JOURNAL OF MATERIALS SCIENCE 20 (1985) 906–916

# Coordination of $Ti^{4+}$ and $Ge^{4+}$ ions in $Na_2O$–$TiO_2$–$GeO_2$ glasses—an approach based on crystallization behaviour, X-ray absorption and IR spectroscopy

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The coordination state of $Ti^{4+}$ and $Ge^{4+}$ ions in $Na_2O$–$TiO_2$–$GeO_2$ glasses has been investigated. Upon crystallization of the glasses, the thermodynamically metastable hexagonal $GeO_2$ crystals containing 4-fold coordinated $Ti^{4+}$ ions together with stable $Na_4Ge_9O_{20}$ crystals containing 6-fold coordinated $Ti^{4+}$ ions were precipitated. The distribution of $Ti^{4+}$ ions between these two crystalline phases is a reflection of the coordination state of $Ti^{4+}$ ions in the starting glass. The majority of $Ti^{4+}$ ions are in 6-fold coordination at a small $TiO_2/Na_2O$ ratio and they are contained in $Na_2Ge_9O_{20}$, while the majority of $Ti^{4+}$ ions are in 4-fold coordination at a large $TiO_2/Na_2O$ ratio and they are contained in $GeO_2$ crystals. Concentrations of 4- and 6-fold coordinated $Ti^{4+}$ ions have been confirmed to be similar to that in $Na_2O$–$TiO_2$–$SiO_2$ glasses as measured by the X-ray absorption spectrometry of $Ti^{4+}$ ions. The coordination state of $Ge^{4+}$ ions in the glasses have been examined by infrared (IR) spectrometry. It is found that in $Na_2O$–$TiO_2$–$GeO_2$ glasses $Ge^{4+}$ ions have 6-fold coordination preferentially, while $Ti^{4+}$ ions have 4-fold coordination except at small contents of $TiO_2$, indicating that the addition of $TiO_2$ to $Na_2O$–$GeO_2$ glasses leads to the replacement of 4-fold coordinated $Ge^{4+}$ ions by 4-fold coordinated $Ti^{4+}$ ions.

## 1. Introduction

The so-called "anomaly" in glasses, that is, the occurrence of a maximum or minimum on a property–composition curve has been reported for alkali– and alkaline earth–borate and germanate systems. The cause for the anomaly is attributed to the change of the coordination state of network-forming cations, $B^{3+}$ and $Ge^{4+}$ ions, on addition of alkali or alkaline earth oxides [1, 2]. So far the anomaly has been extensively investigated from scientific interest, but now it is applied to design properties of practical glasses such as those for the optical wave guide [1].

Glasses containing $TiO_2$, also exhibit an anomalous change of properties with composition, although it is not so marked as in borate and germanate glasses. Accordingly, the coordination of $Ti^{4+}$ ions has been investigated also in these glasses. Rao [3] showed that the plots of thermal expansion coefficient, density and refractive index of $R_2O$–$TiO_2$–$SiO_2$ glasses, where R is an alkali metal, as a function of $TiO_2$ content deviate from additivity. The deviation was attributed to the change of coordination state of $Ti^{4+}$ ions with the $TiO_2$ content of the glass. He proposed that $Ti^{4+}$ ions are in 4-fold coordination at small $TiO_2$ contents and in 6-fold coordination at large $TiO_2$ contents. Takahashi *et al.* [4] re-examined the

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same problem for $Na_2O-TiO_2-SiO_2$ glasses, reaching an opposite conclusion on the change of the coordination number of $Ti^{4+}$ ions with the $TiO_2$ content of glasses. Hanada and Soga [5] supported the conclusion of Takahashi *et al.* on the basis of the chemical shift of $TiK\beta$ X-ray emission spectra of $Na_2O-TiO_2-SiO_2$ glasses. It was found that $Ti^{4+}$ ions are 4-fold coordinated in binary $TiO_2-SiO_2$ [6] and $TiO_2-GeO_2$ [7] glasses. Recently, the extended X-ray absorption fine structure (EXAFS) technique [8] has revealed that in $TiO_2-SiO_2$ glasses $Ti^{4+}$ ions are in 4-fold coordination except at very small $TiO_2$ content.

