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Quantum-Chemical Modeling of Titanium Centers in Titanosilicate Glass

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Abstract—Quantum-chemical simulation of cluster models for a number of titanium centers in titanosilicate glasses has been performed with GAMESS software within the local-density-functional approach, using the BLYP functional, which is known to ensure the best agreement with experimentally determined vibrational frequencies. For each center, we have determined its equilibrium configuration, vibrational frequencies, infrared absorption intensities, and the intensity and degree of depolarization of Raman bands. The results indicate that the totally polarized Raman band near 1030 cm^{-1} is due to single four-coordinate Ti atoms, whereas the partially polarized Raman band near 940 cm^{-1} is contributed by both single (totally depolarized Raman scattering) and double (partially polarized Raman scattering) four-coordinate Ti centers, which accounts for the fact that the relative intensities of these bands depend on TiO_2 concentration. We also show that negatively charged four-coordinate Ti atoms can only be formed through electron excitation, in particular, optical excitation, and that hopping transport of electrons between neutral and negatively charged four-coordinate Ti atoms may be responsible for optical losses of up to 10 dB/km, which should be considered the minimum theoretical level of losses in titanosilicate glasses. The so-called Ti^{3+} centers may be both six- and three-coordinate Ti atoms, but not four-coordinate.

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INTRODUCTION

Titanosilicate glasses containing ≤10% titania offer low transmission losses in the range 1.0–1.6 μm and strong Raman bands with Raman shifts from 500 to 1200 cm^{-1}, which makes them potential materials for fiber optics. To assess the potential of titanosilicate glasses for use in Raman fiber lasers and optical amplifiers for advanced optical fiber communication systems, it is necessary to know how titanium atoms are incorporated in the titanosilicate glass network and to investigate the properties of the resulting titanium centers: their structure and vibrational spectrum and the intensity of the corresponding Raman, absorption, and luminescence bands. In the present paper, these issues are addressed theoretically, using quantum-chemical approaches to model titanium centers.

Consider literature data on the incorporation of titanium atoms in the silica glass network.

Coordination. Sandstrom et al. [1] investigated titanosilicate glasses containing 3.4, 7.5, and 9.5 wt % TiO_2. According to their results, most of the Ti atoms in those glasses substitute for Si atoms to form TiO_4 tetrahedra. In addition, at TiO_2 contents of 7.5 and 9.5 wt % they identified six-coordinate Ti atoms, 5 and 18% of the total amount of Ti, respectively. According to the x-ray absorption spectroscopy data reported by Henderson and Fleet [2], Ti atoms substitute for Si to form TiO_4 tetrahedra in titanosilicate glasses containing ≤11.6 mol % (14.9 wt %) TiO_2. In a later x-ray absorption study by Henderson et al. [3], the Ti atoms in homogeneous TiO_2–SiO_2 glasses were shown to be five-coordinate at TiO_2 contents below 3.6 wt % and predominantly four-coordinate (with a very small fraction of five-coordinate atoms) at higher TiO_2 contents. Six-coordinate Ti atoms were not detected. Anderson et al. [4] found only four-coordinate Ti atoms in titanosilicate glasses containing 8 mol % TiO_2. Larger coordination numbers (six-coordinate Ti) only appeared at TiO_2 contents of 18 mol % and above. At 41 mol % TiO_2, the dominant species was six-coordinate titanium. As pointed out by Henderson and Fleet [2], homogeneous titanosilicate glasses can only be prepared at moderate TiO_2 contents. Glasses containing 8.3 mol % TiO_2 are stable toward TiO_2 crystallization at room temperature, while those containing about 15 mol % TiO_2 are metastable. At the same time, Zhai et al. [5] obtained stable homogeneous glasses at TiO_2 contents of 10 and 20 mol %. According to experimental and theoretical studies reported by Petkov et al. [6], the average coordination number (CN) of Ti in amorphous TiO_2 samples prepared by different procedures ranges from 4.5 to 5.6. It seems, therefore, likely that the content of five-coordinate Ti atoms is high in all

noncrystalline substances containing sufficiently large amounts of titania.

Vibrational spectra. Bobovich [7] studied Raman scattering in barium orthotitanate, Ba_2TiO_4, which is known to contain Ti in tetrahedral coordination. The Raman band at 745 cm^{-1} was attributed to the totally symmetric mode of the TiO_4 tetrahedron. A Raman scattering study of Na_2O–TiO_2–SiO_2 multicomponent glasses of different compositions [8] showed that, at Na_2O concentrations exceeding the TiO_2 concentration, the spectra contained a strong band in the range 875–980 cm^{-1}, consisting of two components (polarized at 920 cm^{-1} and depolarized at 960 cm^{-1}). At an inverse relationship between the Na_2O and TiO_2 concentrations, the spectra contained a broad polarized Raman band in the range 710–790 cm^{-1}. The Ti atoms were assumed to be four-coordinate (TiO_4 tetrahedra) in the former case—so that the features at 920 and 960 cm^{-1} were attributable to Ti–O stretches—and five-coordinate in the latter. Varshal et al. [9] reported the Raman spectra of various titanosilicate glasses, R'_2O–TiO_2–SiO_2 (R' = Li, Na, K) and R"O–TiO_2–SiO_2 (R" = Mg, Ca, Ba), and compared them with data for crystalline analogs. The following conclusions were drawn from their results:

1. In the Raman spectra of TiO_2 (anatase and rutile), $MgTi_2O_5$, $PbTiO_3$, and $K_2TiSi_3O_9$ crystals, no bands attributable to octahedrally coordinated Ti atoms can be identified. Such bands are only observed for titanosilicates in which the TiO_6 octahedra share corners to form chains (605 cm^{-1} in sphene, $CaTiO_5$, and 765 cm^{-1} in narsarsukite, $Na_2TiSi_4O_{11}$).

2. The signature of five-coordinate Ti atoms in crystalline materials is a strong Raman band in the range 775–900 cm^{-1}, which arises from stretching vibrations of the O=Ti double (titanyl) bond in the O=Ti(O–Si)$_4$ "hemioctahedron." This band was observed in the spectra of the $K_2Ti_2O_5$ and La_2TiO_5 titanates and in those of titanosilicates, such as fresnoite, $Ba_2TiSi_2O_8$, and natisite, Na_2TiSiO_5. The significant variation in the frequency of this band with composition was attributed to the influence of cations on the O=Ti bond length.

3. A characteristic band of four-coordinate Ti atoms in crystals is the one at 900–1000 cm^{-1} (solid solution of TiO_2 in cristobalite, $6TiO_2 \cdot 94SiO_2$).

4. The properties of four- and five-coordinate Ti atoms in glasses differ little from those in crystals, so that the Raman spectrum of a glass is an envelope of the spectra of its crystalline analogs. Vibrations of O=Ti double bonds involving five-coordinate Ti atoms are represented by a band at 800–860 cm^{-1}, and those of the TiO_4 tetrahedra give rise to a band in the range 920–960 cm^{-1}. At the same time, the properties of six-coordinate Ti atoms change significantly in going from crystals to glasses, and, accordingly, the Raman spectra of glasses differ markedly from those of crystalline analogs. Six-coordinate Ti atoms in glasses are believed to be responsible for the kink at 700–750 cm^{-1} in their Raman spectra.

An important result is that Varshal et al. [9] determined the composition limits of five-coordinate Ti atoms in titanosilicate glasses.

Chandrasekhar et al. [10] investigated IR absorption and Raman scattering in quartz glass doped with 1.3 to 14.7 wt % TiO_2. They observed Raman bands at 945 and 1115 cm^{-1} due to Ti atoms; the latter band was totally polarized. The IR spectrum showed a band at 945 cm^{-1}. The corresponding vibrations were identified as the F_2 and A_1 vibrational modes of isolated TiO_4 tetrahedra in the quartz glass network.

Chmel et al. [11] reported the IR reflection and Raman spectra of SiO_2–TiO_2 glasses containing 4–6 mol % TiO_2. They observed IR and Raman bands at 935 cm^{-1} and a Raman band at 1015 cm^{-1}. Their integrated intensity was found to rise linearly as the TiO_2 content was increased to <5 mol %. Those bands were assigned to vibrations of Ti–O bonds in isolated TiO_4 tetrahedra. At TiO_2 contents above ≃4 mol %, they revealed a Raman band at 700 cm^{-1}, which was assigned to vibrations of Ti–O bonds in TiO_6 octahedra. The intensity of that band increased with increasing TiO_2 content.

