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Evolution of structural defects of SiO_2-TiO_2 glasses with a change in TiO_2 concentration from zero to phase separation

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The thermal expansion coefficient (TEC) of binary glasses SiO_2-TiO_2 decreases as the TiO_2 concentration grows. At concentration of TiO_2 in the range of 4−6 mol% (in dependence of the applied synthesis method) TEC becomes negative; at concentration of 8−11 mol% devitrification occurs. A combination of photoluminescence (PL) and IR reflection techniques were applied for studying the evolution of point and structural defects in the range of TiO_2 concentration from zero to phase separation. The precision measurements of density showed its drop at TiO_2 content of 7.9 mol% thus evidencing the conversion of glass into a polycrystalline substance consisting of SiO_2 and TiO_2 crystallites. In the TiO_2 concentration range of compatibility of oxides, an ensemble of point defects comprises ≡SiO−Si≡ and $\equiv Ti-O^-$ centers as well as ≡Si−Si≡ and ≡Si−Ti≡ neutral oxygen-vacancies. At the dopant concentration specific for phase separation (TiO_2 7.9 mol%), the PL-active groups of ≡Si−Ti≡ go away, while the IR-detectable Si−O−Ti bridges remain stable.

Keywords: SiO_2-TiO_2 glass, point defects, structural defects, photoluminescence, IR spectroscopy.

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1. Introduction

The production of silicate-titanate glass with zero coefficient of thermal expansion (TEC) has been patented by Corning Inc in 1943. Glasses of the SiO_2-TiO_2 system are characterized by not only low TEC but also by very good optical properties. Therefore, these materials are widely used as transparent protective coatings [1] (in particular, for materials with low TEC) as well as to apply effective antireflection layers on single-crystal and polycrystal silicon solar cells [2].

The TiO_2 oxide itself can be a glass former, however it changes the sixfold coordination to fourfold and fivefold coordination when embedding into the glass network of SiO_2 [3,4]. The SiO_2-TiO_2 homogenous composition is stable until some limit concentration of TiO_2, at which an irreversible phase splitting takes place. Investigations of such binary glasses have shown that at a concentration of titanium oxide in the composite material over ~ 8 mol%, the glass devitrification takes place. The transition from vitreous state to polycrystalline state is accompanied by a sharp change in physico-mechanical properties of the material. At the same time, the literature gives different values of the critical concentration of titanium oxide: 8.5 wt%/6.4 mol% (also, inclusions of crystallites were observed [5]), 11.5 wt%/8.6 mol% [5,6] and 12 wt%/9 mol% [6,7], depending on the method of binary glass synthesis. As a rule, in sol-gel synthesized glasses, the range of compositions with low TEC is wider than in the glasses produced by high temperature hydrolysis of silicon chloride and titanium chloride [1].

Until mid 10s, the professional community in the field of glass believed that density of TiO_2-SiO_2 glasses does not depend on the content of TiO_2 (it should be taken into account that all measurements of density in the aforementioned period were conducted with an accuracy of up to two decimal places [8]). A possible explanation of this phenomenon was that the higher specific weight of the injected titanium oxide (4.23 g/cm^3 versus 2.00 g/cm^3 of SiO_2), related to the bigger size of TiO_4 tetrahedra increased free volume in the glass [9 and references in it]. However, precision measurements performed in the laboratory of Corning Glass Works in 2020 [10] have shown that density of the TiO_2-SiO_2 decreases from 2.2005 g/cm^3 down to 2.1985 g/cm^3 in the region of compatibility of oxides. The discovered change in density can cause gradual distortion of the silicon-oxygen framework with the injection of heavy titanium atoms and, respectively, change the composition of structural defects.

This report is focused on changes in the structure of the defect ensemble in the SiO_2-TiO_2 composite with change in its composition from pure SiO_2 to phase separation. The modification of glass-forming network is manifested in the photoluminescence (PL) and in the IR-spectrum. The pure silicon dioxide does not generate PL because it has no direct optical transitions. However, a photoemission takes place due to the presence of point defects in glass-forming oxides [9]. IR reflection spectra of SiO_2-TiO_2 glasses are sensitive to accumulation of bridging groups of Si−O−Ti due to substitutions of Ti → Si in the TiO_2-doped silicate network.

