

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

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Abstract. The absorption spectra of titanosilicate glasses with the titanium concentration $\sim 0.1\%–3\%$ by weight were investigated in the wavelength range 225–460 nm. These glasses were synthesised in a steady laser plume in an atmosphere of air or nitrogen at normal pressure. Synthesis in these two atmospheres gave rise to Ti ions of different valence in the glasses. For the same Ti concentration the intensity of the characteristic absorption bands of titanium in its reduced states (Ti^{2+} , Ti^{3+}) with maxima at $\lambda \sim 278$ and 306 nm were 3–6 times higher when the synthesis took place in nitrogen. The enhancement of the 278 nm band was approximately half that of the band at 306 nm. Clear-cut strong absorption in the UV range at 260–280 nm as well as strong absorption in the visible range at 400–500 nm, observed for the first time for titanium-doped silica glass, were the results of a record-high concentration of Ti^{3+} ions, compared with the concentrations found in bulk glass samples prepared by other technologies such as melting, reduction of Ti^{4+} ions, and plasma hydrolysis.

The nature and efficiency of formation of oxygen-deficient centres (ODCs) in pure silica glasses, including those doped with transition-metal ions, have been the subject of many investigations [1–3]. The presence of ODCs can be detected spectroscopically because these centres have wide absorption and luminescence bands in the UV, visible, and near-IR parts of the spectrum. Applications of these materials are based on their photorefractive properties or luminescence utilised in quantum-electronic devices [4, 5].

The ODCs form either during synthesis of glass under reducing conditions [2], or as a result of irradiation with electrons, ions, and γ rays, and by exposure to a reducing gaseous atmosphere. Both mechanisms of formation of ODCs (by external ‘shock’ action and by reduction of SiO_2 resulting from a chemical reaction with an unoxidised metal) are active when silica glass plates are bombarded with beams consisting of transition-metal ions [1, 6, 7].

There is as yet no method for reliable identification of the valence state of Ti ions in silica glass on the basis of their

UV absorption spectra. A characteristic distinction of the absorption spectrum of silica glass doped with Ti^{3+} ions, which distinguishes it from pure silica glass, is a shift of the UV absorption edge towards longer wavelengths (~ 300 nm) [2, 8]. Annealing of such a glass in a nitrogen or hydrogen atmosphere gives rise to wide absorption bands with maxima at $\lambda \sim 450$ and ~ 780 nm, which are attributed to Ti^{3+} ions [8, 9].

Judging by the published data, the absorption spectra recorded in the range 180–900 nm are similar for Ti-doped silica glass and Al_2O_3 crystals [6, 8–12], so that the results of optical investigations of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ laser crystals can be applied to silica glass. The absorption in the spectral ranges 190–220 nm [13], 230 nm [12], and 240–300 nm [14] is attributed to Ti^{4+} ions; that in the regions ~ 250 and 450–550 nm [13], 220 and 400–500 nm [14], and also at 270 nm [12] is associated with Ti^{3+} ions; and the absorption at 246 and 315 nm [14] is due to Ti^{2+} ions.

Si-ODCs were found in bulk silica glass samples grown in a steady laser plume in a nitrogen atmosphere at normal pressure [3]. The same synthesis method was used to produce titanosilicate glasses, including those with a variable Ti^{3+} concentration [15]. Titanium was selected because of its high reactivity in reduction of SiO_2 . We investigated titanium-doped silica glasses, in which formation of ODCs occurs during synthesis in a steady laser plume.

The glasses were synthesised making use of an electric-discharge cw CO_2 laser with an output power of ~ 100 W. The target was a silica glass tube inside which there was a titanium foil strip, ~ 2 mm wide and ~ 0.1 mm thick, extending over the whole length of the tube generatrix. The tube was filled with fine SiO_2 powder of the ‘especially pure’ grade. Glasses were synthesised in air or in a nitrogen atmosphere at normal pressure. The chemical composition of the glasses was investigated with a Camebax SX50 x-ray microanalyser (in steps of ~ 10 μm). Optical measurements were made on longitudinal sections of ~ 0.45 mm \times 3 mm \times 10 mm dimensions prepared from the axial parts of the samples and used in our optical measurements.