It was shown that $Ge^{4+}$ ions are also present in both 4- and 6-fold coordination in germanate glasses [9]. As already mentioned, the addition of alkali oxides to $GeO_2$ glass which is composed of $GeO_4$ tetrahedra produces only 6-fold coordinated $Ge^{4+}$ ions. The maximum concentration of 6-fold $Ge^{4+}$ ions of about 25% occurs at 20 mol% alkali oxides [10].

Ternary $Na_2O-TiO_2-GeO_2$ glasses are very interesting since the glasses contain two types of network-forming cations, $Ti^{4+}$ and $Ge^{4+}$, which are assumed to play a dual part. So far, no works have been reported on the coordination state of $Ti^{4+}$ and $Ge^{4+}$ ions in these glasses. In the present work, structure analysis of $Na_2O-TiO_2-GeO_2$ glasses has been made in terms of coordination states of $Ti^{4+}$ and $Ge^{4+}$ ions. The coordination number of $Ge^{4+}$ was examined by infrared (IR) spectroscopy, and that of $Ti^{4+}$ ions was determined on the basis of the crystallization behaviour of glass and X-ray absorption spectroscopy.

## 2. Experimental details

### 2.1. Glass samples

Four series of glasses were subjected to measurements. The compositions of the glasses are given in Table I. The compositions of the first and second series are represented as $(10\text{-}x)Na_2O \cdot xTiO_2 \cdot 90GeO_2$, and $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ in mol%, respectively, in which $TiO_2$ gradually replaces $Na_2O$. In the third and fourth series, that is, $5Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$ and $xTiO_2 \cdot (100\text{-}x)GeO_2$ glasses, $TiO_2$ replaces $GeO_2$.

Reagent grade $Na_2CO_3$, $TiO_2$ (anatase) and α-quartz type $GeO_2$ of high purity (7 N) were used as starting materials. The 30 g batches were melted in platinum crucibles in air in an electric furnace. The melting temperature ranged from 1200 to 1500° C, depending on the composition of glass. The melts were poured out onto an iron plate. Glasses were annealed at temperatures 10 to 20° C lower than the respective glass transition temperatures.

TABLE I Composition and peak temperature of crystallization ($T_c$) of the glass

| Glass | Composition (mol%) | | | $T_c$ (° C) |
|---|---|---|---|---|
| | $Na_2O$ | $TiO_2$ | $GeO_2$ | |
| *Series 1* | | | | |
| 11 | 9.0 | 1.0 | 90.0 | 621 |
| 12 | 8.0 | 2.0 | 90.0 | 622 |
| 13 | 7.0 | 3.0 | 90.0 | 631 |
| 14 | 5.0 | 5.0 | 90.0 | 639 |
| 15 | 4.0 | 6.0 | 90.0 | 663 |
| 16 | 3.0 | 7.0 | 90.0 | 641 |
| 17 | 1.0 | 9.0 | 90.0 | 642 |
| *Series 2* | | | | |
| 21 | 18.0 | 2.0 | 80.0 | 609 |
| 22 | 17.0 | 3.0 | 80.0 | 623 |
| 23 | 16.0 | 4.0 | 80.0 | 620 |
| 24 | 14.0 | 6.0 | 80.0 | 633 |
| 25 | 13.0 | 7.0 | 80.0 | 639 |
| 26 | 11.0 | 9.0 | 80.0 | 651 |
| 27 | 9.0 | 11.0 | 80.0 | 658 |
| 28 | 6.0 | 14.0 | 80.0 | 689 |
| 29 | 5.0 | 15.0 | 80.0 | 666 |
| *Series 3* | | | | |
| 31 | 5.0 | 2.0 | 93.0 | 626 |
| 32 | 5.0 | 4.0 | 91.0 | 639 |
| 33 | 5.0 | 7.5 | 87.5 | 657 |
| 34 | 5.0 | 10.0 | 85.0 | 667 |
| 35 | 5.0 | 12.5 | 82.5 | 662 |
| 36 | 5.0 | 15.0 | 80.0 | 666 |
| *Series 4* | | | | |
| 41 | – | 2.4 | 97.6 | – |
| 42 | – | 3.2 | 96.8 | – |
| 43 | – | 6.4 | 93.6 | – |
| 44 | – | 9.6 | 90.4 | – |
| 45 | – | 12.7 | 87.3 | – |