Absorption, luminescence, and ESR spectra. To assess the coordination of Ti atoms in crystals and glasses, Varshal et al. [12] took advantage of resonance Raman scattering. From frequency-dependent resonance Raman scattering cross sections, they determined the effective electronic absorption frequencies in a number of titania-containing crystals and glasses. They obtained 364 and 397 nm for four-coordinate Ti atoms (TiO_4) in $6TiO_2 \cdot 94SiO_2$ glass and Ba_2TiO_4 crystals, respectively; 430 nm for five-coordinate Ti atoms (O=Ti(O–Si)$_4$) in natisite (Na_2TiSiO_5) and fresnoite ($Ba_2TiSi_2O_8$) crystals and $40BaO \cdot 20TiO_2 \cdot 40SiO_2$ glass; and 425 nm for six-coordinate Ti atoms (TiO_6) in rutile (TiO_2) and sphene ($CaTiO_5$) crystals.

Koepke et al. [13] revealed absorption at wavelengths below 380 nm, due to four-coordinate Ti atoms (TiO_4) in titanosilicate glass-ceramics, accompanied by 460-nm luminescence.

Lebedev and Medvedkov [14, 15] observed absorption in the range 200–250 nm and luminescence at 420 nm in titanosilicate glasses containing 0.1–6 wt % TiO_2, which were assigned to four-coordinate Ti.

Dianov et al. [16] and Lebedev et al. [17] reported absorption bands at wavelengths below 300 nm (most likely, near 270 nm) and at 500 and 680 nm in titanosilicate glasses containing 0.1–6 wt % TiO_2. Those absorptions were attributed to Ti^{3+} centers. In addition, they observed structureless absorption at wavelengths

of up to 1300 nm and luminescence at 690 nm, which was brighter at lower TiO_2 concentrations.

The assumption that TiO_2-doped quartz glass contains Ti^{3+} centers warrants special attention. Most workers refer to analogy with titanium-doped sapphire, Al_2O_3:Ti. Titanium substituting for a trivalent Al ion in sapphire must be in the oxidation state 3+ and, hence, can be regarded as a Ti^{3+} center. At the same time, titanium substituting for a tetravalent Si ion in quartz glass is in the oxidation state 4+ and must be regarded as a Ti^{4+} center. Six-coordinate Ti atoms in the quartz glass network are also tetravalent, forming two extra bonds by a donor–acceptor mechanism—transfer of two electrons from neighboring oxygens. Thus, Ti^{3+} centers in titanosilicate glass should be regarded as defects. It is reasonable to assume that Ti^{3+} centers may be produced, e.g., by ionizing radiation (probably, including UV) [18, 19] or may be formed as oxygen-deficient centers during glass preparation under reducing conditions or in an oxygen-deficient environment [20].

The structure of Ti^{3+} centers in titanosilicate glasses is the subject of much controversy. According to Amosov et al. [18], they result from "radiochemical reduction" of $Ti^{(4+)-}$ centers, i.e., from electron capture at tetrahedrally coordinated Ti atoms, leading to monoclinic distortion of the TiO_4 tetrahedron. In addition, Amosov et al. [19] assume that the Ti^{3+} center may be an analog of the E' center, a three-coordinate Ti atom resulting from the disruption of one of the Ti–O bonds in the TiO_4 tetrahedron. In a number of reports [14–17, 20], mention was made of sixfold (octahedrally) coordinated Ti atoms as Ti^{3+} centers, but without analyzing the origin of the unpaired electron in such centers.

Main properties. Analysis of literature data makes it possible to formulate the current views on titanium centers in titanosilicates.

1. The signatures of four-coordinate Ti atoms (TiO_4) in titanosilicates are

the IR absorption band at $\simeq$940 cm^{-1} and two Raman bands in the ranges 900–945 (partially polarized) and 960–1115 cm^{-1} (totally polarized),

(electronic) optical absorption at wavelengths shorter than 400 nm (<250 nm in titanosilicate glasses), and luminescence near 450 nm.

2. The signatures of five-coordinate Ti atoms are

the strong Raman band in the range 775–900 (in different crystals) or 800–860 cm^{-1} (in different glasses), due to stretching vibrations of the O=Ti double (titanyl) bond in the $O{=}Ti(O{-}Si)_4$ pyramid and

(electronic) optical absorption at $\lambda \simeq 430$ nm, accompanied by no luminescence.

3. The signatures of six-coordinate Ti atoms (TiO_6 octahedra) are

the Raman band whose frequency varies from $\simeq$600 cm^{-1} in crystalline $CaTiO_5$ (sphene) and 700–750 cm^{-1} in different glasses to 765 cm^{-1} in crystalline narsarsukite ($Na_2TiSi_4O_{10}$) and

(electronic) optical absorption at $\lambda \gtrsim 410$ nm (no luminescence has been observed).

4. Ti^{3+} centers in titanosilicate glasses result in three absorption bands, located at $\lesssim$300, 500, and 680 nm, and luminescence at 690 nm.

It should be emphasized that these views are derived predominantly from experimental data.

The main purpose of this work is to check the models underlying these views using quantum-chemical simulation.

QUANTUM-CHEMICAL SIMULATION

Titanium centers were simulated using cluster models. Dangling bonds on the surface of clusters were saturated with hydrogen atoms. All calculations were performed with GAMESS software [21] within the local-density-functional approach, using the BLYP functional, which is known to ensure the best agreement between calculated and experimentally determined vibrational frequencies. We used the basis sets and ECP effective potentials proposed by Stevens et al. [22]. In addition, the basis sets included *d*-state polarization functions, one for each oxygen or silicon atom ($\zeta = 0.80$ and 0.395, respectively). As shown by Amado and Ribeiro-Claro [23, 24], this basis ensures good description of the properties of the systems in question. For hydrogen atoms, we used the standard 3-21G basis.

For all of the centers studied, we performed direct optimization of the geometry of the corresponding clusters. After inferring the equilibrium configuration of each center, we calculated its vibrational frequencies, the intensity of IR absorption bands, and the intensity and polarization of Raman bands. In what follows, the intensity of IR absorption bands is given in $D^2/(a.u.m.\ Å^2)$. For neutral centers, we indicate Raman intensities normalized by the intensity of the Raman band at 1032 cm^{-1} in the Ti^0_{IV} center (see below). Unfortunately, we failed to calculate the absolute Raman intensities for charged centers. For such centers, we report Raman intensities normalized by the intensity of the Raman band due to the totally symmetric mode of the corresponding center.

For some centers, we calculated the energies of excited electronic states and the oscillator strengths of the transitions involved by the configurational interaction (CI) method. In constructing the CI matrix, we took into account six to eight doubly filled orbitals and the same number of empty orbitals, as well as excited electronic configurations, up to threefold. This choice was dictated by our computational facilities and, as shown by control calculations for a number of diatomic molecules, enabled calculation of the energy and oscillator strengths of electronic transitions with a relative accuracy of 10–15%.

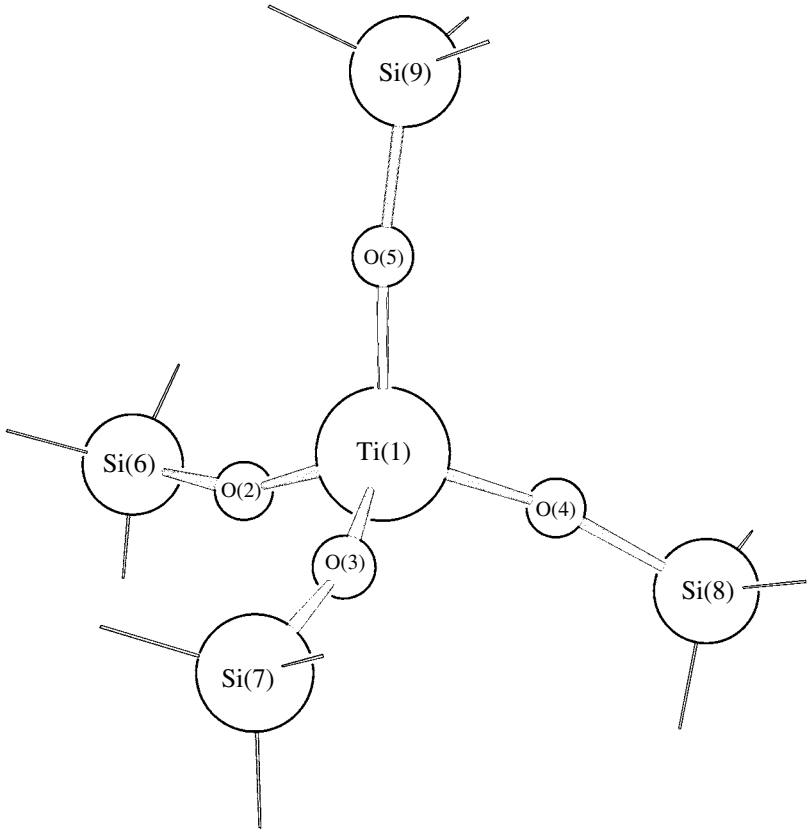

Fig. 1. Simulated configuration of the Ti^0_{IV} center.

