OPTICAL PROPERTIES OF Ce–Ti-CONTAINING SILICATE GLASSES

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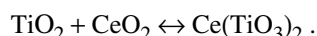**and G. K. Hlushonok**[b]

Silicate glasses doped with ceria and titania have been studied. Such co-doping determines the specific coloration of the glasses with adjustable absorption in the visible spectral region. Based on measurements of optical transmittance and photoluminescence and studies of electron paramagnetic resonance, it was established that the features of their optical properties are due to the formation of chromophore centers incorporating cerium and titanium ions.

Key words: *silicate glass, ceria, titania, chromophore centers, transmission spectrum, absorption coefficient, photoluminescence, electron paramagnetic resonance.*

Introduction. Optical materials containing transition and rare-earth ions are widely used in optics and quantum electronics to fabricate laser glasses that are stable to the action of UV radiation and to develop thermally stable light filters, etc. Interest in the use of Ce and Ti compounds in optical materials grew because of their use to prepare yellowish-orange glasses with consistent optical characteristics and high thermal stability [1]. Such glasses are used to fabricate various items for household and technical purposes and to imitate precious stones. It is important to establish the nature of the coloring effect and the valence and coordination state of the Ce and Ti ions in glasses used as filters for light emitters in the electrical industry because the optical characteristics must be controlled and stabilized.

Optical properties of glasses with both Ce and Ti oxides present in various proportions (silicate, phosphate, borate glasses and thin films) have been studied several times [2–4]. However, there are significant discrepancies in the explanation of the nature of the coloring and the determination of the valence state of the Ce and Ti ions in the glass matrix. According to one study [2], compounds such as $Ce(TiO_3)_2$ and $Ce(Ti_2O_5)_2$ with tetravalent Ce and Ti are formed. Another study [3] explains the yellow color by the effect of Ce and Ti ions on the total optical absorption. Yet another study [4] linked the appearance of the characteristic yellowish-orange color in silicate glasses with Ce and Ti to the formation of colored complexes between Ce^{3+} and Ti^{4+} ions. The involvement of both CeO_2 and TiO_2 in the generation of optical characteristics of films was also proposed [5, 6] but the chemical forms of the compounds were not elucidated.

According to the known chemical properties of Ce and Ti compounds and in accordance with thermodynamic analysis, the following processes in glasses containing both elements are possible

$$CeO_2 \leftrightarrow Ce_2O_3 + O_2 , \quad TiO_2 \leftrightarrow Ti_2O_3\,(TiO_x) + O_2 ,$$

$$CeO_2 + Ti_2O_3 \leftrightarrow Ce_2O_3 + TiO_2 ,$$

$$TiO_2 + CeO_2 \leftrightarrow Ce(TiO_3)_2 .$$

Compounds in the Ce–Ti–O system with different stoichiometry are also probable [7, 8]. Based on the possibility that these and more complicated processes are possible, it can be assumed that Ce and Ti ions are present in the glass ma-

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TABLE 1. CeO_2 and TiO_2 Content in Studied Glasses (mass%) and Forbidden-Band Gap (E_g, eV) Determined from Optical Absorption Data

Series 1					Series 2				
Sample No.	CeO_2	TiO_2	CeO_2/TiO_2 mole ratio	E_g, eV	Sample No.	CeO_2	TiO_2	CeO_2/TiO_2 mole ratio	E_g, eV
1	5.0	0.0	1/0	3.40	6	5.0	15.0	1/6.5	3.04
2	5.0	7.0	1/3.3	3.32	7	4.0	15.0	1/8.2	3.16
3	5.0	9.0	1/3.9	3.25	8	3.0	15.0	1/10.4	3.23
4	5.0	11.0	1/4.8	3.21	9	0.0	15.0	0/1	2.54
5	5.0	13.0	1/5.6	3.14					
6	5.0	15.0	1/6.5	3.04					

trix in various oxidation states, e.g., Ce^{3+}, Ce^{4+}, Ti^{3+}, and Ti^{4+}, and that CeO_x and TiO_x nonstoichiometric oxides with intermediate oxidation states are also present.

The goal of our work was to study the optical properties and establish the valence state of Ce and Ti ions in silicate glass matrices that are promising for the preparation of thermally stable light filters (e.g., colored light bulbs for vehicles).