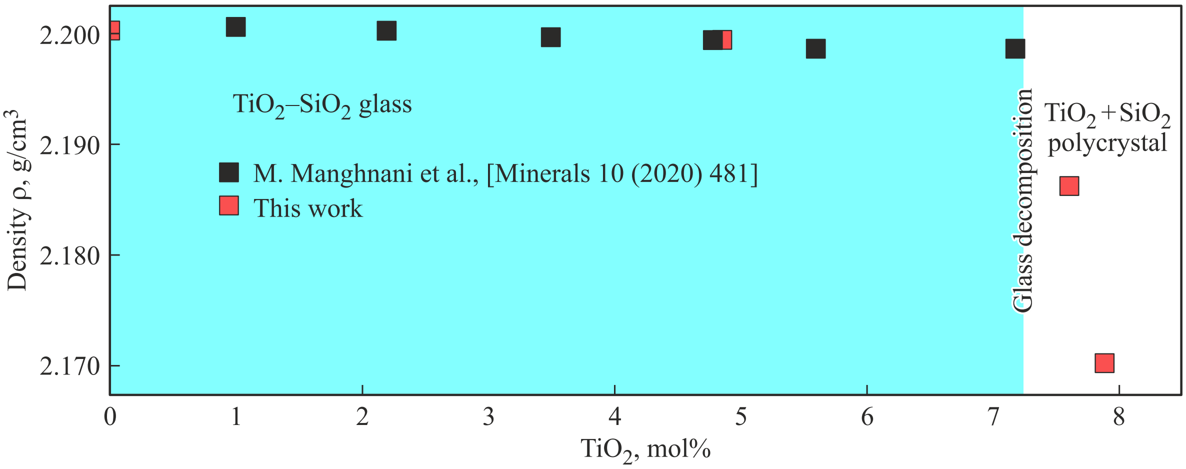

Figure 1. Density of SiO_2-TiO_2 glasses in the range of linear decrease depending on the content of TiO_2.

The injection of titanium affects mechanical properties of SiO_2-TiO_2 binary oxides in the concentration region of their stability [11–13]. The transformation of a glassy structure to the polycrystalline state at the critical concentration of TiO_2 causes a rearrangement of spatial heterogeneity in the solid body, which can have an effect on the specifics of its destruction. In this study the morphology of mechanically damaged surface of titanium-doped silica glass has been evaluated in the range of TiO_2 content from zero to phase separation.

2. Samples and equipment

Glasses of the SiO_2-TiO_2 system were synthesized by high-temperature heating in the flame of a hydrogen torch of $SiCl_4$ and $TiCl_4$ chlorides with a final TiO_2 content of 0, 5.0, 7.3 and 7.9 mol%. The target concentrations were selected taking into account that with the use of this synthesis method the thermal expansion of binary glass linearly decreases from $5 \cdot 10^{-7}/°C$ to $-5 \cdot 10^{-7}/°C$ with TEC crossing the zero level at a TiO_2 content of 5.6 mol% [12]. With a concentration of titanium oxide above 8–9 mol%, the glass devitrification takes place [6].

The precision measurement of sample density was carried out by hydrostatic weighing on a Simadzu AUW 120D analytical balance with a SMK-301 attachment; the distilled water was stabilized at 20.0°C. The accuracy of result reproduction at repeated measurements was $\pm 0.0006\,g/cm^3$.

The PL spectra are recorded using an AvaSpec-ULSi2048L-USB2 OEM fiber-optic spectrometer by AVANTES. The spectra were excited by a LED with an emission wavelength of 370 nm. The IR reflection spectra were recorded with an InfraSpek FSM 1201 Fourier-spectrometer.

To determine mechanical resistance of synthesized glasses, the surface of samples was damaged by a sharpened striker, on which a load of 100 g fell from a height of 70 cm. Changes in the damage morphology were recorded by means of optical photography.

3. Results

In the above-mentioned study [10], density ρ of SiO_2-TiO_2 glasses was measured in the range of its maximum linear decrease from the content of titanium oxide, i.e. in the range of component compatibility. Fig. 1 shows the data of authors of [10] supplemented by the measurements of this study out of the abovementioned region. It can be seen that the density decreases abruptly at $\rho = 7.3$ mol% and becomes even lower at 7.9 mol%.