Single neutral four-coordinate titanium atom (Ti^0_{IV}). A single neutral four-coordinate Ti atom in titanosilicate glass was represented by a $Ti(–O–SiH_3)_4$ cluster in the form of a TiO_4 tetrahedron surrounded by four SiH_3 groups, which modeled SiO_4 tetrahedra. The equilibrium configuration of the Ti^0_{IV} center is shown in Fig. 1, and its geometric parameters are listed in Table 1.

Table 1. Geometric parameters of the simulated configurations of Ti_{IV} centers

Atoms	Bond length, Å			Atoms	Bond angle, deg		
	Ti^0_{IV}	Ti^-_{IV}	Ti^{2-}_{IV}		Ti^0_{IV}	Ti^-_{IV}	Ti^{2-}_{IV}
Ti(1)–O(2)	1.827	1.908	1.918	O(2)–Ti(1)–O(3)	108.0	110.9	100.0
Ti(1)–O(3)	1.826	1.905	1.888	O(2)–Ti(1)–O(4)	109.2	107.8	104.4
Ti(1)–O(4)	1.827	1.905	1.898	O(2)–Ti(1)–O(5)	109.7	110.6	135.2
Ti(1)–O(5)	1.826	1.901	1.900	O(3)–Ti(1)–O(4)	109.1	110.5	116.1
				O(3)–Ti(1)–O(5)	110.0	107.7	98.6
				O(4)–Ti(1)–O(5)	110.8	109.5	103.2
Si(6)–O(2)	1.675	1.667	1.669	Ti(1)–O(2)–Si(6)	160.0	142.4	133.1
Si(7)–O(3)	1.674	1.671	1.685	Ti(1)–O(3)–Si(7)	164.7	143.5	152.2
Si(8)–O(4)	1.673	1.666	1.672	Ti(1)–O(4)–Si(8)	165.1	144.4	136.5
Si(9)–O(5)	1.673	1.655	1.652	Ti(1)–O(5)–Si(9)	172.9	157.0	150.5

According to our calculations, the frequency of the totally symmetric vibrations A_1 of the TiO_4 tetrahedron in the center of Ti_{IV}^0 accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 1050 cm^{-1}; the relative intensities of the corresponding IR absorption and Raman bands are 0.06 and 1.00, respectively; and the degree of depolarization of the Raman band is 0.001. The frequency of the threefold degenerate vibrations F_2 of the TiO_4 tetrahedron, also accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 945 cm^{-1}; the sum intensities of the IR absorption and Raman bands for the three degenerate modes are 92.32 and <0.01, respectively; and the degree of depolarization of the Raman band is 0.750. For the analogous vibrations accompanied by symmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, we obtained the following results: the frequency of the A_1 mode of the TiO_4 tetrahedron is 480 cm^{-1}; the intensities of the IR absorption and Raman bands are 0.01 and 0.03, respectively; the degree of depolarization of the Raman band is 0.005; the frequency of the F_2 mode of the TiO_4 tetrahedron is 582 cm^{-1}; the sum intensities of the IR absorption and Raman bands for the three degenerate modes are 0.73 and 0.05, respectively; and the degree of depolarization of the Raman band is 0.740.

According to calculation results, the electronic absorption in the Ti_{IV}^0 center is only significant at photon energies above 9 eV ($\lambda \lesssim 140$ nm).

Single negatively charged four-coordinate titanium atoms (Ti_{IV}^- and Ti_{IV}^{2-}). Singly and doubly negatively charged four-coordinate Ti atoms in titanosilicate glass were simulated using the same cluster as in the case of the neutral center Ti_{IV}^0, but the cluster had a charge of $-1e$ and $-2e$, respectively.

As follows from the calculations for the neutral center Ti_{IV}^0, extra electrons in the Ti_{IV}^0 center must be localized at the empty d orbital of the central Ti atom. Since the Ti d states are degenerate, it is reasonable to expect that the initially tetrahedral structure of the Ti_{IV} center will be Jahn–Teller distorted. Indeed, according to our calculations the TiO_4 tetrahedron is compressed along one of the C_2 axes in both charge states. The compression is stronger in the two-electron center. The geometric parameters of the equilibrium configurations of the Ti_{IV}^- and Ti_{IV}^{2-} centers are listed in Table 1.

Our calculations show that, in the Ti_{IV}^- center, the frequency of the totally symmetric vibrations of the distorted TiO_4 tetrahedron, accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges (an analog of the A_1 mode in the neutral center Ti_{IV}^0), is about 970 cm^{-1}, the intensity of the corresponding IR absorption band is 1.71, the intensity of the Raman band is taken to be 1.00 for charged Ti_{IV} centers, and the degree of depolarization of the Raman band is 0.056. In the Ti_{IV}^{2-} center, the frequency of this mode is 913 cm^{-1}; the IR absorption and Raman intensities are 4.06 and 0.15, respectively; and the degree of depolarization of the Raman band is 0.136.

The threefold degenerate mode F_2 of a regular tetrahedron corresponds to the following modes in the distorted tetrahedron of Ti_{IV}^-: the twofold degenerate mode E near 829 cm^{-1} and the A_1 mode at 865 cm^{-1}, also accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges. The sum intensities of the IR absorption and Raman bands for the two degenerate modes E are 19.54 and 2.12, respectively, and the degree of depolarization of the Raman band is 0.742. For the A_1 mode, the intensities of the IR absorption and Raman bands and the degree of depolarization of the latter are 9.36, 1.23, and 0.714, respectively.

In the Ti_{IV}^{2-} center, the threefold degenerate mode F_2 of the neutral center, accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, corresponds to the A_1 mode at 855 cm^{-1} and the twofold degenerate mode E near 783 cm^{-1}. For the A_1 mode, the intensities of the IR absorption and Raman bands and the degree of depolarization of the latter are 2.41, 0.15, and 0.077, respectively. The sum intensities of the IR absorption and Raman bands for the two degenerate modes E are 3.50 and 0.40, respectively, and the degree of depolarization of the Raman band is 0.508.

In both charge states, the frequencies of the vibrations of the distorted tetrahedron that are accompanied by symmetric Ti–O and Si–O stretches in the Ti–O–Si bridges fall in the range 400–520 cm^{-1}. In contrast to those of a regular tetrahedron, individual modes of the distorted tetrahedron are severely mixed and are difficult to identify.

In addition, our calculations indicate that the Ti_{IV}^- center is characterized by electronic absorption near 3 eV (wavelength near 415 nm), due to a Ti d–d transition. The calculated lifetime of the corresponding excited state is on the order of 1 ms.

Pairs of neutral four-coordinate titanium atoms ($2Ti_{IV}^0$). Pairs of neutral four-coordinate Ti atoms ($O_3Ti–O–TiO_3$) in titanosilicate glass were modeled using an $(H_3Si–O–)_3Ti–O–Ti(–O–SiH_3)_3$ cluster, containing two TiO_4 tetrahedra bridged by an oxygen and surrounded by six SiH_3 groups, modeling SiO_4 tetrahedra. The equilibrium configuration of the $2Ti_{IV}^0$ center is shown in Fig. 2, and its geometric parameters are listed in Table 2. In this configuration, the TiO_4 tetrahedra are tilted approximately 40° about the Ti–Ti axis off the D_{3h} configuration. Since the local symmetry of the