Experimental. We studied aluminosilicate barium–strontium glasses that are used to prepare items for the electrical industry to which Ce and Ti oxides were added over 100% (i.e., keeping the ratio of main glass components constant). Series 1 glasses were synthesized with a constant content of CeO_2 (5 mass%) and variable TiO_2 (samples No. 1–6); Series 2, with constant content of TiO_2 (15 mass%) and variable CeO_2 (samples No. 6–9). Table 1 lists the content of CeO_2 and TiO_2 in the samples. This range of CeO_2 and TiO_2 ratios is of great interest for application as light filters in automobile lamps [9].

Glasses were synthesized in a gas furnace at $T = 1450^{\circ}C$. The resulting glasses were evenly colored throughout the whole volume. Optical transmission spectra were recorded on an MC 122 spectrophotometer in the wavelength range 350–760 nm for samples 0.4 mm thick; photoluminescence spectra, on a Fluoromax-2 spectrophotometer (Xe lamp excitation source, $\lambda_{ex} = 325$ nm to give the maximum luminescence intensity for the studied glasses). EPR spectra were recorded on an ERS-220 radiospectrometer in the X-band (9.45 GHz) at 298 and 77 K. The high-frequency modulation amplitude (100 kHz) was 1.0 and 5.0 G. The g-factor in spectra of the glasses was determined using a certified standard containing Mn^{2+} ions in a ZnS lattice. The g-factors were $g = 2.0267 \pm 0.0002$ and 1.9858 ± 0.0002 for the third and fourth Mn^{2+} lines. The same standard containing $2.2 \cdot 10^{14}$ centers was used to measure the concentration of paramagnetic centers.

Results and Discussion. *Optical transmission.* Series of transmission spectra of glasses with various CeO_2 and TiO_2 contents showed that the absorption band edge gradually shifted to longer wavelength with a constant CeO_2 content and increasing TiO_2 (Fig. 1a). Such a shift of the absorption band can be characterized as the formation of a Ce–Ti complex according to the optical behavior of an analogous one formed in solutions [2]. The spectrum of glasses containing only CeO_2 (curve 1) differed markedly from the others and had lower absorption in the short-wavelength region and a larger curvature in the portion corresponding to the absorption band edge. The shape of the spectra was practically the same for all Ce–Ti samples in Series 2 glasses with a constant content of TiO_2 and variable CeO_2 (Fig. 1b). The absorption band edge also shifted to longer wavelength with increasing CeO_2 content.

According to the optical behavior of Ti in glasses [10, 11], Ti^{3+} ions typically have absorption bands in the long wavelength part of the spectrum. Such absorption was observed only for glasses containing TiO_2 (sample 9). Furthermore, its spectrum was very different from the others in the studied wavelength range. Such absorption was not observed in all other spectra (with non-zero CeO_2 content, samples 1–8). This indicates that all Ti is present in the tetravalent state or forms very small quantities of Ti^{3+} ions that do not have a noticeable effect on the shape of the spectrum if both TiO_2 and CeO_2 are present.

Absorption spectra of glasses containing Ce^{3+} and Ce^{4+} ions have characteristic absorption bands in the range 250–400 nm [12, 13]. However, it was rather complicated to identify one valence state or the other of the Ce ions
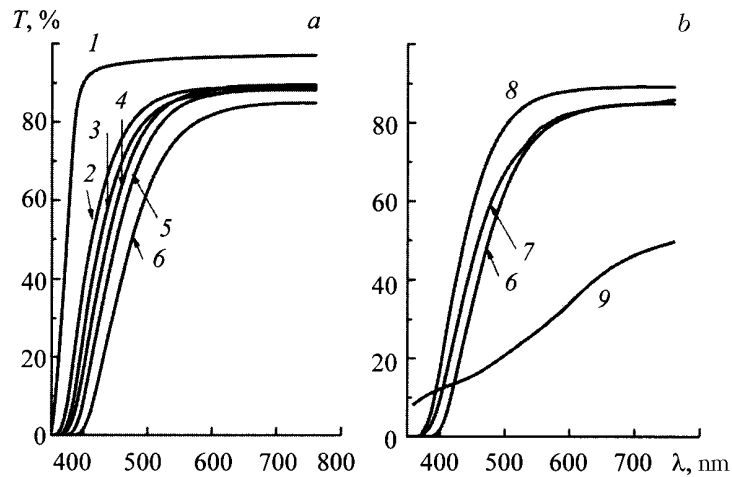
Fig. 1. Transmission spectra of Ce–Ti glasses with constant content of CeO$_2$ (a) and TiO$_2$ (b); sample thickness 0.4 mm; sample numbers according to Table 1.

because of the large overlap of the Ce^{3+} and Ce^{4+} absorption bands and the effect of the amorphous glass environment. Thus, absorption in the range 220–315 nm was characteristic of Ce^{3+} ions taking into account the effect on it of the glass matrix [12]. However, this range in our instance fell in the absorption band of the glass matrix.

