

Absorption spectra and luminescence of oxygen-deficient centres in titanosilicate glass synthesised in a steady laser plume. II. Luminescence

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Abstract. The luminescence spectra of titanosilicate glasses, grown in a steady laser plume in an atmosphere of air or nitrogen at normal pressure, were investigated in the spectral range 260–500 nm. The luminescence was excited by the second harmonic of a cw Ar⁺ laser ($\lambda = 257$ nm) and was observed for glasses synthesised in air and nitrogen atmospheres throughout the investigated range of the titanium concentrations by weight (from $\sim 0.1\%$ to $\sim 6\%$). When the titanium concentration was less than 1%, the luminescence spectrum of glass grown in a nitrogen atmosphere had a band with a maximum at $\lambda \sim 280$ nm associated with silicon oxygen-deficient centres and a correlated new strong band with a maximum at $\lambda \sim 380$ nm. An increase in the Ti concentration from $\sim 0.1\%$ to $\sim 0.4\%$ resulted in an exponential fall (by a factor of ~ 4) of the intensity of the 280 nm luminescence band accompanied by a rise of approximately 30% in the intensity of the luminescence in the 380 nm band. Luminescence in the range 350–500 nm was observed in glass grown in a nitrogen atmosphere when the titanium concentration was $\sim 1\%$ – 2% . Glass grown in air there had a wide band in the luminescence spectrum with its maximum near ~ 440 nm (titanium concentration $\sim 2\%$) and a band attributed to the Ti⁴⁺ luminescence (with a maximum near ~ 420 nm when the titanium concentration was 3% – 6%).

Luminescence of titanium-ion-doped silicate, borate, phosphate, and fluorophosphate glasses had not been detected before because the electronic levels of the metal ions are not split by the crystal field of the glass host [1, 2]. Attention was drawn in Ref. [3] to a similarity of the absorption spectra of Ti-ion-doped silica glasses and Al₂O₃ crystals, so that a corresponding similarity could be expected also in respect of luminescence. Extensive data on the Ti luminescence of Ti³⁺:Al₂O₃ laser crystals grown under reducing conditions are available. The observed luminescence bands have maxima at $\lambda \sim 425$ nm (when the excitation is provided by a source with the wavelength 253.7 nm) [4] and at $\lambda = 420$ nm (excitation by two-photon absorption at 532 nm) [5]. The blue luminescence is attributed to the formation of anion

vacancies. The absorption and luminescence bands with maxima near ~ 230 and 420 nm respectively are attributed in Refs [6, 7] to the isolated Ti⁴⁺ ions, but it is pointed out that the precise nature of the bands is not clear [7]. The same luminescence, but emitted from the surface layers of a crystal, appears when the excitation is delivered in the ~ 255 nm absorption band [8]. The luminescence is emitted also by crystals grown under oxidising conditions when the excitation is provided in the ~ 250 and 266 nm bands [9, 10].

It was shown in Ref. [3] that the synthesis of titanosilicate glasses in a steady laser plume gives rise to titanium oxygen-deficient centres (ODCs) and that the concentration of these centres is high. A comparative investigation of the photoluminescence of the samples of glasses grown in oxidising (air) and neutral (nitrogen) ambient atmospheres is reported below.

The conditions during synthesis and the nature of the investigated samples were described in Part I [3]. In the present study, luminescence was excited by cw UV radiation with $\lambda = 257$ nm (second harmonic of an Ar⁺ laser) and of ~ 500 W cm⁻² intensity. A sample was oriented at a small angle relative to the optic axis of a monochromator and perpendicular to the UV beam. The distribution of the luminescence along an investigated sample was studied by moving it perpendicular to the UV beam axis. Spatial resolution achieved in this system was governed by the width of the entry slit of the monochromator and amounted to 0.1 mm.