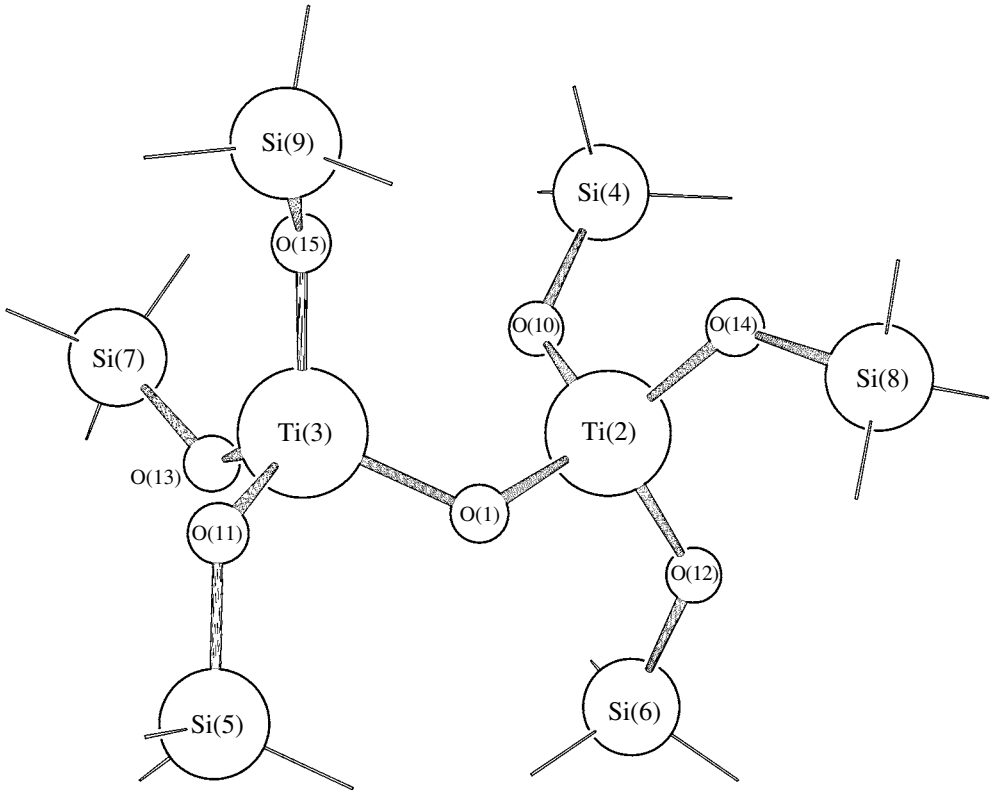

Fig. 2. Simulated configuration of the $2Ti^0_{IV}$ center.

$2Ti^0_{IV}$ center is C_3, it is convenient to interpret its vibrational modes as combinations of modes of two neighboring TiO_4 tetrahedra.

According to our calculations, the highest frequency modes of the $2Ti^0_{IV}$ center are those at 942 and 918 cm^{-1}. The 942-cm^{-1} mode is an in-phase combination of the totally symmetric (breathing) modes of the two TiO_4 tetrahedra and is accompanied by symmetric Ti–O stretches in the Ti–O–Ti bridge and antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges. The 918-cm^{-1} mode is an out-of-phase combination of the same modes of the two TiO_4 tetrahedra and is accompanied by antisymmetric Ti–O stretches in the Ti–O–Ti bridge and antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges. The intensities of the respective IR absorption bands are 0.16 and 3.86, the intensities of the Raman bands are 0.42 and <0.01, and the degrees of depolarization of the Raman bands are 0.019 and 0.376, respectively. In addition, there are two twofold degenerate modes at 876 and 858 cm^{-1}, which are combinations of the twofold degenerate modes E of the two TiO_4 tetrahedra. These vibrations are accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges. The former mode involves bends of the Ti–O–Ti bridge, and the latter involves its rocking about the immobile oxygen. The overall IR absorption intensity for the two degenerate components of the former mode is 56.26, the total Raman scattering intensity is <0.01, and the degree of depolarization of the Raman band is 0.609. For the latter mode, the overall IR absorption intensity for the two degenerate components is 21.89, the total Raman scattering intensity is 0.02, and the degree of depolarization of the Raman band is 0.557.

All of the above modes represent stretching vibrations since they involve insignificant Ti displacements in the TiO_4 tetrahedra. There are also their bending analogs, which involve significant Ti displacements and have much lower frequencies, in particular, vibrations at 755 and 660 cm^{-1}, accompanied, respectively, by antisymmetric and symmetric Ti–O stretches in the Ti–O–Ti bridge. The intensities of the corresponding IR absorption bands are 33.75 and 0.81, the intensities of the Raman bands are 0.02 and 0.01, and the degrees of depolarization of the Raman bands are 0.702 and 0.745, respectively. Also prominent are two twofold degenerate modes at 632 and 548 cm^{-1}, which are combinations of the twofold degenerate modes E of the two TiO_4 tetrahedra. These modes involve, respectively, rocking of the bridge about the immobile oxygen and bends of the Ti–O–Ti bridge. The overall IR absorption intensity for the two degenerate components of the former mode is 1.04, the total Raman scattering intensity is 0.08, and the degree of depolarization of the Raman band is

Table 2. Geometric parameters of the simulated configurations of $2Ti_{IV}$ centers

Atoms	Bond length, Å			Atoms	Bond angle, deg		
	$2Ti^{0}_{IV}$	$2Ti^{-}_{IV}$	$2Ti^{2-}_{IV}$		$2Ti^{0}_{IV}$	$2Ti^{-}_{IV}$	$2Ti^{2-}_{IV}$
				Ti(2)–O(1)–Ti(3)	119.8	99.2	94.6
Ti(2)–O(1)	1.830	1.869	1.853				
Ti(2)–O(10)	1.821	1.890	1.940	O(1)–Ti(2)–O(10)	114.7	125.6	130.4
Ti(2)–O(12)	1.808	1.860	1.902	O(1)–Ti(2)–O(12)	111.7	100.9	98.9
Ti(2)–O(14)	1.804	1.852	1.891	O(1)–Ti(2)–O(14)	104.0	111.5	114.1
Ti(3)–O(1)	1.837	1.877	1.878				
Ti(3)–O(11)	1.805	1.875	1.945	O(1)–Ti(3)–O(11)	101.6	94.9	91.2
Ti(3)–O(13)	1.813	1.854	1.876	O(1)–Ti(3)–O(13)	110.4	117.0	117.9
Ti(3)–O(15)	1.810	1.850	1.888	O(1)–Ti(3)–O(15)	114.9	121.5	127.7
Si(4)–O(10)	1.722	1.694	1.657	Ti(2)–O(10)–Si(4)	128.4	127.4	129.1
Si(5)–O(11)	1.713	1.689	1.668	Ti(3)–O(11)–Si(5)	127.9	125.5	122.5
Si(6)–O(12)	1.710	1.682	1.671	Ti(2)–O(12)–Si(6)	130.6	130.1	129.1
Si(7)–O(13)	1.714	1.696	1.680	Ti(3)–O(13)–Si(7)	129.7	127.3	124.8
Si(8)–O(14)	1.709	1.686	1.675	Ti(2)–O(14)–Si(8)	129.3	125.4	119.3
Si(9)–O(15)	1.714	1.686	1.664	Ti(3)–O(15)–Si(9)	131.3	132.1	130.2

0.527. For the latter mode, the overall IR absorption intensity is 1.12, the total Raman scattering intensity is 0.19, and the degree of depolarization of the Raman band is 0.062.

The other, lower frequency modes of the $2Ti^{0}_{IV}$ center are difficult to identify because of the severe mixing of modes involving different atomic displacement.

Pairs of negatively charged four-coordinate titanium atoms ($2Ti^{-}_{IV}$ and $2Ti^{2-}_{IV}$). Pairs of singly and doubly negatively charged four-coordinate Ti atoms in titanosilicate glass were simulated using the same cluster as in the case of the neutral centers, but the cluster had a charge of $-1e$ and $-2e$, respectively. Like in the Ti^{0}_{IV} center, the extra electrons must be localized at the initially empty Ti *d* orbitals, giving rise to Jahn–Teller distortions of the initial structure of the Ti^{0}_{IV} center. The geometric parameters of the simulated equilibrium configuration of the $2Ti^{-}_{IV}$ and $2Ti^{2-}_{IV}$ centers are listed in Table 2.

Our calculations indicate that, as a result of relaxation, about half of the extra charge density is about evenly divided between the two Ti atoms: the Mulliken effective charge on either Ti atom is $+0.67e$ in the $2Ti^{0}_{IV}$ center, $+0.49e$ in $2Ti^{-}_{IV}$, and $+0.38e$ in $2Ti^{2-}_{IV}$. The rest of the extra charge density is distributed over the oxygens of the two TiO_4 tetrahedra. This is accompanied by an increase in Ti–O bond length in both tetrahedra and a reduction in Ti–O–Ti bond angle. The addition of either electron causes the tetrahedra to tilt by about –4° about the Ti–Ti axis, so that the symmetry of the $2Ti_{IV}$ centers approaches D_{3h}.

