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# Optical absorption and infrared studies of some silicate glasses containing titanium

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The optical absorption and infrared (IR) spectra of mixed alkali silicate glasses in the system $3SiO_2$–$(1-x)Na_2O$–$xK_2O$ + 2.5–20 g of $TiO_2$ were measured. Absorption bands due to $Ti^{3+}$ ions, at 500 and 570 nm, were observed in the spectrum of $Na_2O$-free glasses. The intensities of such bands were followed with the variation in $TiO_2$ content from 2.5 to 20 g (per 100 g of glass). The incorporation of titanium oxide as $Ti^{3+}$ in the $Na_2O$-free glass, conferring a violet hue to it, was explained on the basis of the acidity–basicity character of the glass. The IR measurements have been used to explore the structural changes throughout the compositional variations.

## 1. Introduction

The optical properties of trivalent titanium ($Ti^{3+}$) in various host materials attracted growing interest after the demonstration of $Al_2O_3$:$Ti^{3+}$ crystals as a solid-state laser with a wide range of tunability [1, 2]. For glass hosts, such properties and related information concerning site symmetry and energy levels which are responsible for the observed absorption bands in silicate, borate, phosphate and fluorophosphate have been published [3–5]. Glasses as laser hosts have the advantage of easy and mass production at low cost, compared with single crystals. For both single crystals and glass materials, $Ti^{4+}$ ions should be eliminated during their preparation, because the residual infrared (IR) absorption near 850 nm due to $Ti^{3+}$–$Ti^{4+}$ pairs causes degradation of the emission efficiency [6].

Under ordinary conditions of melting, it is difficult to obtain $Ti^{3+}$ in silicate glasses [7], since a titanium ion is incorporated in its higher valence state $Ti^{4+}$. The latter has the electronic configuration $3d^{\circ}$ which does not produce any absorption in the visible region of the spectrum. It is necessary to force the melting atmosphere to shift the redox equilibrium $Ti^{3+}$–$Ti^{4+}$ to obtain optically detectable amounts $Ti^{3+}$. However, the stabilization of $Ti^{3+}$ ions is easier to achieve for glasses with more acidic composition such as borosilicate and phosphate [8] glasses.

In this study the formation of $Ti^{3+}$ ions in silicate glasses, under ordinary conditions, has been achieved and investigated by optical and IR absorption techniques.

## 2. Experimental procedure

The glasses studied were classified into two series (Table I). In the first series, the composition of the glasses was changed by replacing $K_2O$ for $Na_2O$, while the amount of the additive oxide, $TiO_2$, remains constant (10 g per 100 g of glass.). On the other hand, in the second series, the amount of the additive oxide, $TiO_2$, was varied while the base composition was held constant ($3.0SiO_2$–$1.0K_2O$).

Samples were prepared from reagent-grade chemicals and acid-washed silica. Batch materials to produce 75 g of glass were weighed, thoroughly mixed and melted in a Pt–2% Rh crucible at 1450 °C for 6 h in an electric furnace with air as the furnace atmosphere. Melting was carried out such that, after each interval of 2 h, the melt was poured on a Pt plate and the quenched glass was remelted. This process was repeated three times. After the last stage of melting, the melt was cast as rectangular slabs and annealed at 550 °C for $\frac{1}{2}$ h after which the furnaces was switched off to cool to room temperature. The glass samples obtained were either colourless or faint or dense violet in colour.

The absorption spectra in the ultraviolet and visible regions of the polished samples were obtained with a recording Uvikon 860 spectrophotometer (Kontron Swiss Co.). The optical absorption coefficients were calculated as

$$\alpha = 2.303 \log(I_0/I)\, d$$

where $d$ is the thickness of the specimen, $I_0$ the intensity of the incident beam and $I$ the intensity of the transmitted beam. These calculations allow comparison of the spectra of different samples. For IR measurements the KBr pellet technique was used. 2 mg of each glass powder was added to 200 mg KBr and used as the mixture constituting the pellets. The IR measurements were carried out between 200 and 2000 $cm^{-1}$ using a Unicam SP 1100 spectrophotometer.