The distribution of the maximum of the absorption band, attributed to Si-ODCs, was determined earlier [3] for a sample of pure silica glass synthesised in a nitrogen atmosphere. The maximum was found to be approximately constant along the length of the sample. Naturally, this was observed also for longitudinal distributions of the maxima of the Si-ODC luminescence bands (at 280 and 460 nm). Moreover, the germanium impurity was removed in the course of synthesis and this suppressed the Ge luminescence bands observed in the glass target [11].

The longitudinal distributions of the maxima of the luminescence bands of titanium-doped silica glass grown in a nitrogen atmosphere were qualitatively different (Fig. 1a). A characteristic feature of these distributions was the occurrence of major changes in the luminescence band maxima. There was a correlation between fluctuations of the maxima of the Si-ODC luminescence band (280 nm) and of a new (380 nm) luminescence band. The luminescence intensity maxima corresponded to minima of the Ti concentration. The spectral distributions of the luminescence intensity (Fig. 2) were determined for those parts of the sample (Fig. 1a) where the maxima of the $\lambda = 280$ nm luminescence intensity were found at the coordinates $x = 0.6, 1.4,$ and 2.9 mm, respectively. A comparison of the maxima of the

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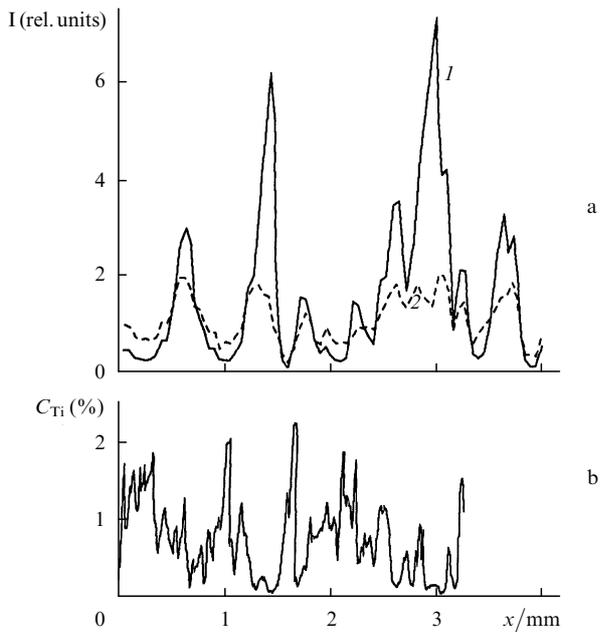


Figure 1. Longitudinal distributions of the intensity of the luminescence band maxima at $\lambda = 280$ nm (1) and 380 nm (2) (a) and of the concentration of titanium by weight C_{Ti} in a sample synthesised in a nitrogen atmosphere (b).

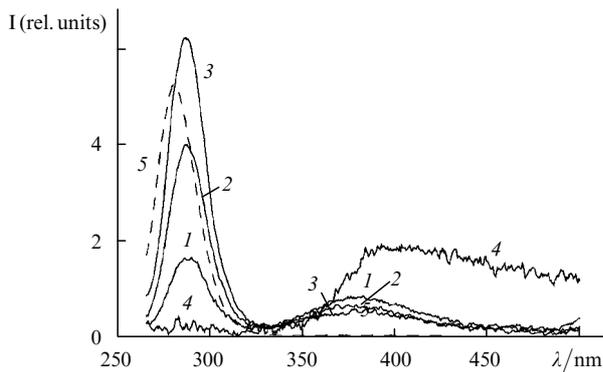


Figure 2. Luminescence spectra recorded in sections of a glass sample with the coordinates $x = 0.6$ mm (weight concentration $C_{Ti} = 0.4\% - 0.5\%$, curve 1), 1.4 mm ($\sim 0.2\%$, curve 2), and 2.9 mm ($\sim 0.1\%$, curve 3) in a part of the sample with $C_{Ti} \leq 2\%$ (curve 4), and the luminescence spectrum of pure silica glass (curve 5) synthesised in a nitrogen atmosphere.

