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Luminescence of Ti^{3+} ions in silica glass

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Abstract. **The $d-d$ luminescence of Ti^{3+} ions was first observed in the double Ti/SiO_2 system at room temperature. Silica glass doped with titanium was synthesised in a steady-state laser plume. The luminescent state was obtained by producing oxygen-deficient centres in the chemical reaction between Ti and SiO_2. Comparison of the luminescence and absorption spectra of the titanium-doped silica glass with the spectra of a Ti^{3+}:Al_2O_3 crystal suggests that the 690-nm luminescence band belongs to Ti^{3+} ions.**

Keywords: *laser plume, titanium-doped silica glass, absorption and luminescence spectra*

In some fields of quantum electronics and especially in fibre optics, silica glass is more widely used than crystals. For this reason, the search for dopant ions producing luminescent centres in glass, which are promising for the creation new laser media, is still urgent. In the visible spectral range, transition-metal ions can serve as such dopant ions.

In this paper, we continue the study [1, 2] of titanium-doped silica glass, which was synthesised in a laser plume. This glass was earlier studied by the methods of absorption, luminescence, and Raman spectroscopy [3 – 6]. The Raman spectra indicated to the presence of titanium in Si – O – Ti complexes in the glass [3] and also showed that the matrix was amorphous. The absorption spectra were measured in the range from 225 to 460 nm with a spatial resolution of $\sim 0.2 - 0.3$ mm [4, 5] which was determined by the diameter of the probe radiation beam. In the range from 190 to 900 nm, this resolution was ~ 6 mm [6]. In the UV region, the absorption band was detected in the range from 260 to 280 nm, which is characteristic for a Ti^{3+}:Al_2O_3 laser crystal containing a great amount of Ti^{3+} ions (compared to Ti^{4+} ions). The absorption spectrum in the visible and near-IR regions represented a broad structureless band [6].

Upon excitation of the glass regions with a low concentration of titanium by a second harmonic of a cw Ar^+ laser at ~ 257 nm, two luminescence bands were detected located in the UV region at 280 and 380 nm [4, 5]. Upon excitation into the 490-nm absorption band of Ti^{3+} ions [6], very weak luminescence was observed in the region of 600 nm (we failed to determine accurately the maximum of this band).

Our studies showed that a chemical reaction between Ti and SiO_2 results in the formation of previously unknown oxygen-deficient luminescent centres. However, the experimental data available are insufficient for the assignment of these centres to any known valence state of Ti. Therefore, the question of the presence of luminescent centres in this glass, which would contain titanium ions Ti^{3+} (in the $3d^1$ state), as in a Ti^{3+}:Al_2O_3 laser crystal, is of great interest.

Titanium-doped silica glass represented a polished plate of size $\sim 4\,\mathrm{mm} \times 10$ mm and thickness ~ 0.45 mm. The distribution inhomogeneity of the titanium concentration varied from tenth fractions to $1\,\% - 2\,\%$ [4]. Regions containing titanium at a higher concentration were more deeply coloured. The coloured regions represented bands oriented along the four-millimetre side of the plate perpendicular to the ten-millimetre side, which was parallel to the growth axis of the glass in a laser plume [4, 5]. We also used a titanium-doped corundum plate of size $\sim 10\,\mathrm{mm} \times 10$ mm and thickness ~ 1 mm for comparative spectral studies.

The transmission spectra were recorded with a Lambda 900 (Perkin – Elmer) spectrophotometer. Luminescence was excited at room temperature at 532 nm by 200-ns pulses of the second harmonic from a *Q*-switched Nd:YAG laser operating with a pulse repetition rate of 1.2 kHz. The luminescence of the titanium-doped glass plate was excited through its 0.45-mm end along the 4-mm side by a laser beam of diameter ~ 1 mm, which was made weakly divergent after passing through a long-focus lens ($F \sim 10$ cm). The luminescence, which was well observed as a column of size $1\,\mathrm{mm} \times 4\,\mathrm{mm} \times 0.45$ mm, was projected on the monochromator slit. A similar scheme was used for detecting luminescence of a Ti^{3+}:Al_2O_3 crystal.