### 2.2. Crystallization

For crystallization powdered glass samples were heated up to a temperature 50° C higher than the crystallization peak temperatures at a heating rate of 5° C $min^{-1}$ and then were cooled in air. The peak temperatures were determined beforehand by differential thermal analysis (DTA).

### 2.3. X-ray diffraction

The species of crystals precipitated in glasses were identified by X-ray diffraction technique. Lattice constants of the crystals were evaluated from *d*-values of their several diffraction lines using the least-square method. For these purposes, the nickel-filtered $CuK\alpha$ radiation was used. Reagent grade $CaCO_3$, the lattice parameters of which were corrected with high purity silicon powders, was used as an internal standard. The fraction of precipitated crystal phase was determined from the ratio of the intensity of its most intense diffraction peak to that of the co-precipitated crystal phase.

### 2.4. Measurement of X-ray absorption spectrum

The X-ray absorption spectrum near the Ti*K* absorption edge (4972 eV) was measured with a conventional X-ray machine. An analysing crystal, LiF, was mounted at the goniometer head. The specimens for the X-ray absorption measurement were prepared as films. The powdered glass sample was mixed with ethylene dichloride–formvar solution to make a thin slurry. The slurry was dried on a Teflon strip to form a film of thickness less than 0.2 mm. The copper target tube was used as a source of white X-rays. The film was placed at the incident beam. The intensity of the transmitting X-rays was measured at $2\theta$-intervals of 0.05° in the diffraction angle range of 74.5° to 76.5° in $2\theta$. The absorption coefficient, $\mu x$, was then estimated. The details of the procedure have been reported previously [11].

### 2.5. IR spectroscopy

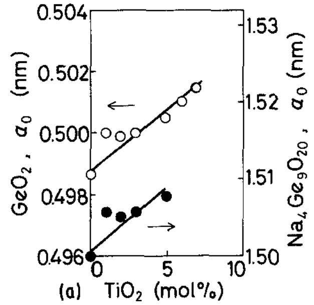
IR spectra of the glasses over the wavelength range of 400 to 1400 $cm^{-1}$ were measured using an IR spectrometer (Nihon Bunko Co, A-202). About 1 mg of glass powders was mixed with 150 mg of dried KBr and pressed into a disk for the measurement.

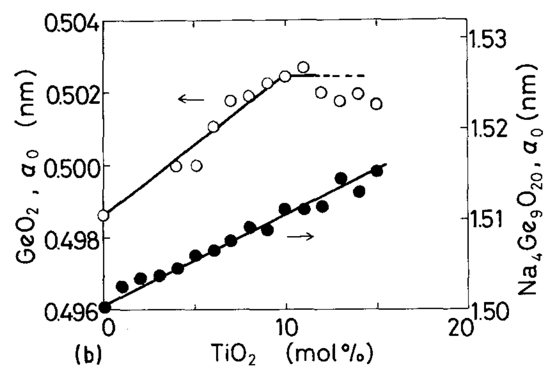
## 3. Results

### 3.1. Crystallization behaviour of glasses

On heating glasses of series 1 to 3, $GeO_2$ crystal with the hexagonal $\alpha$-quartz type structure and $Na_4Ge_9O_{20}$ with the tetragonal structure were precipitated. A very small amount of tetragonal $GeO_2$ was co-precipitated with these two crystals in $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ glasses with $x$ larger than 14. Only hexagonal $GeO_2$ crystal was precipitated in $TiO_2$–$GeO_2$ glasses.