$\lambda = 280$ nm luminescence intensity and of the Ti concentration showed that a strong exponential fall of the $\lambda = 280$ nm luminescence intensity in the sections with $x = 0.6$, 1.4, and 2.9 mm was accompanied by a systematic increase in the Ti concentration to $\sim 0.1\%$, $\sim 0.2\%$, and $0.4\% - 0.5\%$. Going over from the first to the last of these sections we found that the intensity of the $\lambda = 380$ nm luminescence increased by about 30% and the increase was nearly proportional to the distance. In one of the zones with a minimum of the $\lambda = 280$ nm luminescence there was a much wider luminescence band in the spectral range 350–500 nm (curve 4 in Fig. 2). The 280 nm band was not observed for the samples grown in air and the $\lambda \approx 440$ nm luminescence was observed for the Ti concentrations from $\sim 1\%$ to 2% (curve 2 in Fig. 3).

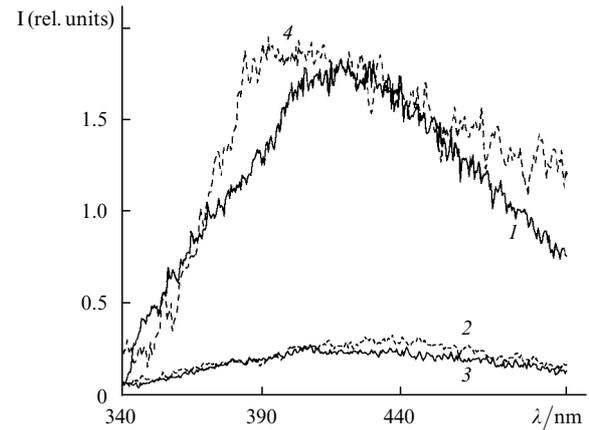


Figure 3. Luminescence spectra of glasses with the weight concentrations of titanium 6% (1), less than 2% (2), and 2%–3% (3), grown in air, when titanium was introduced in the form of a foil (1, 2) or as a TiO_2 powder (3), and also of a sample grown in a nitrogen atmosphere with $C_{Ti} \leq 2\%$ (4).

The luminescence with the maximum at $\lambda \sim 420$ nm was observed for two air-grown samples [12, 13]: in one of them the Ti concentration was $\sim 2\% - 3\%$ (Ti was introduced into the target in the form of a fine TiO_2 powder) and in the other (Fig. 3) it was approximately 6% (Ti was introduced in the form of a foil). A similar band was reported for a $Ti^{3+} : Al_2O_3$ crystal when it was excited in the spectral range 230–266 nm; this band is currently attributed to the Ti^{4+} ions [6, 8–10] (it had been attributed earlier to the Ti^{3+} ions [4, 14]). The investigated silica glass and the Ti^{3+} -doped corundum are known to contain a crystalline TiO_2 phase with an oxygen deficit. This is supported indirectly by the observation that the presence of TiO_2 crystallites specifically gives rise to the Ti^{4+} luminescence of phosphate glasses [2]. The presence of this crystalline phase is needed also to account for the Ti^{3+} luminescence, but in this case the structure should be similar to that of Ti_2O_3 crystals, for example Al_2O_3 . The $TiO_2 \rightarrow Ti_2O_3$ reaction is induced by annealing a crystal in a hydrogen atmosphere [2] and completeness of this transformation is deduced from the disappearance of a strong 144 cm^{-1} band (associated with bending vibrations of the Ti–O–Ti bonds) in the Raman scattering spectrum (such a band is typical of TiO_2 crystals [12]). In contrast to glasses grown earlier and characterised by higher titanium concentrations [12], the samples investigated in the present study did not have a Raman scattering band at 144 cm^{-1} . This indicated a lower sensitivity of Raman spectroscopy, compared with luminescence analysis, in detection of this crystalline phase.