## 3. Results

The absorbance (optical density (OD) ) of the studied glasses are shown in Figs 1 and 2. Fig. 1 shows the

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TABLE I Glass composition and some physical properties

| Series | Glass | Composition (mol) | | | $TiO_2$ additive (g per 100 g of glass) | Colour | Density ($g\,cm^{-3}$) |
|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $K_2O$ | $Na_2O$ | | | |
| I | 1 | 3 | — | 1 | 10 | Colourless | 2.540 |
| | 2 | 3 | 0.2 | 0.8 | 10 | Colourless | 2.500 |
| | 3 | 3 | 0.4 | 0.6 | 10 | Colourless | 2.492 |
| | 4 | 3 | 0.6 | 0.4 | 10 | Colourless | 2.465 |
| | 5 | 3 | 0.8 | 0.2 | 10 | Colourless | 2.418 |
| | 6 | 3 | 1 | — | 10 | Violet | 2.460 |
| II | 7 | 3 | 1 | — | 2.5 | Colourless | 2.397 |
| | 8 | 3 | 1 | — | 5 | Colourless | 2.253 |
| | 9 | 3 | 1 | — | 7.5 | Pale violet | 2.416 |
| | 10 | 3 | 1 | — | 12.5 | Deep violet | 3.038 |
| | 11 | 3 | 1 | — | 15 | Violet | 2.454 |
| | 12 | 3 | 1 | — | 17.5 | Colourless | 2.458 |
| | 13 | 3 | 1 | — | 20 | Colourless | 2.460 |

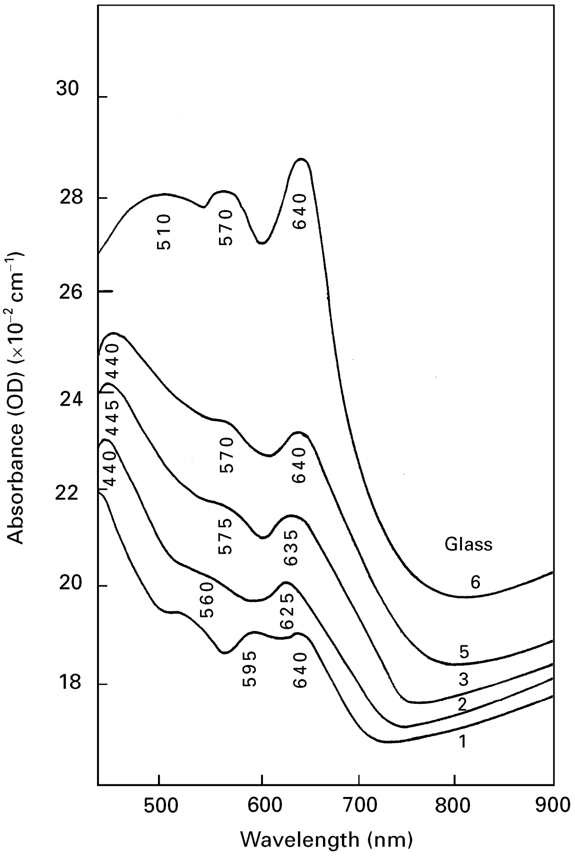

*Figure 1* Absorption spectra of glasses doped with 10 g of $TiO_2$ per 100 g of glass (series I in Table I).