Fig. 2 shows optical photos of local damages on sample surfaces exposed to the point strike. The shock wave in a pure glassy SiO_2 and a TiO_2 content of 5 mol% caused a local destruction in the form of truncated cone. At a TiO_2 concentration of 7.3 mol% brittle cracks appeared radially to the crater. At a TiO_2 concentration of 7.9 mol% the damage has a form of disordered pattern typical for the destruction of polycrystalline solid bodies.

PL spectra of pure glossy SiO_2 in the range of 450–700 nm are shown in Fig. 3, *a*. To track details of the evolution of overlapped bands with the change in concentration of TiO_2 in the composite material, the PL spectra were approximated by a set of Gaussian oscillators. All components of spectra are referred to point defects in the silicate matrix.

$\equiv Ti-O^-$ and $\equiv Si-O^-$ centers have the same band position (~ 600 nm) in the spectrum [13] (Fig. 3, *b*). The symmetric profile of the sum spectrum goes round the doublet of Gaussian components of 500–550 nm, which belongs to defects of $\equiv Si-Si\equiv$, i.e. to a neutral oxygen-vacancy (NOV) [14,15]. The defect consists of two identical structural units with different localization in the matrix that surrounds singularities [16,17] (for example, with two types of stoichiometric distortions [18]). An analogue to

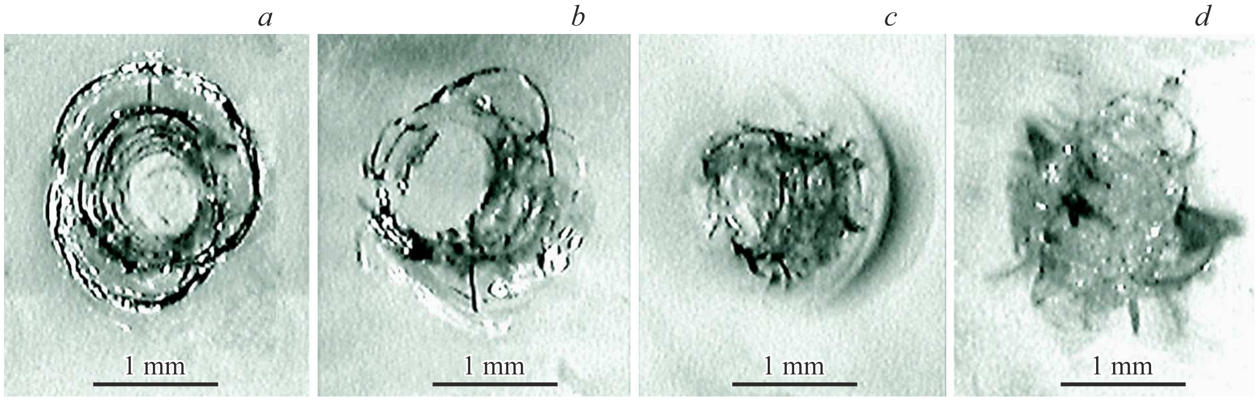

Figure 2. Optical photos of the localized strike-damaged surface of the SiO_2-TiO_2 composite with a TiO_2 content of 0 (*a*), 5.0 (*b*), 7.3 (*c*), 7.9 (*d*) mol%.