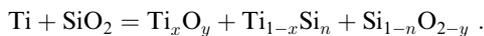
The zones of the glass samples with the Ti concentration ranging from a few tenths of a percent to $\sim 2\%$, grown in nitrogen or in air (in both cases there was no $\lambda = 280$ nm luminescence), were characterised by a shift of the luminescence maximum in the direction of longer wavelengths (Figs 2 and 3). For a glass sample grown in nitrogen the $\lambda = 380$ nm luminescence band was accompanied by a band at longer wavelengths, whereas the spectrum of the air-grown sample had one wide band with a maximum at $\lambda \sim 440$ nm (Fig. 3). The nature of this shift should be governed by modification of the ODCs containing titanium as a result of an increase in the Ti concentration in the glass. A further increase in the Ti concentration resulted in the for-

mation of oxygen-deficient TiO_2 clusters with a typical (for these clusters) luminescence at $\lambda \sim 420$ nm.

When the synthesis took place in an oxidising atmosphere (air), this structural transformation was influenced by a reduction in the oxygen deficit in the resultant Ti_2O_3 - and then TiO_2 -type clusters. A reduction of the oxygen deficit in titanium oxides lengthened the Ti–O bonds (the radius of a metal atom was considerably less than the radius of an oxygen atom) and modified the electron structure of the luminescence-emitting centres (the electron structure of the emitting metal ion was determined specifically by the interaction with oxygen atoms) and, consequently, the emission wavelength changed (~ 440 nm, curve 2 in Fig. 3). This effect clearly occurred also in a ZnO crystal annealed in oxygen, which shifted the luminescence band maximum from 380 to 400 nm [15].

A strong reduction in the intensity of the $\lambda = 280$ nm (Si-ODC) luminescence was observed also in the investigated glass when the titanium concentration was increased from $\sim 0.1\%$ to $\sim 0.4\%$, but this was most probably unrelated to a reduction in the Si-ODC concentration. The Si-ODC concentration in the doped glass was of the same order of magnitude as that in pure silica glass grown in nitrogen, and was governed solely by an increase in the oxygen deficit when the ambient air atmosphere was changed to nitrogen. This was confirmed by the presence of the $\lambda = 280$ nm luminescence band in the spectrum of a synthesised sample of pure silica glass only when it was grown in nitrogen.

On the other hand, introduction of unoxidised Ti into the original target obviously produced an oxygen-deficient glass. The generalised reaction can be represented as follows:



Consequently, the bulk of the ODCs should be present in the structures containing either just titanium ions or both titanium and silicon ions. The example of $\text{Ti}:\text{Al}_2\text{O}_3$ shows that initiation of the photoprocesses between the ODCs requires not only a high Ti^{3+} concentration, but also a low Ti^{4+} concentration in the material, since otherwise the exciting radiation is absorbed by the Ti^{4+} ions and a photocurrent is not detected [6]. When glasses are synthesised in a laser plume, an increase in the dopant concentration increases the concentrations not only of the Ti^{3+} but also of the Ti^{4+} ions [3]. Therefore, the strong fall of the $\lambda = 280$ nm luminescence is a consequence of a stronger absorption in the excitation and luminescence bands as the titanium concentration is increased. The slight change in the $\lambda = 380$ nm luminescence is governed by the low optical density of sections with the Ti concentration approximately $0.1\%–0.4\%$ (the thickness of these sections was ~ 0.45 mm).

The chemical interaction of Ti and SiO_2 should give rise to new absorption and luminescence bands other than those attributed to the Si-ODCs and those typical of the Ti ions. This was indeed observed experimentally (one of the absorption bands was found at 250–280 nm [3] and there was a luminescence band at $\lambda = 380$ nm). Luminescence was excited at room temperature near the maximum of the ~ 258 nm absorption band found by calculation earlier [3]. Under the same excitation conditions a $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystal did not luminesce (a strong red luminescence typical of the Ti^{3+} ions appeared at temperatures below 120 K [6]). Moreover, the very fact that luminescence was emitted by titanosilicate glass in the absence of a crystalline phase (when there was no luminescence band at $\lambda = 420$ nm) indicated, by analogy with

a pure oxygen-deficient silica glass, the presence of ODCs containing both silicon and titanium atoms. We can assume that titanium atoms are incorporated in a structure similar to that of the Si-ODCs.