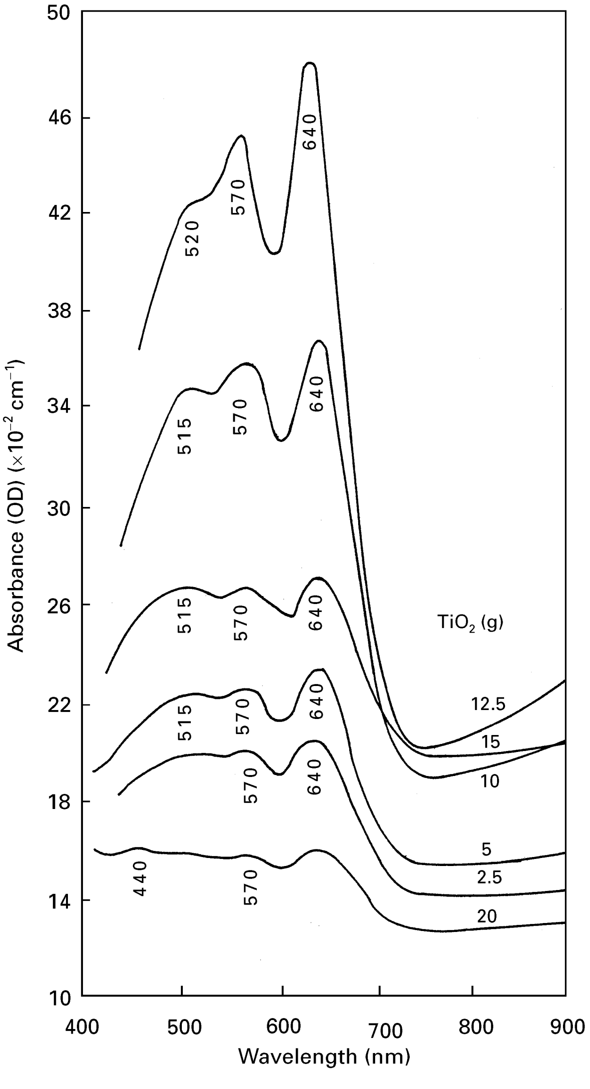

*Figure 2* Absorption spectra of 3.O$_2$SiO–1.0K$_2$O glasses doped with different amounts of $TiO_2$ added per 100 g of glass.

effect of substituting $K_2O$ for $Na_2O$ (series I in Table I) on the absorption spectra. It can be seen that a distinct band appears at 440 nm. This band has been identified for the first time in the work of Bausa *et al.* [7] and was attributed to the presence of the two states, $Ti^{3+}$ and $Ti^{4+}$. The intensity of this band decreases at first with increasing proportion of $K_2O$ at the expense of $Na_2O$ (curves 1, 2 and 3 in Fig. 1), and then it increases as the $K_2O$ becomes the predominant oxide over $Na_2O$. The absorption spectrum (curve 1) shows two less intense absorption peaks at 570 and 635 nm. On replacing $Na_2O$ by $K_2O$ the 570 nm band shifts to shorter wavelengths, reaching 510 nm in glass 5. The band at 635 nm shifts to 620 nm and then splits into two bands at 640 and 595–570 nm with increasing amount of $K_2O$ replaced. The calculated crystal field of the former peak (i.e., 570 nm) in the form of the *Dq* parameter (17 545 $cm^{-1}$) agrees with that associated with the $^2T_2$–$^2E$ transition between the split levels of the 3d configuration of $Ti^{3+}$ in the octahedral crystal-field approximation. The latter peak at 635 nm is due to the transition between the sublevels $T_{2g}$ ground state and the $E_{2g}$ excited state of the $3d^1$ configuration of $Ti^{3+}$, which is present in an octahedral cubic field [8]. The two aforementioned absorption bands (about 570 and 635 nm) show sudden increases in their intensities as all the $Na_2O$ was replaced by $K_2O$ in the spectrum of glass 6. Such changes in the spectrum of $Na_2O$-free glass compared with $Na_2O$-containing glasses account for the violet hue of this glass (see Table I).

Fig. 2 shows the effect of increasing the amount of $TiO_2$ on the absorption spectra of glasses with the base composition $3.0SiO_2$–$1.0K_2O$ (series II, in Table I). The colour of these glasses has been observed to change from colourless to deep violet as the $TiO_2$ content was increased from 2.5 to 12.5 g (per 100 g of glass). Further additions result in a sharp decrease in the intensity of the violet colouration of the glasses and becomes colourless as the $TiO_2$ content reaches the value of 20 g.

The aforementioned progress in the glass colouration can be monitored in Fig. 2. The increase in violet colouration is accompanied by a development of the bands at 570 and 640 nm. On the other hand, the area of the broad absorption envelope which extends from 400 to 550 nm is reduced. This reduction in the area, which is mainly in the shorter-wavelength region, implies a decrease in the band at 440 nm. The addition of $TiO_2$ beyond 12.5 g results in a decrease in the intensities of the observed bands, i.e., at 510, 570 and 640 nm.

Fig. 3 shows the IR transmission spectra of glasses of series I. In the spectra of such glasses the characteristic absorption bands of silicate glasses at approximately 440, 745, 860 and 995 $cm^{-1}$ are observed. Another two bands can be seen at about 1570 and 1410 $cm^{-1}$. The former was attributed previously [9] to molecular $H_2O$ bending vibrations. All the bands concerning the silicate group vibrations are observed to shift toward lower wavenumbers with increasing $K_2O$ content. This trend is reversed in the spectra of $Na_2O$-free glass (glass 6). This is accompanied by a dramatic decrease in the intensities of the Si–O–Si and O–Si–O bands located at about 995, 745 and 440 $cm^{-1}$.