The change of the lattice constants, $a_0$, of the $GeO_2$ and $Na_4Ge_9O_{20}$ crystals with the $TiO_2$ content of starting glasses is shown in Figs. 1a, b and c for series 1, 2 and 3, respectively. The increase in the lattice constant, $a_0$, of the $GeO_2$ and $Na_4Ge_9O_{20}$ crystals is attributed to the substitution of $Ti^{4+}$ ions for $Ge^{4+}$ ions. Fig. 2 shows the $a_0$ of $Ti_xGe_{1-x}O_2$ and $Na_4Ge_{9-x}Ti_xO_{20}$ solid solutions which were made by crystallizing glasses of the corresponding compositions. It has been confirmed that no compounds other than the hexagonal $GeO_2$ type crystal crystallize out of the former glasses, and $Na_4Ge_9O_{20}$ type crystal out of the latter glasses, as long as the $TiO_2$-content is not too large. Accordingly, the change of $a_0$ of $GeO_2$ and $Na_4Ge_9O_{20}$ with the $TiO_2$ content of glass





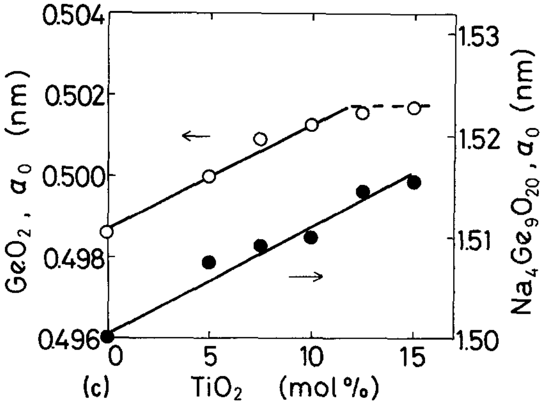


*Figure 1* Lattice constants $a_0$ of the hexagonal $GeO_2$ and the $Na_4Ge_9O_{20}$ type crystal precipitated in (a) $(10\text{-}x)$ $Na_2O \cdot xTiO2 \cdot 90GeO_2$ glasses, (b) $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80Ge_2$ glasses and (c) $5Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$ glasses.

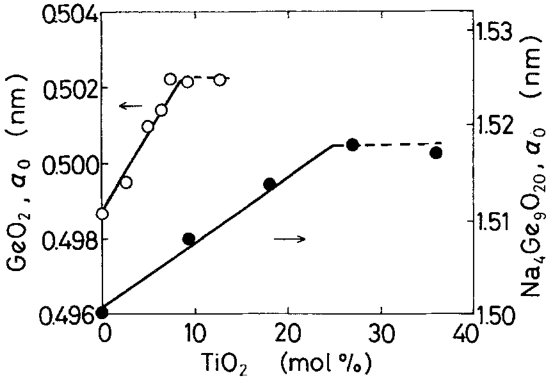
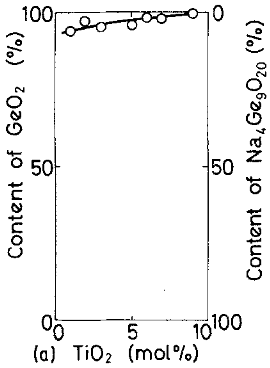


*Figure 2* Lattice constants $a_0$ of the solid solution of $Ti_xGe_{1-x}O_2$ (hexagonal $GeO_2$ type crystal) and $Na_4Ti_xGe_{9-x}O_{20}$ plotted against $TiO_2$ content.