The absorption spectra were recorded when radiation from a deuterium lamp was focused on the entry slit of a monochromator, where a sample was located. The spatial distribution of the absorption was measured by moving the investigated sample along the monochromator entry slit perpendicular to the optic axis of the system. An aperture stop kept constant the diameter (0.2–0.3 mm) of the beam passing through the sample. Measurements were made by the lock-in detection method employing a phase-sensitive voltmeter. The optical system for measurements in the spectral range 225–460 nm made it possible to determine the

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distribution of the spectral parameters, for example, along the axis of a section in steps of 0.05 mm. Longitudinal axes of the sections coincided with the direction of growth of the samples and, therefore, such distributions represented time dependences of the properties of the investigated material obtained under varying conditions during synthesis.

An analysis of the distribution of the absorption band maximum of pure silica glass along the long dimension of a sample of Si:ODC (248 nm) revealed that it was approximately constant along the whole length of the section ($\alpha_{248} \approx 0.78 \text{ cm}^{-1}$). Hence, the protection of a growing sample from oxygen in the growth atmosphere was reliable.

Sections of the synthesised titanosilicate samples had clearly distinguishable stripes. Alternate dark and bright stripes forming parts of a circle had convex sides directed opposite to the substance being deposited and they reproduced the moving melt-solidification region. In a quantitative expression the appearance of strong and weakly coloured stripes occurred at titanium concentrations $\sim 3.8\%$ and $\sim 2.2\%$, respectively, for samples synthesised in a nitrogen atmosphere, and at concentrations $\sim 3.0\%$ and $\sim 1.6\%$ growth took place in air. Such a structure of the material of our samples resembled (including distribution of stripes also perpendicular to the growth direction) the striped nature of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystals associated with fluctuations of the Ti concentration [16].

Samples used in the present investigation were synthesised employing a silica target of transverse cross section larger than required for steady-state evaporation [15, 17]. Moreover, the position of the foil in the target tube around the evaporation spot was also uneven. For these reasons, titanium reached the evaporation zone nonuniformly [15, 17] and samples had regions with practically zero concentration of the dopant (Fig. 1). The scatter of the maximum Ti concentrations was considerably less than the scatter of the concentrations themselves. This occurred because target evaporation occurred at the boiling temperature of silica glass and it was this temperature that determined the degree of doping when the initial mass fraction of Ti in the target was kept constant [16]. Steady-state evaporation of a rod of silica glass wrapped uniformly with a titanium foil along its perimeter did not produce such 'dips' of the Ti concentration in the grown sample [15].

However, inhomogeneous doping proved useful in identification of the influence of the concentration of titanium on

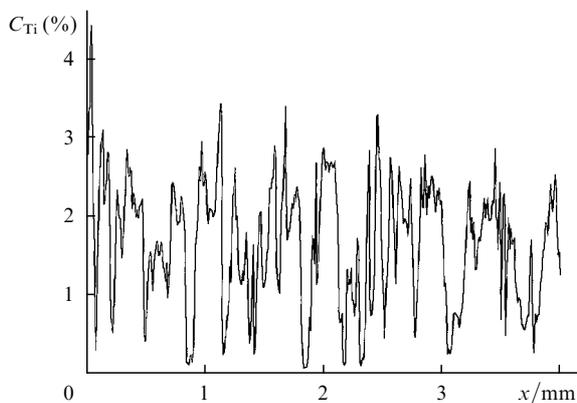


Figure 1. Longitudinal distribution of the titanium concentration C_{Ti} by weight in a section of a sample which was grown in air.