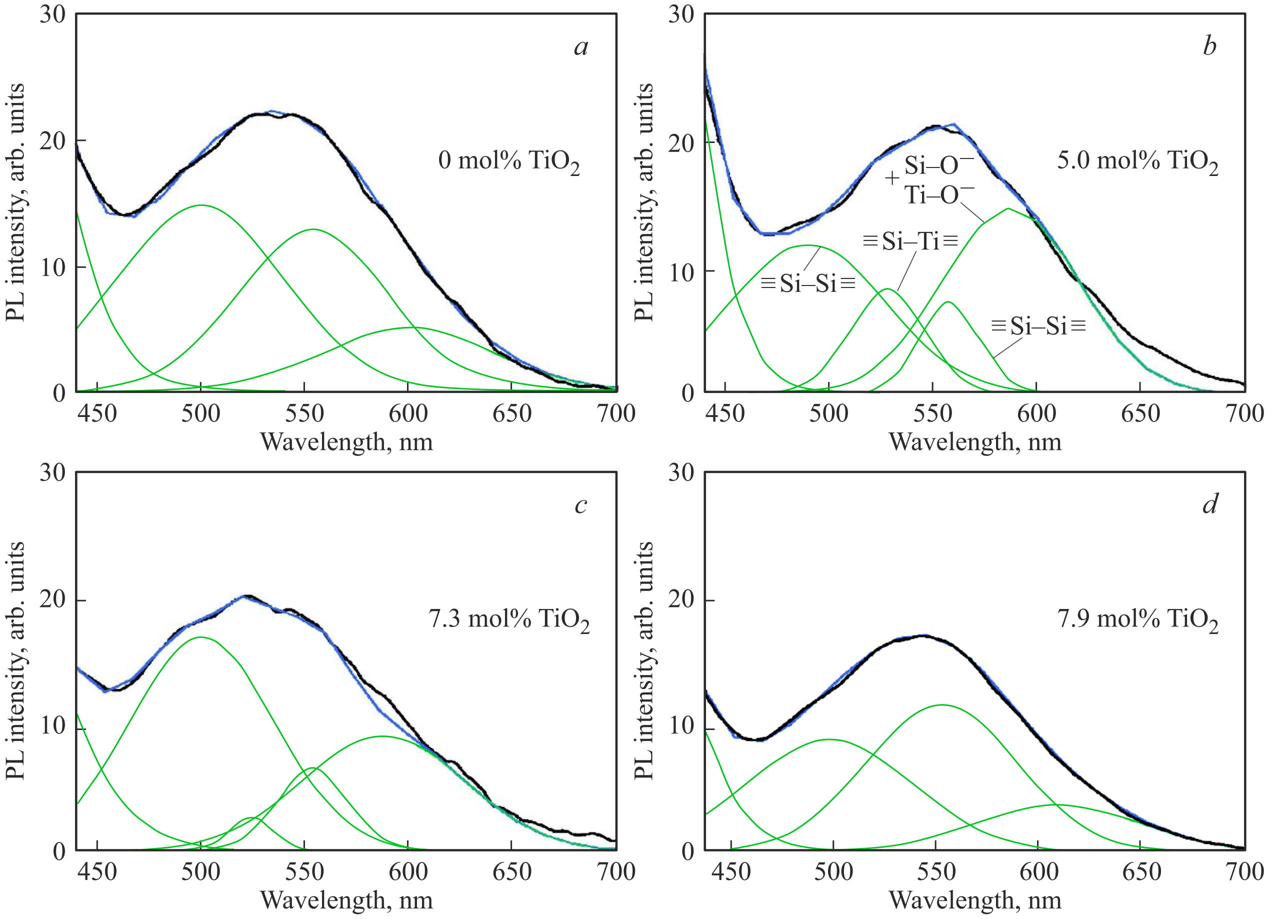

Figure 3. PL spectra of pure (*a*) and titanium-doped SiO_2 (*b–d*) in the spectral region of point defects. Thick wavy lines show experimental spectra, thin lines show calculated Gaussian outlines; thick smooth lines show numerical approximation of spectra.

the 550 nm band in the matrix spectrum is the 530 nm in the TiO_2-doped glass, which is provisionally considered as a hybrid defect with NOV (≡Si−Ti≡) in the spectrum (Fig. 3, *b, c*). The difference in positions of bands of defects between ≡Si−Si≡ and ≡Si−Ti≡ allowed monitoring the presence of atoms injected into the silicate network.

Fig. 3, *b* shows that the concentration of hybrid NOV centers in SiO_2 doped with 5 mol% of TiO_2 is comparable with that of pure silicate NOV defects, while in the sample containing 7.3 mol% of TiO_2 the presence of hybrid centers is significantly lower (Fig. 3, *c*). The FL spectrum of a glass containing 7.9 mol% of TiO_2 (Fig. 3, *d*) is completely