shown in Fig. 2 is assumed to be caused by the incorporation of $Ti^{4+}$ ions in the crystals. The saturation in the increase of $a_0$ of $GeO_2$ at about 9 mol % $TiO_2$ and $Na_4Ge_9O_{20}$ at 27 mol % $TiO_2$ indicates that the solubility limits of $Ti^{4+}$ ions in these crystals are 9 and 27 mol %, respectively. It is clear that in $GeO_2$ type crystal $Ti^{4+}$ ions replace tetrahedrally coordinated $Ge^{4+}$ ions. In $Na_4Ge_9O_{20}$, where 4/9 of $Ge^{4+}$ ions are in 6-fold coordination and 5/9 of them are in 4-fold coordination [12], $Ti^{4+}$ ions replace only 6-fold coordinated $Ge^{4+}$ ions. This was confirmed on the basis of the diffraction intensity change of 1 0 1, 2 2 0, 2 0 0 and 2 0 2 lines with the content of incorporated $Ti^{4+}$ ions. Then, the data given in Fig. 2 enable us to estimate the contents of $Ti^{4+}$ ions in the $GeO_2$ and $Na_4Ge_9O_{20}$ type crystals precipitated in glasses of series 1 to 3 from the $a_0$ values shown in Fig. 1.

The fraction of the hexagonal $GeO_2$ and $Na_4Ge_9O_{20}$ type crystals in the crystallized glass which was estimated using the diffraction intensity is shown as a function of the $TiO_2$ content of the starting glass in Figs. 3a, b and c for series 1, 2 and 3, respectively. In any of series 1 glasses (Fig. 3a), the amount of hexagonal $GeO_2$ crystal is much larger than that of the $Na_4Ge_9O_{20}$ type crystal. Glasses of series 2 with $TiO_2$ contents smaller than a few mol % give the $Na_4Ge_9O_{20}$ type crystal along with a small amount of the hexagonal $GeO_2$ type crystal. The content of the latter crystal is seen to increase rapidly around 5 mol % $TiO_2$. For series 3, the major crystalline species is the hexagonal $GeO_2$, irrespective of the $TiO_2$ content.

The content of each crystalline phase and the content of incorporated $Ti^{4+}$ ions thus obtained are assumed to give the distribution of 4- and 6-fold coordinated $Ti^{4+}$ ions between the precipitated crystals. The fraction of 4-fold coordinated (or 6-fold vice versa) $Ti^{4+}$ ions thus evaluated is plotted against the $TiO_2$ content of the starting glass in Fig. 4a, b and c for series 1, 2 and 3, respectively. In crystallized glasses of series 1, a



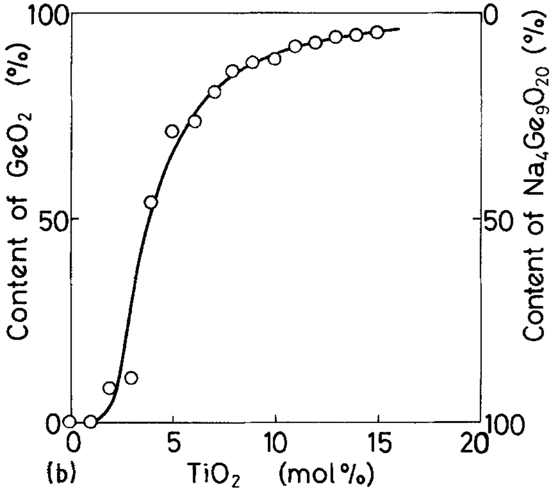
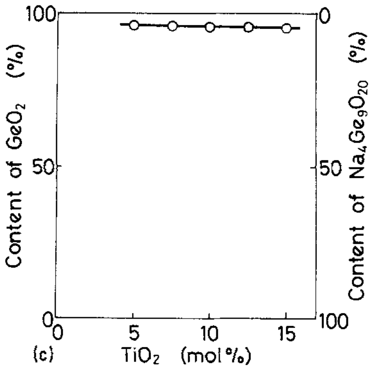


*Figure 3* Contents of the hexagonal $GeO_2$ and $Na_4Ge_9O_{20}$ in the crystallized glasses of compositions (a) $(10\text{-}x)Na_2O \cdot xTiO_2 \cdot 90GeO_2$, (b) $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ and (c) $5Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$.