The highest frequency modes of the $2Ti^{-}_{IV}$ and $2Ti^{2-}_{IV}$ centers are, respectively, in-phase and out-of-phase combinations of the totally symmetric (breathing) modes of the two TiO_4 tetrahedra and are accompanied, respectively, by symmetric and antisymmetric Ti–O stretches in the Ti–O–Ti bridge and antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges. In the $2Ti^{-}_{IV}$ center, the frequencies of these modes are 917 and 872 cm^{-1}, the intensities of the corresponding IR absorption bands are 4.30 and 19.18, the intensities of the Raman bands are 1.00 and 0.32 (Raman intensities are normalized by the intensity of the 917-cm^{-1} band), and the degrees of depolarization of the Raman bands are 0.067 and 0.049, respectively. In the $2Ti^{2-}_{IV}$ center, the frequencies of these two modes are 900 and 860 cm^{-1}, the intensities of the IR absorption bands are 13.74 and 6.56, those of the Raman bands are 1.00 and 2.36 (Raman intensities are normalized by the intensity of the 900-cm^{-1} band), and the degrees of depolariza-

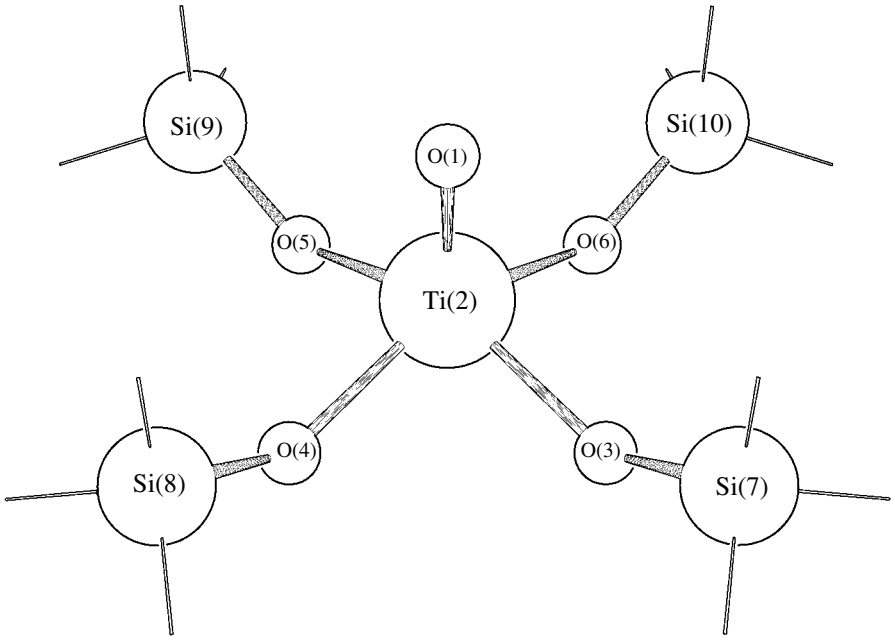

Fig. 3. Simulated configuration of the Ti_V^0 center.

tion of the Raman bands are 0.022 and 0.044, respectively.

In the $2Ti_{IV}^-$ center, four vibrational modes, at 860, 850, 825, and 820 cm^{-1}, are combinations of the twofold degenerate modes E of the two TiO_4 tetrahedra, with antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges and bends of the Ti–O–Ti bridge (the first two modes) or its rocking about the immobile oxygen (the last two modes). For the first two modes, the intensities of the IR absorption bands are 30.79 and 8.88, the Raman scattering intensities are 0.13 and 0.45, and the degrees of depolarization of the Raman bands are 0.095 and 0.445, respectively; for the last two modes, 25.37 and 3.53, 0.17 and 0.98, and 0.362 and 0.393, respectively. In the $2Ti_{IV}^{2-}$ center, the frequencies of the analogous vibrational modes are 855, 840, 820, and 795 cm^{-1}; the intensities of the IR absorption bands are 10.12, 4.86, 3.26, and 1.18; the Raman scattering intensities are 0.45, 2.56, 1.78, and 2.30; and the degrees of depolarization of the Raman bands are 0.537, 0.215, 0.474, and 0.321, respectively.

For the modes at 719 and 577 cm^{-1} in the $2Ti_{IV}^-$ center, accompanied, respectively, by symmetric and antisymmetric Ti–O stretches in the Ti–O–Ti bridge, the intensities of the IR absorption bands are 0.80 and 2.01, those of the Raman bands are 0.06 and 0.01, and the degrees of depolarization of the Raman bands are 0.088 and 0.673, respectively. In the $2Ti_{IV}^{2-}$ center, the frequencies of the analogous modes are 733 and 581 cm^{-1}, the intensities of the IR absorption bands are 2.24 and 3.20, the Raman scattering intensities are 0.73 and 0.19, and the degrees of depolarization of the Raman bands are 0.042 and 0.160, respectively.

As in the case of the neutral center, other modes of the $2Ti_{IV}^-$ and $2Ti_{IV}^{2-}$ centers are difficult to identify because they involve displacements of many atoms.

Single five-coordinate titanium atom (Ti_V). A single five-coordinate Ti atom in titanosilicate glass was represented by an O=Ti(O–Si)$_4$ cluster. The TiO_4 tetrahedron, which has one nonbridging oxygen, is linked to four SiO_4 tetrahedra. The cluster has a total charge of $-2e$, which represents donor–acceptor electron transfer from two three-coordinate oxygens to a Ti atom in the glass (a cluster containing such oxygens is too large to be simulated on our computer). The equilibrium configuration of the Ti_V center is displayed in Fig. 3, and its geometric parameters are listed in Table 3. Clearly, the local symmetry of the Ti_V center is C_{4v}. A characteristic feature of this center is the double bond between the Ti atom and nonbridging oxygen.

According to our calculations, the Ti_V center has two totally symmetric A_1 modes, related to stretches of the double bond O=Ti, with frequencies of 1053 and 919 cm^{-1}. In both modes, O=Ti stretches are accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, but in the former mode all of the oxygens move in phase, whereas in the latter mode the nonbridging oxygen moves out of phase with the four bridging oxygens. The intensities of the IR absorption and Raman bands and the degree of depolarization of

the Raman bands are, respectively, 1.01, 1.00, and 0.095 for the former mode and 2.61, 1.21, and 0.013 for the latter mode (intensities are normalized by the intensity of the 1053-cm^{-1} Raman band).

In addition, there are vibrations that are also accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, but with no motion of the atoms in the O=Ti double bond: these are the twofold degenerate E mode at 992 cm^{-1} (the overall intensities of the IR absorption and Raman bands for the two degenerate modes are 47.66 and 0.04, respectively, and the degree of depolarization of the Raman band is 0.745) and the B_1 mode at 978 cm^{-1} (the intensities of the IR absorption and Raman bands are 0.14 and 1.79, respectively, and the degree of depolarization of the Raman band is 0.750).

Note also the twofold degenerate E modes at 511 and 498 cm^{-1}, which are combinations of O=Ti rocking and Ti–O–Si rocking and bending, respectively. The overall intensities of the IR absorption and Raman bands for the two degenerate components and the degree of depolarization of the Raman band are, respectively, 8.06, <0.01, and 0.734 for the former mode and 6.30, <0.01, and 0.745 for the latter.

Finally, there is a totally symmetric A_1 mode, which involves synchronous bending of the four Ti–O–Si bridges (each in its own plane) and concurrent translational motion of the O=Ti pair as a whole along the double bond. The frequency of this mode is 518 cm^{-1}, and the IR absorption intensity, Raman scattering intensity, and degree of depolarization of the Raman bands are 6.32, 0.13, and 0.557, respectively.

In the cluster model used for the Ti_V center, electronic absorption is only significant at photon energies above 7 eV ($\lambda \lesssim 180$ nm). Note, however, that three-coordinate oxygen atoms, which must be present in the glass network together with Ti_V centers, are characterized by absorption in the range 3–4 eV (400–300 nm) [25].

Single neutral six-coordinate titanium atom (Ti^0_{VI}). A single neutral six-coordinate Ti atom in titanosilicate glass was represented by a $Ti(–O–SiH_3)_6$ cluster, in which the TiO_6 octahedron is surrounded by six SiH_3 groups, modeling SiO_4 tetrahedra. The cluster has a total charge of $–2e$, which represents donor–acceptor electron transfer to a Ti atom in the glass. The simulated equilibrium configuration of the Ti^0_{VI} center is displayed in Fig. 4, and its geometric parameters are listed in Table 4.

The simulated equilibrium configuration of the Ti^0_{VI} center possesses O_h symmetry, but the octahedron is slightly distorted (most likely, because of the small cluster size and interaction between the outer SiH_3 groups). Nevertheless, the highest frequency modes of the Ti^0_{VI} center can be identified using irreducible representations of the O_h group. In particular, the frequency of the totally symmetric A_{1g} mode, accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 932 cm^{-1}, the intensity of the IR absorption band is 0.34, the intensity of the Raman band is taken to be 1.0, as with the other charged clusters, and the degree of depolarization of the Raman band is 0.003. The frequencies of the threefold degenerate mode F_{2u} are approximately 860 cm^{-1}, the sum intensities of the IR absorption and Raman bands for the three degenerate components are about 29.1 and 3.24, respectively, and the degree of depolarization of the Raman band is 0.750. Lower frequency modes are difficult to identify because of the severe mode mixing caused by the distortion of the octahedron.