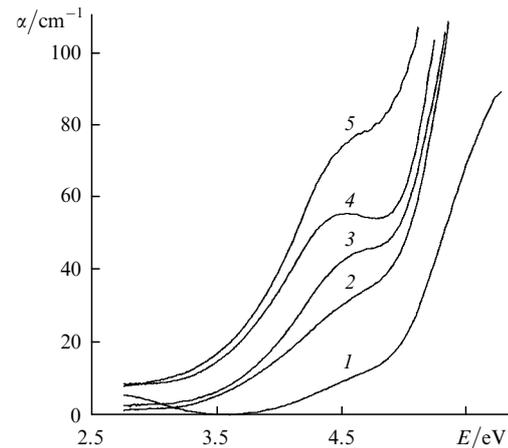


Figure 2. Absorption spectra of glasses grown in a nitrogen atmosphere with the titanium concentrations by weight less than 0.4% (2) 0.6%–0.8% (3), 1%–1.2% (4), and $\sim 1.6\%$ (5). The titanium concentration was not determined for curve 1, but it was less than for curve 2.

the absorption and luminescence of our material. A strong variation of the intensity of the absorption bands from point to point, associated with fluctuations of the Ti concentration, was observed for all the samples. Typical spectra of several regions of a sample grown in a nitrogen atmosphere are given in Fig. 2. Exposure of such a sample to UV radiation with $\lambda = 257 \text{ nm}$ and of power density in excess of 500 W cm^{-2} (the second harmonic of a cw Ar^+ laser) reduced the absorption in the region of $\sim 200 \text{ nm}$ and also altered the intensity of the luminescence emitted during such exposure. Clearly, this exposure induced photochemical reactions involving titanium ions and further studies would be needed to obtain information on these reactions.

All the spectra, including those of the samples grown in air, had a system of UV bands of approximately Gaussian profile with maxima at $E = 3.6 \text{ eV}$ (half-width $\sim 0.46 \text{ eV}$), 4.05 eV (0.48 eV), 4.45 eV (0.42 eV), 4.8 eV (0.45 eV), 5.3 eV (0.45 eV), and 5.6 eV (0.44 eV), where $E = 1240 \text{ nm eV}/\lambda$ (Fig. 3). The positions of the band maxima and their broadening were found with errors of ± 0.05 and $\pm 0.03 \text{ eV}$, respectively. When the titanium concentration was less than 0.4% (curve 1 in Fig. 2), the spectrum had a definite absorption band in the visible part of the spectrum and

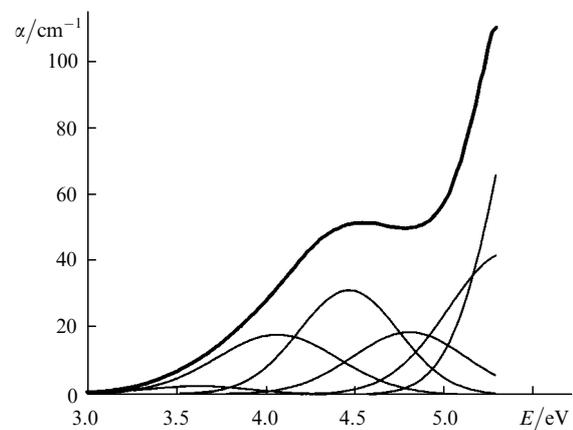


Figure 3. Example of an approximation of the absorption spectrum represented by curve 4 in Fig. 2 by a system of Gaussian bands.

its maximum was at 2.64 eV (half-width 0.46 eV). Usually, however, there was only structure-free absorption in the visible part of the spectrum: this absorption amounted to $\sim 10\text{--}30\text{ cm}^{-1}$ and it increased with increase in the Ti concentration. The constant component of such absorption was ignored in calculations of the UV band intensities.

The structural configuration of the titanium complexes in silica glasses was governed by the amount of titanium which was introduced and by the glass fabrication technology. Titanium was usually introduced into silica glass in the form of the oxide TiO_2 (this was done in the melting and laser hydrolysis technologies). Initially, the Ti^{4+} ions replaced isomorphously the Si^{4+} ions in the glass network and formed TiO_4 complexes. An increase in the titanium concentration resulted in the formation of a structure of the TiO_6 type, including TiO_x clusters, preferable from the energy point of view. An increase in the coordination number of the titanium ions lengthened the Ti–O bonds and, consequently, favoured deviations from stoichiometry in complexes containing few Ti^{3+} ions. The Ti^{3+} ions in an octahedral environment were responsible for the absorption bands with their maxima located in the spectral range 400–500 nm [10].