The appearance of silicides or a high Ti^{3+} concentration lowers by more than an order of magnitude the electrical resistivity of glass [16]. Therefore, we measured the electric resistance of a solidified melt of a target in which the titanium concentration (converted to full oxide) was at least 80% [12]. Between the points separated by a distance of $\sim 2–3$ mm, when the solidified melt thickness was ~ 3 mm, the resistance was ~ 1 k Ω (this was true also between two points inside the solidified melt), which corresponded to a resistivity ~ 100 Ω cm. The electric resistivity of the targets containing Cu was several orders of magnitude higher. Therefore, oxygen-deficient structures containing both Ti^{3+} ions and Ti–Si bonds appeared on the target surface and thus also in the grown samples.

An investigation of silica glass samples surface-modified by ion implantation revealed that an increase in the Ti concentration to $\sim 6.5\%$ increased the fraction of the Ti^{3+} ions in the diamagnetic state (relative to their total number) from 40% to 90% [17] and, as shown in Ref. [3], the Ti^{3+} ions should have a fourfold coordination. Implantation of Ti ions also produced silicides with the highest probable ratio $[\text{Ti}]/[\text{Si}] = 1.1 \pm 0.3$. Irradiation with a beam of 30-keV titanium ions produced samples in which the concentrations of titanium oxides (TiO_2) and of silicides of the TiSi type were in the ratio 1:2 [18, 19]. Unfortunately, the spectroscopic properties of such modified glass were not given in these reports. Therefore, by analogy with the diamagnetic structure of Si-ODCs containing the Si–Si bonds, we can assume that the diamagnetic structure of the Ti–Si ODCs consists of a fourfold-coordinated titanium ion incorporated in the SiO_2 matrix (Ti–O–Si bond) without an oxygen bridge.

The hypothesis that titanosilicides are the structure-forming elements of Ti-ODCs can be checked experimentally by a study of glass samples synthesised in a laser plume. The initial composition of the target must be modified by introducing either titanosilicides or titanium and silicon in its unoxidised state. In the latter case we can expect formation of titanosilicides in the course of a chemical interaction in the melt on the target surface.

This composition of the target should result also in its effective evaporation because of a smaller difference between the boiling temperatures of the components MeSi and SiO_2 [20]. A more reliable identification of the luminescence-emitting Ti or Ti–Si centres would require further investigations of the emission of luminescence by the synthesised glasses when they are excited in the absorption bands at ~ 230 nm (attributed to the Ti^{4+} ions), 250–270 nm (Ti^{3+} , Ti^{4+}), $\sim 305–310$ nm (Ti^{2+}), and ~ 490 nm (Ti^{3+}). This may reveal also possible channels of photochemical reactions which transform the Ti ions.

It is necessary to point out an important feature of the geometry of the target adopted in our investigation: a metal foil was placed inside a silica tube so that during synthesis in air the metal was protected to some extent from the oxidising effect of air. When titanosilicate samples are grown in air, the absence of full oxidising conditions during synthesis was confirmed by colouration of the glasses, by the appearance of characteristic (~ 270 nm) absorption bands, and by the emission of photoluminescence. It was reported in Ref. [20]

that cuprosilicate samples synthesised in air also emitted luminescence.

The adopted synthesis method characterised by the evaporation of a target heated to the boiling temperature of just one of the target components [20] and deposition on the surface at a temperature equal to the melting point of the most refractory component prevented losses of the volatile components during synthesis. In particular, in synthesis of cuprosilicate glasses the number of copper ions in the monovalent or neutral states should be considerably greater than the number of divalent ions. This was due to the fact that the growth of glass occurred at the melting point of silica glass (at least 1700 °C) and the oxide CuO was more volatile than Cu₂O (the boiling temperatures of these oxides were 1180 °C and 1800 °C, respectively [20]). This was confirmed by the luminescence parameters of the glass.