Table 3. Geometric parameters of the simulated configuration of the Ti^0_V center

Atoms	Bond length, Å	Atoms	Bond angle, deg
Ti(2)–O(1)	1.673		
Ti(2)–O(3)	2.040	O(1)–Ti(2)–O(3)	105.7
Ti(2)–O(4)	2.040	O(1)–Ti(2)–O(4)	105.8
Ti(2)–O(5)	2.040	O(1)–Ti(2)–O(5)	105.7
Ti(2)–O(6)	2.040	O(1)–Ti(2)–O(6)	105.7
		O(3)–Ti(2)–O(4)	85.8
		O(3)–Ti(2)–O(5)	148.7
		O(3)–Ti(2)–O(6)	85.8
		O(4)–Ti(2)–O(5)	85.8
		O(4)–Ti(2)–O(6)	148.5
		O(5)–Ti(2)–O(6)	85.8
Si(7)–O(3)	1.610	Ti(2)–O(3)–Si(7)	139.9
Si(8)–O(4)	1.610	Ti(2)–O(4)–Si(8)	139.9
Si(9)–O(5)	1.610	Ti(2)–O(5)–Si(9)	139.9
Si(10)–O(6)	1.610	Ti(2)–O(6)–Si(10)	139.8

Single negatively charged six-coordinate titanium atom (Ti^-_{VI}). A single negatively charged six-coordinate Ti atom in titanosilicate glass was represented by the same cluster as the neutral center Ti^0_{VI}. The cluster has a total charge of $–3e$. The simulated equilibrium configuration of the Ti^-_{VI} center is displayed in Fig. 5, and its geometric parameters are listed in Table 4.

As in the case of four-coordinate Ti atoms, an extra electron must be localized at the Ti d orbital, giving rise

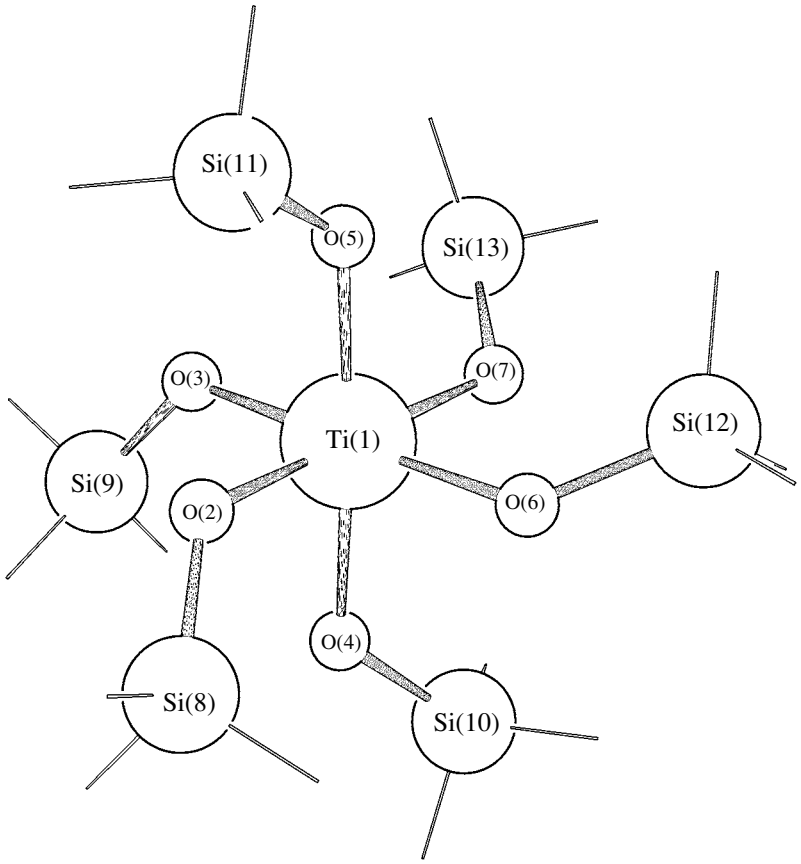

Fig. 4. Simulated configuration of the Ti^{0}_{VI} center.

to Jahn–Teller distortions of the initial structure of the Ti^{0}_{VI} center. Indeed, the TiO_6 octahedron in the simulated equilibrium configuration of the Ti^{-}_{VI} center is monoclinically distorted, so that the local symmetry of the negatively charged center is C_{3v} and not O_h as in the neutral center (Figs. 4, 5). Three Ti–O bonds are shorter (on average, 2.00 Å) than the other three (on average, 2.15 Å), with bond orders of 0.60 and 0.33, respectively. The O–Ti–O angles are, on average, 100.5° between the short bonds and 88.2° between the long bonds. Thus, remaining formally six-coordinate, the Ti atom forms only three normal (short) bonds, whereas the other three (long) bonds are substantially weaker. The unpaired electron is localized largely at the Ti atom (33% of the spin density) and the oxygens involved in the short bonds (approximately 19% of the spin density per oxygen), whereas each of the oxygens involved in the long bonds gains no more than 3% of the spin density.

The highest frequency modes of the Ti^{-}_{VI} center can be identified using irreducible representations of the C_{3v} group. The frequency of the totally symmetric A_1 mode, accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 527 cm^{-1}, the intensity of the IR absorption band is 0.92, the intensity of the Raman band is taken to be 1.0, as with the other charged clusters, and the degree of depolarization of the Raman band is 0.050. In the negatively charged center Ti^{-}_{VI}, the vibrations corresponding to the threefold degenerate mode F_{2u} of the neutral center are split into a twofold degenerate E mode at 662 cm^{-1} (the overall intensities of the IR absorption and Raman bands for the two degenerate modes are approximately 1.34 and 0.50, respectively, and the degree of depolarization of the Raman band is 0.651) and an A_1 mode at 585 cm^{-1} (the intensities of the IR absorption and Raman bands are 0.25 and 0.60, respectively, and the degree of depolarization of the Raman band is 0.704). Lower frequency modes are also difficult to identify.

According to our calculations, the Ti^{-}_{VI} center gives rise to electronic absorptions at 1.7 and 2.4 eV (wavelengths of 730 and 515 nm, and oscillator strengths of 0.05 and 0.15, respectively), due, for the most part, to *d–d* excitations in the three-coordinate titanium ion.

Table 4. Geometric parameters of the simulated configurations of Ti_{VI} centers

Atoms	Bond length, Å		Atoms	Bond angle, deg	
	Ti^0_{VI}	Ti^-_{VI}		Ti^0_{VI}	Ti^-_{VI}
Ti(1)–O(2)	1.985	2.149	O(2)–Ti(1)–O(3)	93.4	88.0
Ti(1)–O(3)	1.991	2.151	O(2)–Ti(1)–O(4)	89.0	87.8
Ti(1)–O(4)	1.993	2.151	O(2)–Ti(1)–O(5)	87.9	95.0
Ti(1)–O(5)	1.987	2.001	O(2)–Ti(1)–O(6)	90.7	95.2
Ti(1)–O(6)	1.993	2.005	O(2)–Ti(1)–O(7)	175.9	174.4
Ti(1)–O(7)	1.992	2.003	O(3)–Ti(1)–O(4)	88.8	88.6
			O(3)–Ti(1)–O(5)	89.2	96.7
			O(3)–Ti(1)–O(6)	175.7	176.8
			O(3)–Ti(1)–O(7)	90.2	95.0
			O(4)–Ti(1)–O(5)	176.2	173.7
			O(4)–Ti(1)–O(6)	90.0	96.3
			O(4)–Ti(1)–O(7)	92.9	98.5
			O(5)–Ti(1)–O(6)	92.2	100.6
			O(5)–Ti(1)–O(7)	90.3	100.1
			O(6)–Ti(1)–O(7)	85.7	100.7
Si(8)–O(2)	1.664	1.638	Ti(1)–O(2)–Si(8)	127.5	130.1
Si(9)–O(3)	1.661	1.644	Ti(1)–O(3)–Si(9)	128.8	131.6
Si(10)–O(4)	1.660	1.641	Ti(1)–O(4)–Si(10)	128.7	136.9
Si(11)–O(5)	1.665	1.653	Ti(1)–O(5)–Si(11)	126.2	128.7
Si(12)–O(6)	1.660	1.646	Ti(1)–O(6)–Si(12)	128.4	127.2
Si(13)–O(7)	1.663	1.650	Ti(1)–O(7)–Si(13)	127.1	130.5

Single three-coordinate titanium atom (Ti^0_{III}). A single neutral three-coordinate Ti atom in titanosilicate glass was represented by a $Ti(–O–SiH_3)_3$ cluster, in which the Ti atom was oxygen-bridged to the Si atoms of three SiH_3 groups, modeling SiO_4 tetrahedra. The simulated equilibrium configuration of the Ti^0_{III} center is displayed in Fig. 6, and its geometric parameters are listed in Table 5. As seen, the local symmetry of the Ti^0_{III} center is D_{3h}.