An improvement in the doping homogeneity shifted towards higher titanium concentrations the concentration limit of coordination modification of titanium complexes and formation of TiO_x clusters. This was observed when the melting technology was replaced with the gas-flame technology and then with the sol–gel technology, which shifted the concentration limit to $\sim 5\text{--}10\%$, $\sim 16\%$, and $\sim 19\%$ [10, 18]. The high homogeneity of introduction of titanium into silica glass during synthesis in a laser plume was confirmed by the observation that a strong colour of the grown glasses began to appear not at thousandths of a percent reported in Ref. [8], but at much higher (by several orders of magnitude, as shown below) Ti^{3+} concentrations.

When synthesis in air was replaced with synthesis in nitrogen the concentration limit of the appearance of strong colouration shifted in the direction of higher titanium concentrations (the shift was from $\sim 2.2\%$ to $\sim 3.8\%$), indicating that the oxidising atmosphere influenced the rate of formation of TiO_6 complexes. When the overall titanium concentration was varied from 0.3% to 3% in the samples grown in the laser plume, the absorption band at $\sim 470\text{ nm}$ was observed clearly only in one case when the titanium concentration was less than 0.4% (curve 1 in Fig. 2). This band could be associated with local fluctuations of the flux density in the plume when the steadiness of the synthesis was not controlled. When ion implantation was employed, such an absorption band was not observed for Ti^{3+} concentrations right up to $\sim 6.4\%$ [6].

The absorption band in the region of $\sim 270\text{ nm}$, representing Ti^{3+} ions, was observed earlier only in a $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystal [12]. It was attributed to the formation of localised excitons. Excitation with light corresponding to this absorption band generated the familiar red luminescence, which confirmed that the structural environment of the Ti^{3+} ions was the same as that responsible for the absorption in the visible part of the spectrum ($\sim 450\text{--}550\text{ nm}$). It is evident from Figs 2 and 3 that strong absorption in the spectral range 270–280 nm (4.4–4.6 eV) with a maximum at $\lambda \sim 278\text{ nm}$ ($\sim 4.45\text{ eV}$) was also observed for the glass samples grown in nitrogen. Such a clear-cut absorption band of this intensity was observed for the first time for titanium-doped silica glass, which indicated a high Ti^{3+} concentration in the glass.

An estimate of the Ti^{3+} concentration based on both these absorption bands [$\sim 470\text{ nm}$ ($\sim 2.64\text{ eV}$) and $\sim 270\text{ nm}$ ($\sim 4.6\text{ eV}$)] could be made making use of spectrum 1 in Fig. 2. These bands, like those of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystals [12], have approximately the same absorption (6.5 and 5.6 cm^{-1} , respectively). Knowing the absorption in the 300–500 and 200 nm bands, we found the Ti^{3+} concentration and the ratio of the Ti^{3+} and Ti^{4+} concentrations: $C_{470}^{\text{Ti}^{3+}} = \alpha_{470}/\epsilon_{470} \approx 6.5\text{ cm}^{-1}/(410\text{ litre mol}^{-1}\text{ cm}^{-1}) \approx 10^{19}\text{ cm}^{-3}$, $C_{470}^{\text{Ti}^{3+}}/C^{\text{Ti}^{4+}} \approx \alpha_{470}\epsilon_{200}/\alpha_{200}\epsilon_{470} \approx 26.8\alpha_{470}/\alpha_{200} = 26.8 \times 6.5\text{ cm}^{-1}/109\text{ cm}^{-1} = 1.6$, where α_{470} , α_{200} , and $\epsilon_{470} = 410\text{ litre mol}^{-1}\text{ cm}^{-1}$, and $\epsilon_{200} = 1.1 \times 10^4\text{ litre mol}^{-1}\text{ cm}^{-1}$ are, respectively the absorption and extinction coefficients for the 300–500 and 200 nm bands [2].