Fig. 4 shows the transmission spectra of glasses of series II. In this figure a decrease in the intensity of the bands related to Si–O–Si and O–Si–O group vibrations can be observed as the amount of additive $TiO_2$ increases. The band at 760 $cm^{-1}$ vanishes in the spectrum of the glass containing the highest addition of $TiO_2$. This is accompanied by a decrease and an increase in the intensities of the bands at 880 nm and 400 nm, respectively, and the appearance of a new band at 830 $cm^{-1}$. The assignments of the bands observed in the spectra of the present glasses are described in Table II.

## 4. Discussion

According to Bausa *et al.* [7] the absorption band at 440 nm is assigned to charge-transfer transitions between $Ti^{3+}$ and $Ti^{4+}$ ions. Hence, it can be used as a measure of the number of $Ti^{3+}$–$Ti^{4+}$ pairs in the glass. The concentration of $Ti^{3+}$–$Ti^{4+}$ pairs follows the relation

$$[Ti^{3+}][Ti^{4+}] = c(1 - c)[TiO_2]^2$$

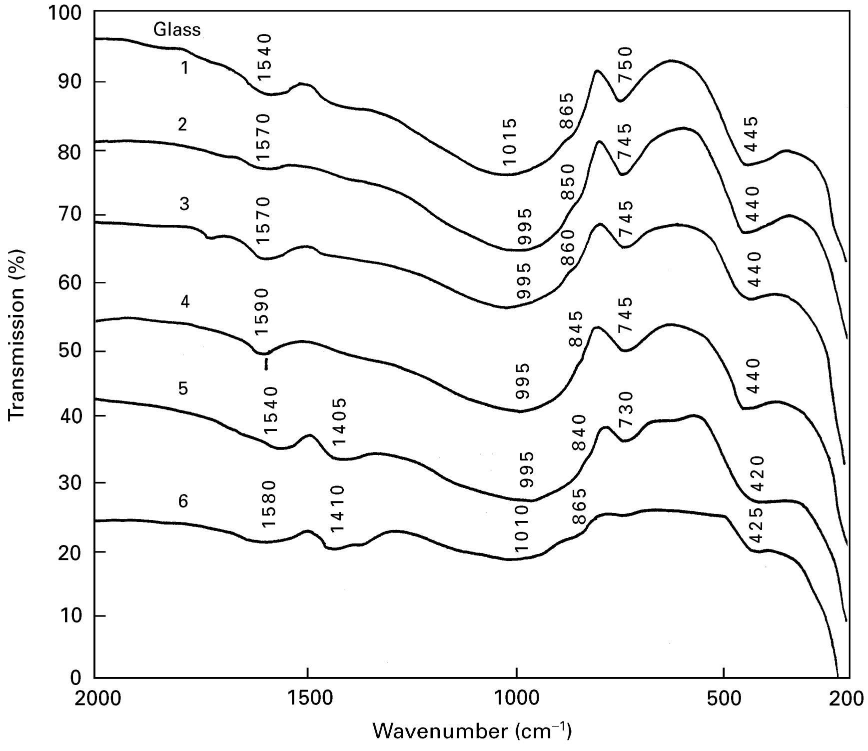

*Figure 3* IR transmission spectra of glasses of different compositions doped with 10 g of $TiO_2$ per 100 g of glass (series I in Table I).