Our calculations attest to the following vibrational properties of the Ti^0_{III} center: The frequency of the totally symmetric mode (A_1'), accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 1017 cm^{-1}, the intensities of the IR absorption and Raman bands are 0.140 and 0.30, respectively, and the degree of depolarization of the Raman band is 0.744. The frequency of the twofold degenerate mode E', also accompanied by antisymmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 953 cm^{-1}, the overall intensities of the IR absorption and Raman bands for the two degenerate components are 65.8 and 0.053, respectively, and the degree of depolarization of the

Table 5. Geometric parameters of the simulated configuration of the Ti^0_{III} center

Atoms	Bond length, Å	Atoms	Bond angle, deg
Ti(1)–O(2)	1.837	O(2)–Ti(1)–O(3)	120.4
Ti(1)–O(3)	1.836	O(3)–Ti(1)–O(4)	119.3
Ti(1)–O(4)	1.836	O(4)–Ti(1)–O(2)	120.0
Si(5)–O(2)	1.674	Ti(1)–O(2)–Si(5)	171.4
Si(6)–O(3)	1.674	Ti(1)–O(3)–Si(6)	173.2
Si(7)–O(4)	1.674	Ti(1)–O(4)–Si(7)	171.5

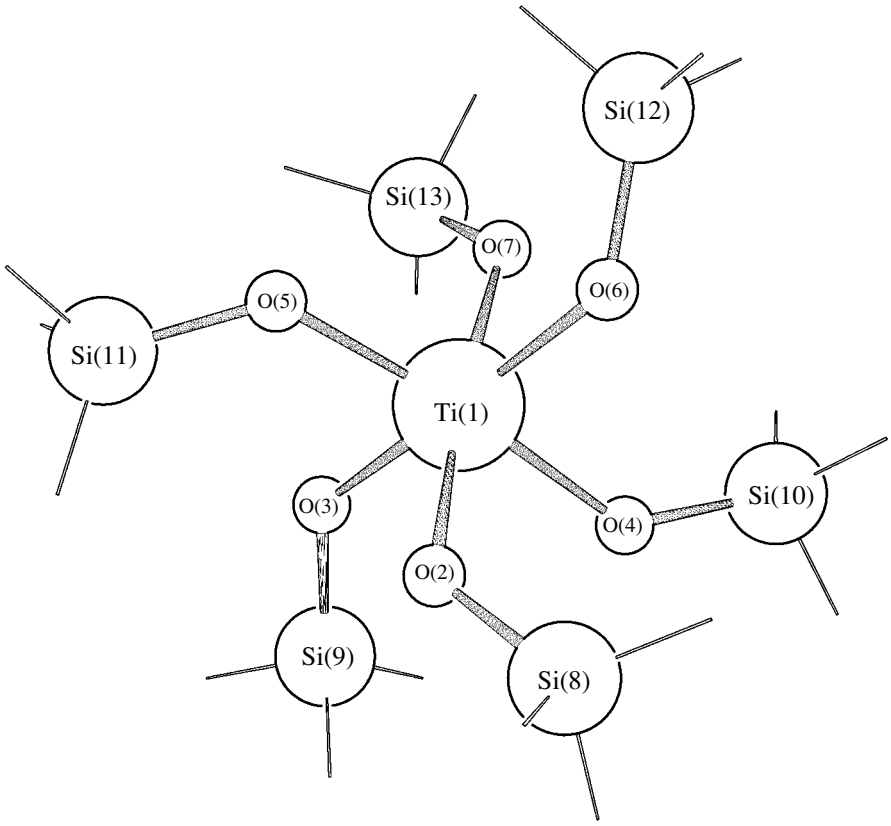

Fig. 5. Simulated configuration of the Ti^{-}_{VI} center.

Raman bands is 0.749. The other degenerate mode E' has a frequency of 575 cm^{-1}, the intensities of the IR absorption and Raman bands are 0.15 and <0.01, respectively, and the degree of depolarization of the Raman bands is 0.747. The frequency of the A_2'' mode, accompanied by Ti–O–Si bending, displacement of the oxygens normal to the plane of the center, and symmetric Ti–O and Si–O stretches in the Ti–O–Si bridges, is 544 cm^{-1}, the IR absorption and Raman scattering intensities are 3.51 and <0.01, respectively, and the degree of depolarization of the Raman band is 0.600.

A characteristic feature of the Ti^{0}_{III} center is the presence of an unpaired electron. According to the simulation results, it must be localized almost entirely (about 97%) at the nonbonding *d* orbital of the central Ti atom.

Our results indicate that the Ti^{0}_{III} center has excited electronic states at 1.7, 4.2, and 8,7 eV, due, for the most part, to *d–d* excitations in the three-coordinate Ti ion. Transitions from these states to the ground state give rise to luminescence near 750, 290, and 140 nm, respectively. The calculated excited-state lifetimes are on the order of 1 ms, 1 μs, and 10 μs, respectively.

DISCUSSION

Our results fully confirm the existing interpretation of the characteristic vibrational properties and electronic transitions of the Ti^{0}_{IV} center. The frequencies calculated for the five- and six-coordinate titanium atoms, Ti^{0}_{V} and Ti^{0}_{VI}, are considerably overestimated (by about 100 cm^{-1}) in comparison with the aforementioned bands observed in experiment and attributed to these centers. The origin of this discrepancy is not yet clear. It may be due to the inherent drawback of the cluster approach that such centers have to be represented by charged clusters (e.g., as mentioned above, the stretching frequency of the O=Ti double bond strongly depends on the cation environment). It, however, cannot be ruled out that the reported interpretations, relying on analogies with crystals, are erroneous. To resolve this issue, further simulation studies are needed, using approaches other than the cluster model.

On the nature of Ti^{3+} centers. As mentioned in the introduction, such centers are believed to be responsi-

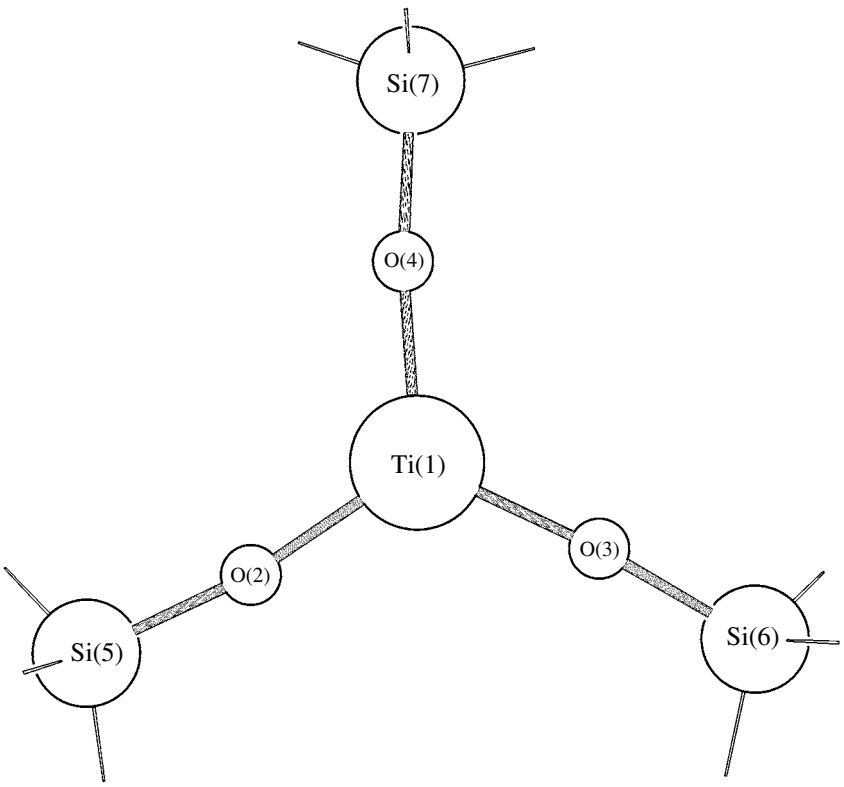

Fig. 6. Simulated configuration of the Ti^{0}_{III} center.

ble for the absorptions at ≲300, 500, and 680 nm. Their vibrational properties are essentially unexplored. The nature of such centers is the subject of controversy. The proposed models include a monoclinically distorted titanium–oxygen tetrahedron, Ti^{-}_{IV}; three-coordinate titanium atom, Ti^{0}_{III}; and six-coordinate titanium atom, Ti^{-}_{VI}. According to the present simulation results, none of these centers are responsible for the three absorption bands commonly attributed to Ti^{3+}. Judging from the IR absorption data only, it seems likely that the so-called Ti^{3+} centers actually represent two types of centers, six- and three-coordinate titanium atoms (Ti^{-}_{VI} and Ti^{0}_{III}), and not four-coordinate atoms (Ti^{-}_{IV}).