The Al_2O_3 and SiO_2 hosts are characterised by similar intensities of the electric fields created by the Al^{3+} and Si^{4+} ions [19]. Therefore, because of the absence of data on silica glass, we could estimate the relative Ti^{3+} concentration on the basis of the $\sim 270\text{ nm}$ absorption band making use of the absorption cross sections of Al_2O_3 [12]. The ratio of the Ti^{3+} and Ti^{4+} concentrations is given by the expression $C_{270}^{\text{Ti}^{3+}}/C^{\text{Ti}^{4+}} \approx \alpha_{270}\sigma_{220}/\alpha_{220}\sigma_{270} \approx 40\alpha_{270}/\alpha_{220} \approx 3.4$, where $\sigma_{270} = 7.36 \times 10^{-19}\text{ cm}^2$, $\sigma_{220} = 28 \times 10^{-18}\text{ cm}^2$ are the absorption cross sections of Ti^{3+} and Ti^{4+} in the spectral ranges 270 and 220 nm.

It is evident that these estimates of the Ti^{3+} concentration do not represent the maximum possible values for the grown samples because in the calculations we used nonmaximum measured intensities of characteristic absorption bands and also because of uncertainty in the values of ϵ and σ . For example, the absorption cross sections given for the $\sim 490\text{ nm}$ band of corundum [12, 20] differed approximately by a factor of 2.5 and were 3–7 times greater than the cross sections given for silica glass in Ref. [8]. In view of the uncertainty of the extinction coefficients and of the absorption cross sections, the discrepancy of the estimates based on the two absorption bands amounting to a factor of almost 2 can be regarded as satisfactory. Therefore, synthesis of titanosilicate glass in a steady laser plume results in the formation of Ti^{3+} ions in concentrations exceeding that of the Ti^{4+} concentration.

The quantitative influence of the ambient atmosphere and of the titanium concentration on the ionic composition of the synthesised glass is demonstrated in Fig. 4, which gives the dependences of the maxima of the absorption bands at 4.45 eV (278 nm) and 4.05 eV (306 nm), attributed to Ti^{3+} and Ti^{2+} , respectively [14], on the titanium concentration.

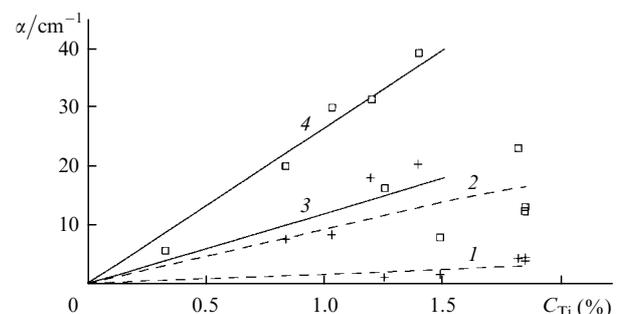


Figure 4. Dependences of the maxima of characteristic absorption bands of glass (points) and their linear approximation (straight lines), plotted for $E = 4.05\text{ eV}$ (1, 3) and 4.45 eV (2, 4) on the titanium concentration C_{Ti} for samples synthesised in air (1, 2) or in nitrogen (3, 4).

The intensities of these absorption bands increased considerably (by a factor of 3–6) when the oxidising nature of the atmosphere (air) was changed to neutral (nitrogen). The increase in the absorption intensity in the 278 nm band was approximately half that in the 306 nm band. The increase in the intensities of the characteristic absorption bands with increase in the total titanium concentration was approximately linear, indicating a constant relative concentration of the reduced ions when the total titanium concentration was increased.

A close analogue of the method of doping silica glass adopted in the present study is a surface change of silica glass in the course of titanium ion implantation [7]. In both cases the final composition of the glasses is the result of the chemical interaction only between Ti and SiO₂. The two synthesis methods differ primarily by the source of energy creating conditions favourable for this interaction. In the course of implantation this energy is released when the surface of a glass interacts with a flux of singly charged metal ions accelerated in an electric field. It is assumed that the chemical interaction then occurs in a small zone of the glass host localised near an ion: this zone is rapidly heated to ~5 kK [21] and it then cools rapidly (is quenched).