Two photoluminescence bands were observed for the first time simultaneously for the samples grown in this way: a violet band (with its maximum in the region of 405 nm) and a yellow band (with its maximum 535 nm); the intensity of the former was approximately 3 times higher (Fig. 4). The $\lambda = 405$ nm luminescence band, observed for the first time, did not appear when nitrogen laser radiation ($\lambda = 337$ nm) excited a silica glass sample doped with copper and grown by a method similar to that described above [21]. Consequently, the $\lambda = 405$ nm luminescence band was associated with copper in a state responsible for the shorter-wavelength absorption band at ~ 260 nm. According to Ref. [22], the presence of these bands could be explained by the existence of monovalent copper ions in the glass. The 405 nm band clearly corresponded to isolated states of the copper ions, which could possibly be also segregated, and the 535 nm band corresponded to oxygen-deficient Cu_xSiO_y complexes.

In this target structure a chemical interaction of copper with the glass would be possible only during the initial oxi-

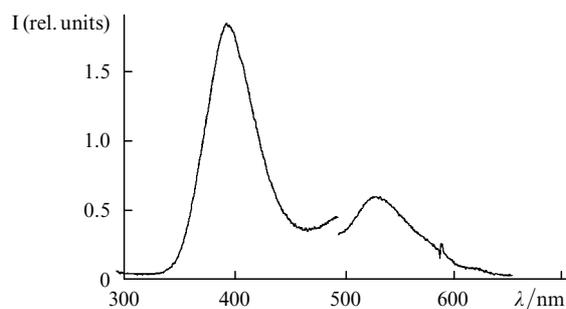


Figure 4. Luminescence spectrum of silica glass doped with Cu ($\sim 0.5\%$) and grown in air.

dation with oxygen from air [20], followed by the formation of compounds of the Cu_xSiO_y type. Therefore, the concentration of such compounds should be considerably less than the concentration of the centres containing just copper and oxygen. On the other hand, synthesis under neutral conditions (for example, in a nitrogen atmosphere) should be accompanied by incorporation of copper in the glass in the form of neutral atoms [13] or, beginning from a certain concentration, as microparticles. In contrast to titanium, in these experiments the copper was found in the intensive evaporation zone (spot) of the target. The metal evaporation regime should then be of transient nature, giving rise to an

inhomogeneous doping of the glass and to loss of the gaseous nature of the evaporation process because of overheating of copper, and should result in the incorporation of the metal (or, which was less likely, of its oxides) in the gas in the form of microparticles [20]. These conclusions were confirmed by the experimental results given in Ref. [21].

We can assume that the photoluminescence of metal-doped silica glasses synthesised in a laser plume should be observed in all those cases when the formation of luminescence centres is associated with a deficit of oxygen in the complexes containing the metal (including the complexes containing silicon and the metal). The oxygen deficit should activate the impurity by the formation of a local impurity level in the band gap in the energy spectrum of silica glass [23].

Layers of doped silica glass with these properties may form also on the surface of a target illuminated nonuniformly with laser radiation in a suitable atmosphere, for example, it should be possible to prepare Cu : SiO₂ layers (or those doped with Ni or Fe) or Si_{1-z}O_{2-y} : M_xO_y, M_xSi_z layers (with, for example, M = Ti, Cr) in a nitrogen atmosphere. Then an effective mechanism for the transport of elements in the melt is thermocapillary convection [20].

These investigations demonstrated that it should be possible to synthesise, particularly in a laser plume, silica glass doped with metals (Ti, Cu) and containing a number (including those not observed earlier) of luminescence centres. The dependence of the spectral properties of this glass on the intensity of the incident radiation [3] indicated that it should be possible to modify this glass photochemically. The influence of optical radiation on chemical transformations in polycrystalline samples containing Ti, Si, O atoms was demonstrated experimentally [24]. Further investigations may reveal potential applications of these glasses, for example, in effective formation of refractive-index gratings, as radiation sources, and as sensors of ionising radiations [25].

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