasses together with CeO₂.

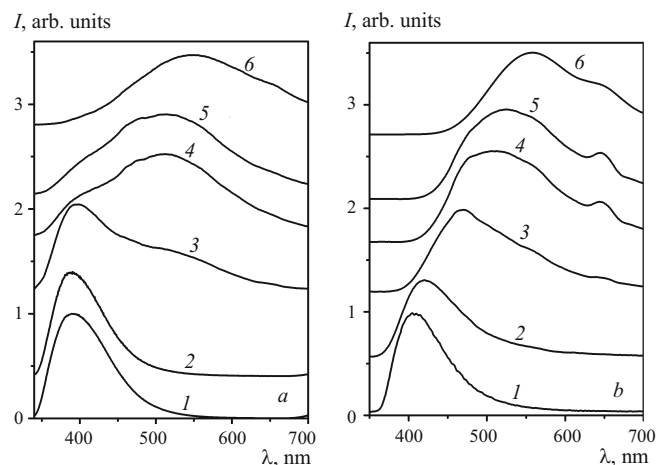


Fig. 2. Photoluminescence spectra of cerium- and titanium-containing glasses (the spectra are normalized at the maximum to 1 and are shifted along the intensity axis by an arbitrary amount). The labeling is the same as in Fig. 1.

The change occurring in the absorption spectrum as the CeO_2 content increases (no TiO_2) can be explained by changes of the valence state of cerium; in the process, predominately Ce^{3+} is formed for low cerium content [7], and as the cerium concentration increases, some Ce^{3+} can be expected to transform into Ce^{4+} [8]. Glasses with different composition, containing Ce^{3+} and Ce^{4+} , are characterized by a series of absorption bands in the range 250–400 nm [7–9], but because of the absorption by the glass matrix only their long-wavelength part can contribute to the spectra presented.

The changes occurring in the spectrum with increasing TiO_2 content (together with CeO_2) as noted above can be explained by assuming that both oxides interact as the glass is formed, and as a result the absorption is determined not by the total contribution of the cerium and titanium ions but rather only by a new oxide phase which is stabilized in the glass. The composition of this phase depends on the ratio $\text{CeO}_2 : \text{TiO}_2$, and the stronger coloring of the glasses with decreasing ratio $\text{CeO}_2 : \text{TiO}_2$ could attest that the number of titanium atoms is greater than the number cerium atoms in the formula for this oxide phase. The large difference between the ionic radii of the cerium and titanium determines the formation of precisely such, more stable, phases — for example, $\text{Ce}_4\text{Ti}_9\text{O}_{24}$ [10].

Photoluminescence. The conclusions that can be drawn from the changes found in the transmission spectra of glasses are limited by the transmission region of the glass matrix itself and by the fact that no distinct individual transmission bands (and, correspondingly, absorption bands) are observed for a given material. In this connection, photoluminescence is a more flexible optical method, since it can be excited at different wavelengths, and emission, as a rule, is represented by emission bands carrying information about the emission centers in the material. For the series of photoluminescence

spectra of the experimental glasses, the excitation wavelength 325 nm (chosen experimentally), at which the absorption by the glass matrix is still not total, was used; this wavelength falls into the region of excitation of cerium and titanium ions forming in the glass.

The photoluminescence spectra obtained for the two series of samples are presented in Fig. 2. The glasses containing only CeO_2 (the curves 1 for both series) have a form that is quite characteristic for materials containing cerium ions — predominately in the form of Ce(III) in glassy and crystalline media [11–13]. This form is due to the fact that the transition $5d \rightarrow 4f$ from the excited state of Ce^{3+} ions occurs into the f level split into ${}^2F_{5/2}$ and ${}^2F_{7/2}$ states [14], and the spectrum consists of at least two bands with different intensities.