The absorption spectrum of the titanium-doped silica glass exhibits an intense UV band, two absorption bands in the visible region at ~ 500 and ~ 680 nm, and a broad structureless tail extending to $\lambda \sim 1300$ nm (curve *1* in Fig. 1). The difference absorption spectrum, which is obtained by subtracting the spectrum of weakly coloured glass region from that of the strongly coloured glass region, the positions of maxima of the bands are more distinct (curve *3* in Fig. 1). In addition, the difference spectrum exhibits the 270-nm absorption band. The main difference between the absorption spectra of the glass and a Ti^{3+}:Al_2O_3 crystal is that the glass has an additional weakly structured absorption at the wavelengths above 500 nm.

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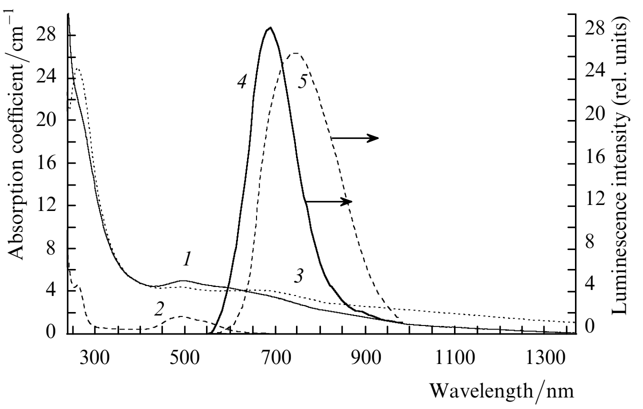

Figure 1. Absorption (*1, 2*) and luminescence (*4, 5*) spectra of titanium-doped silica glass (*1, 4*) and a Ti^{3+}: Al_2O_3 crystal (*2, 5*), and the difference absorption spectrum (in relative units) of strongly and weakly coloured glass regions (*3*).

The luminescence intensity of titanium-doped glass proved to be approximately 800 times lower that that of a Ti^{3+}: Al_2O_3 crystal. The luminescence band of the glass was narrower than in the crystal and was shifted to the blue side (the band maximum was approximately at 690 nm) (curve *4* in Fig. 1).

Note that the absorption and luminescence spectra shown in Fig. 1 are related to different glass regions and cannot be associated with a certain concentration of titanium ions. This is explained by the fact that the weight concentration of titanium is distributed inhomogeneously in the glass and is within $\sim 0.1 - 0.5\,\%$; in addition, the diameter of the probe radiation beam was different in measurements of the absorption and luminescence spectra. One can see from Fig. 1 that the luminescence and absorption bands of the glass are strongly overlapped. This explains the enhancement of luminescence upon the displacement of the exciting beam from the glass region containing a higher amount of titanium, which was more intensely coloured, to the glass region with a lower concentration of titanium.

The spectra presented in Fig. 1 show that, despite a great difference between the structures of the glass (the silicon atom in the tetra-coordinated oxygen environment) and an Al_2O_3 crystal (the aluminium atom in the hexa-coordinated oxygen environment), the absorption and luminescence bands of titanium ions in these matrices are located in the same spectral regions. This is probably explained by the fact that titanium ions replacing silicon in the glass network form, as in an Al_2O_3 crystal, hexa-coordinated complexes. According to the crystal-field theory, which is also widely applied to glasses, the blue shift of the luminescence band in the silica glass means that the crystal field of the glass matrix is higher than that in corundum.

Thus, we have shown that the luminescence centres formed in the titanium-doped silica glass are similar to those present in a Ti^{3+}: Al_2O_3 crystal. The absorption and luminescence spectra of titanium-doped glasses and crystals and, hence, the efficiency of luminescence in these systems can be compared in more detail in studies of glasses synthesised by different methods, which provide a more uniform distribution of titanium in a glass matrix. To reduce the reabsorption of luminescence, the concentration of titanium should be lower than that used in samples studied here.

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