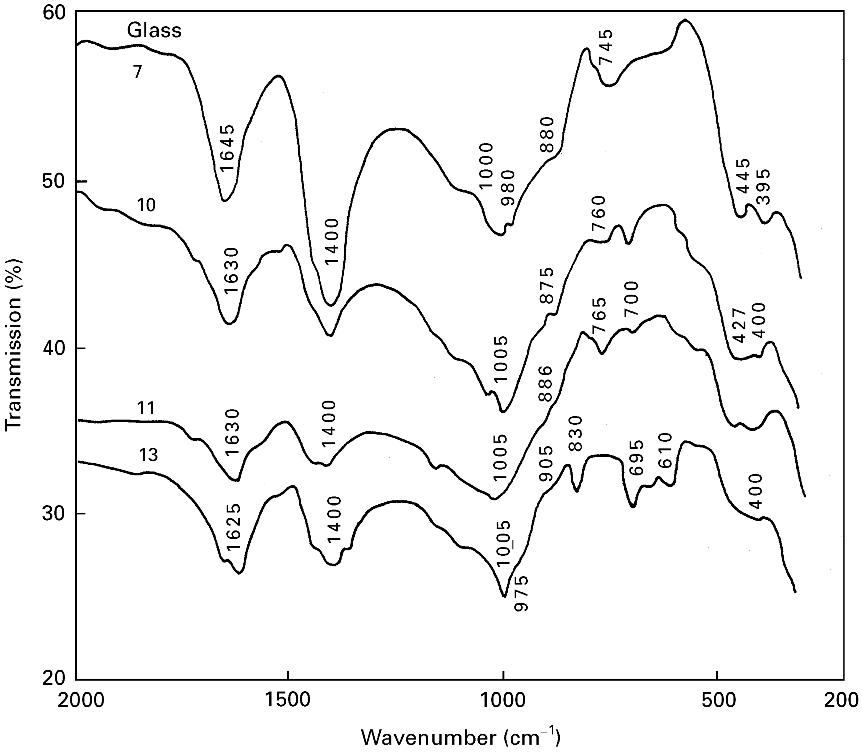

*Figure 4* IR transmission spectra of $3.0SiO_2$–$1.0K_2O$ glasses doped with different amounts of $TiO_2$ added per 100 g of glass.

TABLE II Assignment of the IR bands in the spectra of the glasses studied

| Peak position ($cm^{-1}$) | Assignment | References |
|---|---|---|
| 1015–995 | Si–O antisymmetrical stretching viration | [9–11] |
| 870 | $Si–O^-$ stretching vibration | [9–11] |
| 830 | Ti–O vibration in $[TiO_4]$ | [10] |
| 765–745 | Si–O symmetrical stretching mode | [9–11] |
| 700 | Ti–O–Ti symmetrical vibration | [10] |
| 445–420 | Si–O–Si and O–Si–O bending mode | [9–11] |
| 400 | Ti–O vibration connected with $TiO_6$ unit | [12] |
| 1645–1540 | Molecular $H_2O$ bending vibration | [9] |

TABLE III Values of the basicity parameter, *B*, of the oxides involved in the glasses studied where the values of $SiO_2$ and CaO are normalized as 0 and 1 [6]

| Oxide | *B* |
|---|---|
| $SiO_2$ | 0.000 |
| $TiO_2$ | 0.133 |
| $Na_2O$ | 2.349 |
| $K_2O$ | 3.381 |

where $c$ is the proportionality constant of the production of $Ti^{3+}$ as a function of $TiO_2$, i.e.,

$$[Ti^{3+}] = c[TiO_2]$$

Thus, the decrease in the intensity of this band (440 nm) as $Na_2O$ was replaced by $K_2O$ suggests a decrease in $Ti^{3+}$–$Ti^{4+}$ pair concentration. This may be expected as result of the decrease in the concentration of $Ti^{3+}$ ions rather than $Ti^{4+}$ ions, since the $Ti^{4+}$ ions constitute the predominant species in the $K_2O$-containing glasses. The previous suggestion may be confirmed by the decrease in the intensity of the band at 570 nm corresponding to $Ti^{3+}$ in an octahedral environment, which appears as a shoulder in the spectra of glasses 2, 3 and 5.

Furthermore, it is well known [13] that the increase in oxygen ion activity suppresses any reduced states. Therefore, it must be concluded that the fraction of higher-valence-state ions $Ti^{4+}$ increases as the basicity value, *B* (Table III), expressing the oxygen ion activity of the glass host, is increased. The value of *B* increases as either the ionic radius of alkali or the content of the modifiers is increased. The higher basicity parameter of $K_2O$-containing glasses compared with $Na_2O$-containing glasses enhances the formation of the higher valence state, $Ti^{4+}$. Accordingly, the redox equilibrium $Ti^{3+}$–$Ti^{4+}$ is strongly shifted to the higher valence state with increasing proportion of $K_2O$ in the glass. On the other hand, the $Ti^{4+}$-ion concentration increases, the acidity character is supported, since it is situated in tetrahedral coordination together with $SiO_4$ [10]. This may explain the dramatic increase in the intensity of the bands at 510, 570 and 640 nm and the violet hue of $Na_2O$-free glass (glass 6), since the stabilization of $Ti^{3+}$ is easier to achieve with more acid compositions.