The form of the luminescence spectra is considerably different for glasses containing TiO_2 (see Fig. 2a and b, curves 2–6). The long-wavelength components predominating at high TiO_2 content in the subsequent spectra can be seen even for the minimal content of TiO_2 (see Fig. 2a and b, curves 2). The form of the spectra changes sharply with a transition into the region 12–25% TiO_2 . In the glasses 4–6 of both series there is virtually no contribution from the component comprising the main part of the samples containing only CeO_2 ; however, this can be intensified by re-absorption in the range 400–500 nm in the samples (see Fig. 1). But these spectra are very wide and even neglecting the re-absorbed bands they include at least three components. Thus, glasses with low TiO_2 content can be characterized as including the state Ce^{3+} and a contribution from a new form due to an interaction with TiO_2 . It should be noted that the photoluminescence of Ti^{3+} [15] falls in a longer wavelength region (880–980 nm). Conversely, luminescence in the region 500–560 nm is characteristic for Ti^{4+} ; titanium ions are usually found in complex oxide compounds [16]. Both valence states of titanium are likewise quite easily distinguished according to the absorption spectra. Therefore, the states of Ti^{4+} can be regarded as the main states of titanium for interpreting the observed luminescence spectra of cerium- and titanium-containing glasses.

Comparing pairs of samples with molar ratios $\text{CeO}_2 : \text{TiO}_2 = 0.3 : 1.0$ and $2.0 : 1.0$ and $\text{CeO} : \text{TiO}_2 = 0.3 : 3.0$ and $2.0 : 3.0$ it becomes evident that the spectra for these pairs are very similar, i.e., the effect of the cerium concentration is negligible. This could mean that the state of titanium changes even in the presence of minimal amounts of cerium and the composition of the possible phases (compounds) between cerium and titanium in the cerium- and titanium-containing glasses is not constant, while the properties are smooth functions of the ratio $\text{Ce} : \text{Ti}$ within the quite wide, experimental, range of titanium concentrations.

A similar comparison of sample pairs with a higher titanium concentration (see Fig. 2a and b, curves 4–6) shows that they too are very similar, and increasing the cerium content by more than a factor of 6 (from 1.5 to 10%) produces virtually no shift of the maximum in the luminescence spec-

tra; however, the intensity of the short-wavelength section drops appreciably. Taking the shift of the transmission spectra (see Fig. 1*b*) with increasing the cerium concentration into consideration, the cut-off of the short-wavelength section can be attributed to re-absorption. Thus, the similarity of the photoluminescence characteristics for samples with different cerium content becomes even clearer. The appearance of a small peak at the wavelength 650 nm for glasses with the ratios $\text{CeO}_2 : \text{TiO}_2 = 2.0 : 5.0, 2.0 : 6.5,$ and $2.0 : 10.0$ (see Fig. 2*b*) is for the time being not clear within the framework of the existing data and, since glasses with such composition have been obtained for the first time, suggests that precisely such compositions should be specially studied by additional methods.

XPES. The optical properties examined for cerium- and titanium-containing glasses show that the states of cerium and titanium change appreciably compared to glasses doped only with a single element, and the presence of Ce^{3+} , Ce^{4+} as well as different states of titanium Ti^{4+} , Ti^{3+} in different samples, the latter ion being very unlikely, cannot be ruled out. The XPES method can give additional information, independent of optical methods, about the valence state of these as well as other elements present in the glasses. In the present work XPES results are presented only for one sample ($\text{CeO}_2 : \text{TiO}_2 = 1.0 : 6.5$), where the ratio $\text{CeO}_2 : \text{TiO}_2$ corresponds to that in glass with the most intense color [4], and according to the optical data presented above change of the cerium concentration have only a negligible effect. Glass with such composition can be regarded as representative for both series, presented in optical investigations, with 1.5–1.0% CeO_2 .

Figure 3 shows the x-ray photoelectron (XPE) spectra separately for the elements (Si, O) comprising the base of the glass matrix and for Ce, Ti which form chromophoric centers. The Si 2*p* XPE spectra are noticeably asymmetric (see Fig. 3*a*), which could attest to the presence of silicon states which are different from the usual state for SiO_2 and shifted in the direction of lower bonding energies. Such changes in the position of the Si 2*p* line show that a partial chemical interaction occurs between the glass matrix and color centers formed; the nature of this interaction needs further study, since up to now, according to data obtained by other methods (for example, IR spectroscopy [4]) virtually no changes have been observed in the absorption bands of SiO_2 in the glass matrix indicated. The decrease of the binding energy of the levels Si 2*p* as compared to the energy characteristic for SiO_2 [5] can be attributed to the formation of Ti–O–Si and Ce–O–Si groupings; if such groupings arise, the effective degree of oxidation of some silicon atoms will be somewhat lower than in SiO_2 and alkali silicates.