However, in our case the interaction between titanium and silica glass occurred at much lower temperatures (2–3 kK on the target surface and in the plume, 2 kK on a growth surface [16]) and the conditions were closer to thermal equilibrium. This occurred because of the long durations of the contact between the metal and the glass in the melts on a target and in a growing sample, since the boundaries of the melts moved at velocities of a few millimetres per minute. The intensity of the absorption band with its maximum at ~6.9 eV, attributed by analogy with Ti:Al₂O₃ crystals to the Ti³⁺ ions [22], was used in Ref. [7] to draw the conclusion that 100% of the Ti ions were in the trivalent state. The absence of the ~450 nm absorption bands (and of the corresponding colouration) right up to concentrations of ~6.4% indicated a fourfold coordination of the Ti³⁺ ions [10].

The ratio of the concentration of the silicon ODCs to the concentration of the implanted metal ions, considered as a function of the concentration of the latter, is 1.5–2 for the Ti ions and remains practically constant (exceeding unity slightly) for the Cr, Mn, and Fe ions [1]. Consequently, the formation of silicon ODCs resulted not only from the ‘shock’ damage to the structure of silica glass, but also from the chemical interaction between Ti and SiO₂. The fall of the relative concentration of Si-ODCs from 2 to 1.5 with increase in the titanium concentration was accompanied by the appearance and enhancement of colouration, which could be explained by a change in the coordination number of titanium from 4 to 6 [6]. This should give rise to bonds of the Ti–O–Ti type responsible for the appearance of the ~450 nm absorption band [10] and evidently also responsible for the paramagnetic properties of the glass [23].

Measurements indeed showed that the intensity of the glass colouration and, consequently, the intensity of the ~450 nm absorption band increased with increase in the Ti ion concentration. However, the number of the paramagnetic Ti centres fell as the number of diamagnetic centres increased [6]. It is thus clear that one more real pretender to the role of Ti-ODCs with the diamagnetic properties can be a structure of the Ti–Si type (by analogy with the Si–Si centres in pure silica glass [21]). A considerable concentration of titanium silicides was found [24, 25] in samples which were implanted

with titanium and also those formed under conditions of thermal-equilibrium interaction of Ti with SiO₂, but the silicides with the [Ti]/[SiO₂] ≈ 1.1 ± 0.3 [26] ratio predominated.

The weak colour of our samples grown in a nitrogen atmosphere began to appear, as in the case of implantation, at concentrations in excess of 2%. The colouration intensity also increased with increase in the Ti concentration, but a band typical of Si-ODCs (~248 nm) did not appear in the absorption spectrum of glasses synthesised in a laser plume and the spectrum of silica glass with implanted Ti ions did not reveal unambiguously the absorption band in the region of ~270 nm. The process of implantation is known to be dominated by the ‘shock’ mechanism of the interaction between the metal ions and quartz glass, leading to rupture of bonds in SiO₂ and formation of a large number of Si–Si centres. Nevertheless, the spectra of the glasses grown by both methods should have an absorption band corresponding to Ti–Si complexes. This is clearly one of the bands in the region of ~250–280 nm, but it does not appear clearly in the overall spectrum of glass with implanted titanium ions because of an overlap with a much stronger absorption band of the Si–Si at ~248 nm.

In conclusion, it should be pointed out that, when titanosilicate glasses are synthesised in a laser plume and a metal foil is employed as a target component, a considerable fraction of titanium is in a reduced state (Ti-ODCs in the form of Ti³⁺ ions). The origin of the strong structure-free absorption in the visible part of the spectrum is not very clear, so that we cannot estimate sufficiently accurately the Ti³⁺ concentration (obviously because of the high Ti²⁺ concentration). Additional investigations are needed of the conditions of formation of strong structure-free absorption in the visible and adjoining UV parts of the spectrum. Better understanding of the degree of influence of titanium on the synthesis of silicon ODCs will require determination of the absorption spectrum of the glass at even shorter UV wavelengths, where the absorption bands of the Si and Ti³⁺ centres can be readily distinguished (the maxima of these bands are located at 7.6 and 6.9 eV, respectively [1]) and, therefore, it should be possible to determine the relationship between their concentrations.