On the charge states of single and double Ti_{IV} centers. This issue is connected with the assumption often encountered in the literature that Ti^{3+} centers result from electron capture at tetrahedrally coordinated Ti atoms (Ti^{0}_{IV} centers), leading to monoclinic distortion of the TiO_4 tetrahedron. The present simulation results make it possible to evaluate the relative energies of different charge states of single and double four-coordinate titanium atoms. To this end, one must determine the energies of so-called electrical levels [26, 27]. In a cluster approximation, the energy of an electrical level measured from the conduction band edge is

$$E(n/n+1) = \varepsilon[D^n] - \varepsilon[D^{n+1}] - E_{CBE},$$

where $\varepsilon[D^n]$ is the total energy of the cluster for a charge state of the center with a total change n, corresponding to the equilibrium geometry, and E_{CBE} is the energy of the conduction band edge relative to vacuum ($-E_{CBE}$ is the electron affinity). The electron affinity of glassy SiO_2 has variously been reported as 0.9 to 2.0 eV [27–29]. The most commonly accepted value is probably 0.9 eV. Note that the approach used here allows the position of an electrical level to be determined with an accuracy no better than 0.5 eV [26]. The formation of a new center through the capture of an electron from the conduction band is only possible if the electrical level lies below the conduction band edge, i.e., $E(-1/0) < 0$ or $E(-2/-1) < 0$. Our calculations give $E(-1/0) \simeq 0.9$ eV > 0 for the Ti^{0}_{IV} single center and $E(-1/0) \simeq 1.6$ eV > 0 for the $O_3Ti–O–TiO_3$ double center. On the other hand, $E(-2/-1) \simeq -3.2$ eV < 0 for the Ti^{0}_{IV} single center and $E(-2/1) \simeq -2.0$ eV < 0 for the $O_3Ti–O–TiO_3$ double center. This means that neither single nor double singly negatively charged Ti atoms can be formed through the capture of an electron directly from the conduction

band of v-SiO_2. Consequently, such centers can only be formed through the filling of appropriate states as a result of electron excitation, in particular, optical excitation. However, after having being formed, both single and double singly negatively charged Ti atoms tend to capture extra electrons from the conduction band and to form doubly negatively charged centers. This conclusion, firstly, leads us to assume that, during drawing of titanosilicate glass fibers, some states of four-coordinate titanium atoms may be filled through the absorption of the UV radiation propagating along the fiber from the melt and, secondly, suggests that the forming negatively charged centers can be eliminated by annealing the fiber during drawing.

Concerning the "gray" absorption. A characteristic feature of the optical absorption in titanosilicate glasses is the relatively weak "gray" (almost wavelength-independent) absorption. It is well known that such absorption is characteristic of disordered semiconductors, where it is due to zero-phonon hopping conduction. It is reasonable to assume that the gray absorption in titanosilicate glasses is also due to hopping transport. Let us estimate a characteristic magnitude of this absorption using quantum-chemical simulation results. The linear absorption coefficient α ($I = I_0\exp(-\alpha z)$) associated with (quasi-)free carriers is related to the real part of conductivity by

$$\alpha = \left(\frac{8\pi\sigma(\omega)}{\omega}\right)^{1/2}\frac{\omega}{c},$$

where ω is the frequency of the incident radiation. It is well known (see, e.g., [30]) that, at low temperatures ($T \ll \hbar\omega$), the real part of zero-phonon conductivity at frequency ω, associated with hopping transport between structural defects (including impurity centers), can be estimated as

$$\mathrm{Re}\,\sigma(\omega) = \frac{\pi^2 e^2 \rho^2}{3\gamma}\omega\left(\hbar\omega + \frac{e^2}{\varepsilon r_\omega}\right)r_\omega^4,$$

where

$$r_\omega = \frac{1}{\gamma}\ln\left(\frac{2I_0}{\hbar\omega}\right).$$

Here, I_0 and γ are parameters in the interpolation formula $I(r) = I_0\exp(-\gamma r)$ for the overlapping integral of the wave functions of two defects, ρ is the volume density of states of defects, and ε is the dielectric permittivity of the glass. Clearly, for wavelengths on the order of 1 μm ($\hbar\omega \simeq 1$ eV), we have $\hbar\omega \gg e^2/\varepsilon r_\omega$. Therefore,

$$\frac{\mathrm{Re}\,\sigma(\omega)}{\omega} \simeq \frac{\pi^2 e^2 \rho^2}{3\gamma}\hbar\omega r_\omega^4.$$

The present simulation results can be used to estimate the above parameters: $\gamma^{-1} \simeq 3$ nm, $I_0 \simeq 7$ eV, $r_\omega \simeq 30$ nm, and $\rho \simeq 100\nu$, where ν is the electron concentration in defect states. Consequently, the absorption coefficient α associated with zero-phonon hopping transport between defect states at the frequency corresponding to a wavelength of $\simeq 1$ μm can be estimated as $\alpha \simeq 6 \times 10^{-23}$ cm^{-1} (ν is in cm^{-3}). A TiO_2 content on the order of 1 mol % corresponds to a volumetric concentration on the order of 10^{22} cm^{-3}. Using the estimate reported by Carson and Maurer [31], according to which only 0.004% of the states of titanium centers are filled with electrons, we obtain $\nu \simeq 5 \times 10^{17}$ cm^{-3}. Thus, the absorption in our case must be on the order of $\alpha \simeq 3 \times 10^{-5}$ cm^{-1} $\simeq$ 10 dB/km.

CONCLUSIONS

We performed quantum-chemical simulation of the most important centers formed by titanium atoms in titanosilicate glasses. The following simulation results are of special interest for fiber optics applications:

Single neutral four-coordinate titanium, Ti_{IV}^0, has tetrahedral symmetry. The characteristic vibrational frequencies of this center are 1050 and 945 cm^{-1}. These vibrations give rise to two Raman bands (very strong, totally polarized and weak, depolarized, respectively) and one IR absorption band (945 cm^{-1}). Electronic absorption is only possible in the UV region ($\lambda \lesssim 140$ nm).

Four-coordinate titanium atoms, Ti_{IV}, may form pairs, $2Ti_{IV}$, bridged by an oxygen atom, which are characterized by the absence of the totally polarized Raman band at 1050 cm^{-1}. Instead, their spectra show a highly polarized, strong Raman band near 942 cm^{-1} and partially polarized, very weak Raman band near 918 cm^{-1}. Both Raman bands have IR absorption analogs, of which the band corresponding to the 918-cm^{-1} Raman band is an order of magnitude stronger.

According to the present simulation results, the totally polarized Raman band near 1050 cm^{-1}, characteristic of titanosilicate glass, is due to single neutral four-coordinate titanium, Ti_{IV}^0, whereas the partially polarized Raman band near 945 cm^{-1} is due to comparable contributions of both Ti_{IV}^0 centers and neutral four-coordinate titanium pairs, $2Ti_{IV}^0$. The radiation scattered by these centers is depolarized and strongly polarized, respectively. Thus, both the relative intensities of these Raman bands and the degree of depolarization of the lower frequency band depend on the relative concentrations of single and double four-coordinate titanium centers.

Neither Ti^0_{IV} nor $2Ti^0_{IV}$ centers can capture an electron directly from the conduction band of v-SiO_2. Therefore, Ti^-_{IV} and $2Ti^-_{IV}$ negatively charged centers can only be formed through the filling of appropriate states as a result of electron excitation, in particular, optical excitation. Hopping transport of electrons between neutral and negatively charged centers may be responsible for optical losses of up to 10 dB/km.

The so-called Ti^{3+} centers in titanosilicate glass may represent two types of titanium centers, six-coordinate (Ti^-_{VI}) and three-coordinate (Ti^0_{III}) titanium atoms, whereas four-coordinate titanium atoms, Ti^-_{IV} and $2Ti^-_{IV}$, are unrelated to the Ti^{3+} centers.

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