Assuming that absorption in the glasses was due to the presence of direct-band semiconductors TiO$_2$ and CeO$_2$ [14] whereas the general shape of the spectra near the absorption edge persisted for the binary system TiO$_2$–CeO$_2$, the forbidden-band gap (E_g) could be determined for the studied glasses. For this the square of the linear absorption coefficient α^2 was plotted as a function of photon energy (E): $\alpha^2 = f(E - E_g)$, which for these semiconductors can be used to determine E_g [15, 16]. The absorption coefficient α was calculated by measuring the optical transmission (T) of the samples. Figure 2 shows α^2 as a function of photon energy for all samples; Table 1, E_g values.

The results indicate that the forbidden-band gap changed for all CeO$_2$/TiO$_2$ samples in the limits 3.04–3.32 eV; for glasses containing only CeO$_2$ and TiO$_2$, E_g = 3.40 and 2.54 eV. The smooth change of E_g with changing CeO$_2$/TiO$_2$ ratio was consistent with the formation of complicated compounds between CeO$_2$ and TiO$_2$ of variable composition and similar optical properties. The edge of the self-absorption band gradually shifted to long wavelength with increasing TiO$_2$ content (curves 1–6). This was accompanied by a decrease of E_g. As the amount of CeO$_2$ increased with constant content of TiO$_2$ (15 mass%, curves 6–8), the edge of the absorption band also shifted to longer wavelength. This was accompanied by a decrease of E_g. The resulting values of E_g as functions of the CeO$_2$/TiO$_2$ ratio were not smooth and had a minimum for the sample with CeO$_2$/TiO$_2$ = 1/6.5. On one hand, the presence of such a minimum for E_g was also consistent with the fact that the properties of the material did not result from the sum of the contributions from the pure oxides and, on the other, indicated that compounds of complicated stoichiometry formed with a structure different from any solid solutions of one oxide in the other.

Photoluminescence. Figure 3 shows photoluminescence spectra (PL) of the glasses. The PL spectra, like the transmission spectra, of samples containing both elements (curves 2–8) were usually very different from spectra of glasses containing only CeO$_2$ (curve 1) or only TiO$_2$ (curve 9). The Ce-containing glasses had a complex band with λ_{max} = 400 nm that is characteristic of Ce^{3+} ions in various matrices.

The optical properties of the glasses can be explained by considering the electronic structure of Ce ions. The electron configuration of the outer shell of Ce^{3+} is $4f^1 5s^2 p^6 d^0$; of Ce^{4+}, $4f^0 5s^2 p^6 d^0$. Electronic transitions with light absorption occur in the former between $4f \rightarrow 5d$ shells. Luminescence involves relaxation from the $5d$-states. Excitation of the remaining electrons in the former requires exceedingly high energies that do not fall in the range of optical studies. However, charge-transfer transitions from O^{2-} to Ce^{4+} are possible in the examined energy range for Ce^{4+} in an oxygen environment [17, 18]. The absorption of Ce ions through these mechanisms covers a rather broad range λ = 200–350 nm because the electronic states of the ions depend substantially on the environment [19, 20] but the ex-
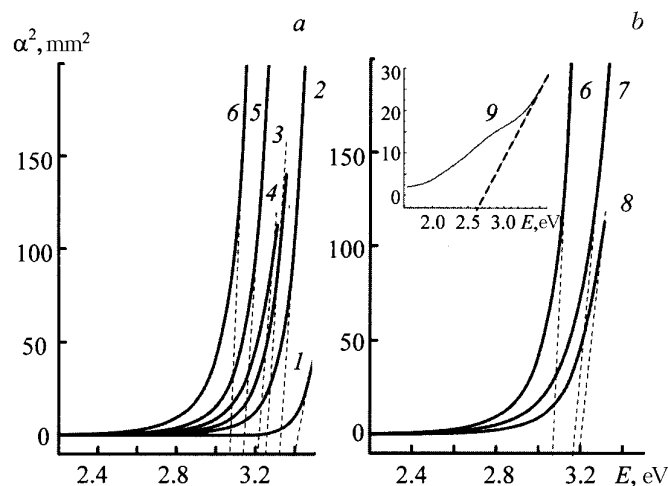
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Fig. 2. Quantity α^2 as a function of photon energy for Ce–Ti glasses with constant content of CeO_2 (a) and TiO_2 (b); sample numbers according to Table 1.