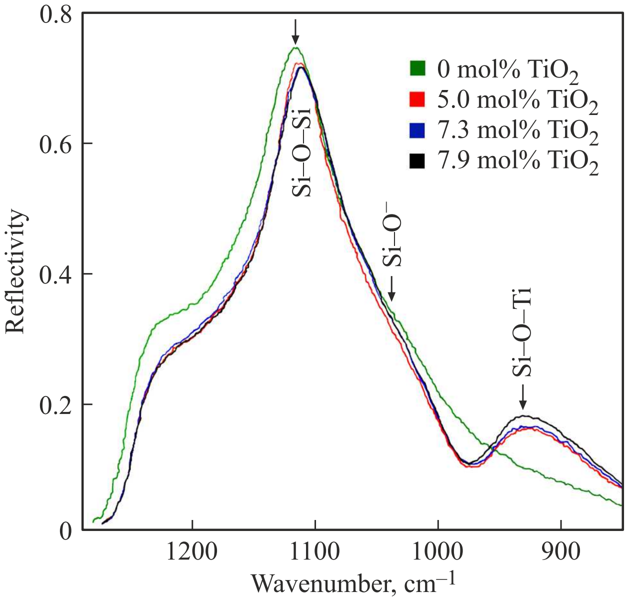

Figure 4. IR reflection spectrum of pure SiO_2 and SiO_2-TiO_2 binary glasses.

free from the 530 cm^{-1} band, which is indicative of the absence of ≡Si−Ti≡ centers. Taking into account the previously shown evidence [6] of the devitrification of binary glasses synthesized from chlorides with a TiO_2 content of about 8 mol%, a conclusion can be made that crystallites of rutile/anatase formed at the phase separation have no Si−Ti bonds. The emergence of the 530 nm band in the spectrum of doped silicon dioxide confirms its reference to hybrid oxygen vacancies.

Fig. 4 shows IR reflection spectrum of pure and doped samples of SiO_2. The prevailing band of 1126 cm^{-1} in the pure material belongs to asymmetric valence oscillations of bridging groups of Si−O−Si. In the spectra of Ti-containing glasses, the band intensity decreases and maximum is shifted to the position of 1116−1120 cm^{-1}. At the same time, in spectra of composites the 935 cm^{-1} band appears.

4. Discussion

The performed density measurements and mechanical tests allowed precise determining of the titanium oxide content that makes the SiO_2-TiO_2 binary glass transforming to a polycrystalline substance. Fig. 1, 2 show that this structural transition is manifested itself at a TiO_2 concentration of 7.3 mol% and is explicit at 7.9 mol%. The sharp decrease in the material density is indicative of large cavities between the formed crystallites.

The use of two spectroscopic methods sensitive to the presence of point defects (PL) and structural arrangement in glasses (IR) allowed evaluating formation/disintegration of the ensemble of weak places in the structural network of the glass and obtaining some characteristics of interatomic bonds depending on the composition of the silicate-titanate compound.

In PL spectra, the highest concentration of ≡Si−Ti≡ centers determined by intensity of the 530 nm band took place at a TiO_2 concentration of 5 mol%. This concentration corresponds to a TEC close to zero [12]. With a TiO_2 concentration of 7.9 mol%, the 530 cm^{-1} band disappears completely due to the crystallization of the titanium dioxide.

As for the IR spectra, the low-frequency shift of the 1126 cm^{-1} band is indicative of a decrease in Si−O−Si angles in the pure SiO_2. The decreased angle of Si−O−Si is typical for cells with threefold and fourfold coordination [19]. The presence of small siloxane rings increases compactness of the glass [20], however, decreases its strength due to the stresses arising in the them [21].

The 935 cm^{-1} band appears in doped glasses only. It is also active in the Raman spectrum of SiO_2-TiO_2 glasses belongs to oscillation of Si−O−Ti bridges [22,23]. In contrast to NOV point defects and centers with nonbridging oxygen of ≡Ti−O$^-$ and ≡Si−O$^-$, hybrid bridges remain stable after the phase splitting. At the same time, it is known [24] that an increase in titanium concentration above the level, which is critical for the compatibility with SiO_2 does not result in increase in the intensity of the 935 cm^{-1} band. This fact means, that residual hybrid bridges are formed only in a glassy material.

5. Conclusion

Active NOV PL-centers in the spectra of titanium-doped SiO_2 manifest themselves as a 550 nm band (≡Si−Si≡) and a 530 nm band (≡Si−Ti≡). The „play“ of intensities of these bands in spectra with a change in the titanium content was observed in the case of PL spectra deconvolution to Gaussian profiles. The ≡Si−Ti≡ groups disappear when the TiO_2 concentration exceeds the level typical for the polycrystallization of components, while the Si−O−Ti bridges, which are active in the IR spectrum, remain stable after the phase separation. The low-frequency shift of the prevailing band in the IR reflection spectrum with the injection of titanium in the SiO_2 is indicative of the formation of three-member and four-member siloxane rings.

Conflict of interest

The authors declare that they have no conflict of interest.

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