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References

1. Hosono H, Weeks R A, Imagawa H, Zuhr R J. *Non-Cryst. Solids* 120 250 (1990)
2. Leko V K, Mazurin O V *Svoistva Kvantsevoogo Stekla (Properties of Silica Glass)* (Leningrad: Nauka, 1985)
3. Lebedev V F, Marchenko V M, Rybaltovskii A O, Tikhomirov V A *Kvantovaya Elektron. (Moscow)* 21 1097 (1994) [*Quantum Electron.* 24 1020 (1994)]
4. Sukharov S B, Batyaev I M *Opt. Spektrosk.* 72 1367 (1992) [*Opt. Spectrosc. (USSR)* 72 765 (1992)]
5. Hosono H *Jpn. J. Appl. Phys.* 1 32 3892 (1993)
6. Whichard G, Hosono H, Weeks R A, Zuhr R A, Magruder R H III *J. Appl. Phys.* 67 7526 (1990)
7. Weeks R A, Magruder R H III *Proceedings of the Second Conference of the European Society of Glass Science and Technology, Venice, 1993* p. 139
8. Carson D S, Maurer R D J. *Non-Cryst. Solids* 11 368 (1973)
9. Kurkjian C R, Peterson G E *Phys. Chem. Glasses* 15 12 (1974)
10. Amosov A V, Kornev V V, Malyskhin S F, Khotimchenko V S *Fiz. Khim. Stekla* 8 361 (1982)

11. Kaminskii A A, Aminov L K, Ermolaev V L, et al. *Fizika i Spektroskopiya Lazernykh Kristallov (Physics and Spectroscopy of Laser Crystals)* (Moscow: Nauka, 1986)
12. Wong W C, McClure D S, Basun S A, Kokta M R *Phys. Rev. B* 51 5682 (1995)
13. Bessonova T S, Stanislavskii M P, Khaimov-Mal'kov V Ya *Opt. Spektrosk.* 41 152 (1976) [*Opt. Spectrosc. (USSR)* 41 87 (1976)]
14. Neustruev V B *Tr. Fiz. Inst. Akad. Nauk SSSR* 79 3 (1974)
15. Lebedev V F, Marchenko V M, Mel'nik N N, Myzina V A *Kvantovaya Elektron. (Moscow)* 23 633 (1996) [*Quantum Electron.* 26 617 (1996)]
16. Shashkov Yu M *Vyrashchivanie Monokristallov Metodom Vytyagivaniya (Growth of Single Crystals by the Pulling Method)* (Moscow: Nauka, 1982)
17. Lebedev V F *Kvantovaya Elektron. (Moscow)* 24 89 (1997) [*Quantum Electron.* 27 86 (1997)]
18. Emili M, Incoccia L, Mobilio S, Fagherazzi G, Guglielmi M *J. Non-Cryst. Solids* 74 129 (1985)
19. Petzold A, Peschmann G *Enamel and Enamelling (Translated into Russian)* (Moscow: Metallurgiya, 1990)
20. Albers P, Stark E, Huber G J. *Opt. Soc. Am.* 3 134 (1986)
21. Hosono H, Weeks R A *Phys. Rev. B* 40 10543 (1989)
22. Tippins H H *Phys. Rev. B* 1 126 (1970)
23. Dmitryuk A V, Karapetyan G O, Maksimov L V *Zh. Prikl. Spektrosk.* 2 153 (1975)
24. Bertocello R, Glisenti A, Granozzi G, Battaglin G, Caccavale F, Cattaruzza E, Mazzoldi P *J. Non-Cryst. Solids* 162 205 (1993)
25. Russell S W, Strane J W, Mayer J W, Wang S Q *J. Appl. Phys.* 76 257 (1994)
26. Battaglin G, Bertocello R, Trivillin F, Cattaruzza E, Mattei G, Mazzoldi P *Proceedings of the Seventh International Congress on Glass, Beijing, 1995 Vol. 3, p. 15*