amined glass matrix absorbs strongly in this range. Absorption in the range $\lambda > 350$ nm was more likely related to interband transitions in semiconductors CeO_2, Ce_2O_3, and TiO_2 or compounds of Ce and Ti oxides. It is noteworthy that the oxidation state of Ce in various materials is ill defined. The valence state is rarely established independently using non-optical methods. A similar ambiguity occurs for the assignment of the luminescence bands [21–24]. The PL of Ce-containing glasses depended on the synthetic conditions of the glasses, the Ce concentration, and the exciting wavelength. In general luminescence spectra were rather broad bands with maxima at 350–470 nm. The luminescence bands shifted slightly to long wavelength on going from oxidizing to reducing conditions. The difference in the absorption spectra was more significant, indicating that most of the Ce under reducing conditions was present as Ce^{3+}. A change of the glass composition affected both the width and intensity of the bands. The concentration dependence was consistent with quenching at concentrations greater than 1%. The results for various types of glasses in general confirm the suppositions formulated above and indicate that doping by other elements has a substantial effect [23–26]. PL of Ce ions in quartz sol-gel glasses [27–29] is also rather effective and sensitive to the sintering conditions and to a lesser extent to the Ce concentration. Luminescence spectra of material sintered in vacuo contain a long wavelength peak (or a spectral component that is well seen even without deconvolution) with a maximum at about 490 nm [27–29].

According to the results, glasses doped with both oxides (Fig. 3, curves 2–8) had luminescence spectra that were very different from spectra of glasses doped with only CeO_2 (curve 1) or only TiO_2 (curve 9). Assignment of luminescence in sample 1 to Ce^{3+} ions was rather simple compared with most materials in which it has been observed. However, the presence of Ti in samples 2–8 caused significant changes due to re-absorption and a possible change of the Ce oxidation state. The shape of PL bands of samples doped with both oxides may be specific for the formed Ti–Ce complexes. However, quantitative identification of the components was complicated by re-absorption in the samples, owing to which the luminescence intensity in the short wavelength range decreased as the amount of Ti in the glasses was increased. The relative intensity of the long wavelength range became more apparent, as a result of which the overall shape of the spectrum changed. It can be concluded that the effective PL of Ce ions in glasses was regulated by the CeO_2/TiO_2 ratio in them.

It was concluded that Ti was present mainly in the tetravalent state according to the results for samples of Ce–Ti-containing glasses (2–8) and the literature [30–32]. Luminescence in the range 500–560 nm that is noticeably different from that at longer wavelength for Ti^{3+} ions is characteristic of Ti^{4+} ions. Also, Ti ions are usually found in complex oxides. Both valence states of Ti, as shown, are also rather easily differentiated by using absorption spectra.

Electronic paramagnetic resonance. EPR spectra of three samples (Fig. 4) containing only TiO_2, only CeO_2, and both oxides were recorded in order to determine if trivalent Ce and Ti ions were present. Two groups of signals corresponding to both measurement temperatures could be identified in the spectra. There were weak signals with *g*-fac-
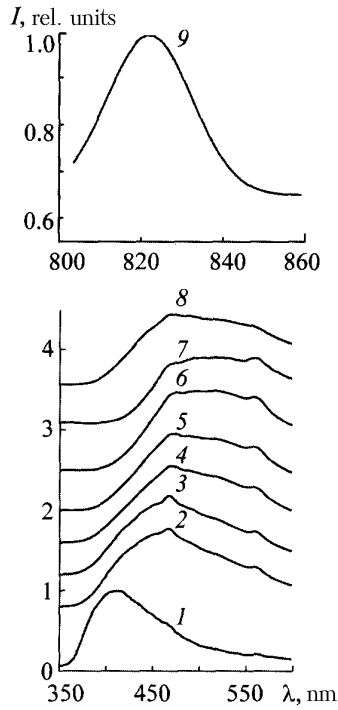
Fig. 3. Photoluminescence spectra of Ce–Ti glasses normalized to a maximum of 1 (shifted along the ordinate by an arbitrary amount; sample numbers according to Table 1).
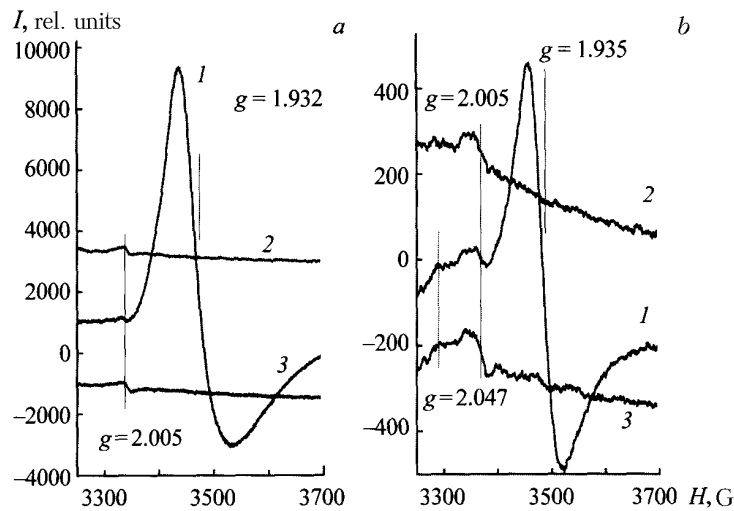