The observed decrease in the intensity of the latter bands (510, 570 and 640 nm) as the added $TiO_2$ exceeds the value of 12.5 g (Fig. 2) may be explained as follows. According to Iwamoto *et al.* [14] the formation of $Ti^{3+}$ ions depends on the dominance of non-bridging oxygen, since it exists mainly as $Ti^{3+}O_3^-O_3^{2-}$ and $Ti^{3+}O_4^-O_2^{2-}$ complex ions. At high $TiO_2$ contents, titanium ions enter the network as $TiO_4$ groups which require more non-bridging oxygen atoms to be involved in the formation of the tetrahedral groups. As the concentration of non-bridging oxygen atoms has been decreased by the formation of such tetrahedral groups, the formation of $Ti^{3+}$ ions is retarded. These conditions favour a shift in the equilibrium of $Ti^{3+}$–$Ti^{4+}$ towards the higher valence state which explains the previously mentioned reduction of the intensities of the bands due to $Ti^{3+}$ ions (510, 570 and 640 nm).

The results of IR studies confirm the previous conclusions. The downshift of the band due to $Si–O^-$ stretching vibrations (865–840 $cm^{-1}$), as the proportion of $K_2O$ increases (Fig. 3), may be related to the lower field strength of $K^+$ ions compared with $Na^+$ ions. The suggestion that titanium is incorporated in a network-forming position $[TiO_4]$ with increasing $K_2O$, except for $Na_2O$-free glass, can be confirmed by the decrease in the intensity of $Si–O^-$ band (850 $cm^{-1}$). Moreover, when $Ti^{4+}$ ions are formed, the polarizability of the oxygen of the $[SiO_4]$ tetrahedron is expected to increase [10]. Hence, the ionic character of these oxygen atoms increase; thus the vibrations corresponding to Si–O–Si and O–Si–O groups shift to lower energies (1015–995, 750–730 and 445–420 $cm^{-1}$).

The entrance of $Ti^{3+}$ ions as previously suggested as a network-modifying complex ion is accompanied by an increase in the intensity of $Si–O^-$ band since it breaks up the silica network at least partially [10], and shift of the bands throughout the spectrum towards higher wavenumber occurs.

As the $TiO_2$ additions reached their maximum value, the titanium ion may enter the structure as $Ti^{4+}$, as confirmed by the observed decrease (Fig. 4) in the intensity of the $Si–O^-$ band and the appearance of a new band at 830 $cm^{-1}$ which was attributed to $[TiO_4]$-group vibrations [10].

The fluctuation in the development of the band at 1400 $cm^{-1}$ suggests its interrelation with the $TiO_4$ vibration. To the knowledge of the present authors this band has not been identified before.

## 5. Conclusion

The addition of 10 g of $TiO_2$ to glasses in the system $3SiO_2–(1-x)Na_2O–xK_2O$ causes violet colouration in glass with the composition $3.0SiO_2–1.0K_2O$. Such colouration is accompanied by the development of the absorption bands at 500, 570 and 640 nm, which are attributed to $Ti^{3+}$ ions.

The effect of increasing the $TiO_2$ content, as an additive oxide, to the $Na_2O$-free glass, from 2.5 to 20 g, shows a progressive increase in the violet colouration up to 12.5 g of $TiO_2$. The colour variation is accompanied by an increase in the intensity of the bands characteristic of $Ti^{3+}$.

The addition of $K_2O$ at the expense of $Na_2O$ is accompanied by strong modifications of the structure revealed by IR spectra. The $[TiO_4]$ groups are expected to increase in numbers in glasses with the highest $K_2O$ content. This increase in the $[TiO_4]$ groups is accompanied by an increase in the polarizability of the $[SiO_4]$ tetrahedron, which increases the acidity character of the glass. Titanium ions are found to prefer to exist in the lower valence state when the $TiO_2$ content is greater than 5 mol% in the present glass.

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