For oxygen, a quite wide but symmetric spectrum is observed at energies corresponding to the O 1*s* level used in XPES of a wide range of oxygen-containing compounds (see Fig. 3*b*). This shape of the spectrum corresponds to the fact that the fraction of oxides with low degrees of oxidation (for

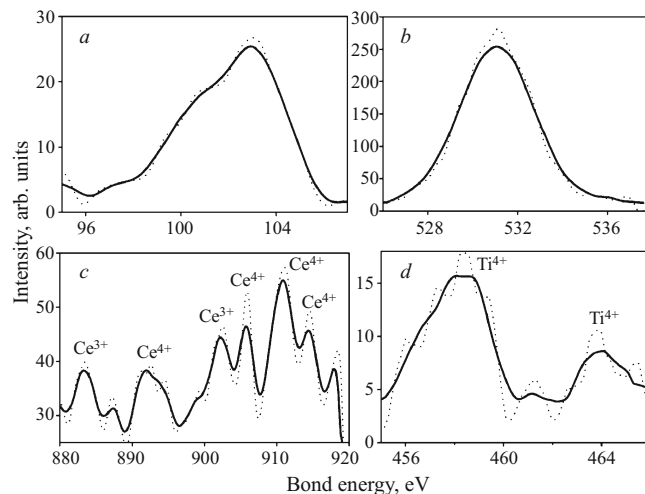


Fig. 3. XPE spectra for the main levels Si 2*p* (*a*), O 1*s* (*b*), Ce 3*d* (*c*), and Ti 2*p* (*d*) of cerium- and titanium-containing glasses with $\text{CeO}_2 : \text{TiO}_2 = 1.0 : 6.5$.

example, Ce_2O_3 and Ti_2O_3) in the experimental glass is small or such oxides are not present at all.

According to the Ce 3*d* lines (see Fig. 3*c*) the presence of cerium atoms in different valence states (Ce^{3+} , Ce^{4+}) follows from a comparison of the XPE spectra of the glasses studied and other cerium-containing materials [17]. The peaks at bond energies 910, 914, 905, and 892 eV could be due to the presence of Ce^{4+} , and the weaker peaks at 883 and 892 eV could be due to Ce^{3+} . It can be concluded on the basis of the ratio of the intensities of the peaks that cerium is present in two valence states but the concentration of Ce^{4+} is appreciably higher.

The XPE spectrum for titanium (see Fig. 3*d*) is not represented by a pair of symmetric peaks for the levels Ti 2*p*_{1/2} and Ti 2*p*_{3/2} easily observed for TiO_2 , but this can be attributed primarily to the Ti^{4+} states [18]. In connection with the low intensity of the entire spectrum of titanium, one reason for which is that the photoemission cross section for titanium is lower than for cerium, it is difficult to make a sound identification of several states, but Ti^{4+} probably predominates.

In summary, it can be concluded on the basis of the XPES results that cerium in glass is present in two states — Ce^{3+} and Ce^{4+} , and the spectrum for titanium is consistent with titanium being present as Ti^{4+} .

Adding cerium and titanium oxides to silicate glass makes it possible to obtain color centers with regulatable visible-range absorption which are of practical interest for manufacturing light filters in the near-UV and visible ranges of the spectrum. Optical transmission and photoluminescence measurements as well as XPES data have shown that the appearance of characteristic coloring is determined not by the total contributions of cerium and titanium ions but rather only by the absorption due to a new oxide phase which is stabilized in the glass. For the composition of the color centers it was determined that titanium is predominately

present as Ti^{4+} and cerium is present in two states — Ce^{3+} and Ce^{4+} , but their coupling complicates the spectroscopic manifestation. The ratio of CeO_2 and TiO_2 introduced into the glass is an effective means for controlling their spectral and color characteristics.

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