Fig. 4. EPR spectra of glasses containing TiO_2 (sample 9) (1), CeO_2 (sample 1) (2), CeO_2 + TiO_2 (sample 6) (3); T = 77 (a) and 298 K (b), modulation amplitude 5 G.

tors 2.047 and 2.005 for all glasses, anisotropic singlets with g = 1.935 (298 K) and 1.932 (77 K) for samples containing only TiO_2, and no signals for other samples, including glasses containing CeO_2 and TiO_2. The nature of the strong signals and the g-factors agreed well with the presence of Ti^{3+} ions in the glass (electronic configuration $3d^1$) [33, 34]. Therefore, Ti^{4+} in the starting TiO_2 was reduced to Ti^{3+} during synthesis of glasses without Ce. However, the results suggest that the process was not complete. The presence of Ce completely suppressed the reduction even

taking into account that the molar content of CeO_2 was several times less than that of TiO_2 (1/6.5 for sample 6). The additional signals with g-factors >2.0 that were observed for all glasses could be ascribed to the presence of oxygen defects (F-centers, non-bridging oxygen in the glass matrix, adsorbed and ionized oxygen) and were found in glasses of various composition [35, 36]. Detectable EPR signals in this range with g-factors 1.9–2.0 were also characteristic for Ce^{3+} ions formed in CeO_2 (without a glass matrix) during heat treatment [37–39]. However, such signals were not observed either for glass containing only CeO_2 (curve 2) or for glasses with both oxides (curve 3). Therefore, the states of Ce ions in the studied glasses and in pure CeO_2 were considerably different. This was more significant for ions in glasses doped with both oxides.

The temperature at which the EPR spectra were recorded had little effect on the nature of the observed signals. However, signals ascribed to oxygen defects were more evident at room temperature because the intensity of the main signal for Ti^{3+} ions was much weaker. An estimate of the concentration of Ti^{3+} from the EPR data (compared with Mn^{2+} internal standard) gave $\approx$0.1 mass% calculated as TiO_2. This was much less than the amount of TiO_2 added to the charge for synthesizing the glass (15 mass%). Therefore, an exceedingly small fraction of the total Ti in the glasses was found in the Ti^{3+} state. Most of it was in the tetravalent state. Thus, Ti^{3+} ions in Ce–Ti glass (sample 6) was completely absent. The characteristic coloration of these glasses was due to the formation of complex compounds between Ce and Ti oxides. The high sensitivity of the EPR method (which makes it possible to detect concentrations much less than 0.1 mass% because the observed spectrum for this concentration of Ti^{3+} is rather strong) suggested that lower Ti oxidation states in Ce–Ti glasses were practically absent whereas the state of Ce ions differed greatly from that typical of heat-treated CeO_2.

Conclusion. The spectral investigations of Ce silicate glasses with various contents of Ce and Ti oxides and EPR data led to a conclusion about the probable oxidation state of these elements in the glass matrix. The appearance of the characteristic color of Ce–Ti glasses was due to the formation of complexes (chromophore centers) from Ce and Ti ions bonded to oxygen ions and stabilized in the glass matrix. The sharp changes of optical transmission, PL, and EPR of Ce–Ti-containing glasses compared to those of glasses doped with only one element were explained by the presence of the complexes. The predominance of Ti as Ti^{4+} and the spectroscopic properties of Ce ions were probably complicated by several factors. Further investigation by optical methods is required to confirm that it is mixed valent.

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