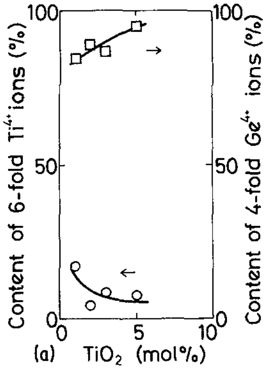


large part of the $Ti^{4+}$ ions is in 4-fold coordination. Furthermore, there is a tendency for 4-fold coordinated $Ti^{4+}$ ions to increase with increasing $TiO_2$ content of starting glasses. The majority of $Ti^{4+}$ ions in crystallized glasses of series 2 with $x$ of 2 to 5 are in 6-fold coordination. The fraction of 4-fold coordinated $Ti^{4+}$ ions increases as $TiO_2$ gradually replaces $Na_2O$, being over 90% at a $TiO_2$ content larger than 15 mol%. The fraction of 4-fold $Ti^{4+}$ ions in crystallized glasses of series 3 is over 90%, independent of the $TiO_2$ content.

The $Ge^{4+}$ ions present in $Na_2O$–$TiO_2$–$GeO_2$ glasses are also divided between the hexagonal $GeO_2$ and the $Na_4Ge_9O_{20}$ type crystal on crystallization of glass. The fraction of 4-fold coordinated (or 6-fold vice versa) $Ge^{4+}$ ions determined in a similar manner to the case of $Ti^{4+}$ ions is shown in Figs. 4a, b and c for glass series 1, 2 and 3, respectively. In series 1 and 2, the amount of 6-fold coordinated $Ge^{4+}$ ions is seen to decrease with increasing $TiO_2$ content of glass. In series 3, however, it is 9 to 10%, independent of the $TiO_2$ content of glass.

## 3.2. X-ray absorption spectra near *K* edge of $Ti^{4+}$ ions in the $TiO_2$-containing germanate glasses

Fig. 5 shows the X-ray absorption near *K*-edge structure (abbreviated as XANES) of $Ti^{4+}$ ions in three reference crystals and a reference glass of the composition of $6.5TiO_2 \cdot 93.5SiO_2$ (mol%), which has been made from metal alkoxides [13]. The $Ti^{4+}$ ions are in 4-fold coordination in $Li_4TiO_4$ and the reference glass and in 6-fold coordination in $TiO_2$ (anatase) and $TiO_2$ (rutile). The difference in the coordination state of $Ti^{4+}$ ions is distinctively reflected on the XANES, as seen in the figure. The spectrum of 6-fold coordinated $Ti^{4+}$ ions in rutile and anatase has a pronounced maximum around 20 to 30 eV, while that of 4-fold $Ti^{4+}$ ions in $Li_4TiO_4$ and the reference glass does not show any remarkable maxima or minima but a monotonic decrease in $\mu x$ in the high energy region. The spectra of $Ti^{4+}$ ions for rutile and anatase are in fairly good agreement with those [14] previously reported, although a peak at 20 eV in the present work is less pronounced compared to the previous ones. The spectra of $Ti^{4+}$ ions in $6.5TiO_2 \cdot 93.5SiO_2$ glass is very similar to that [9] reported for the corresponding glass made by a melting method. The slight difference in the spectrum of 4-fold coordinated $Ti^{4+}$ ions between $Li_4TiO_4$ and the glass may be due to the difference in connectivity of the $TiO_4$ tetrahedra. The $TiO_4$ tetrahedra are



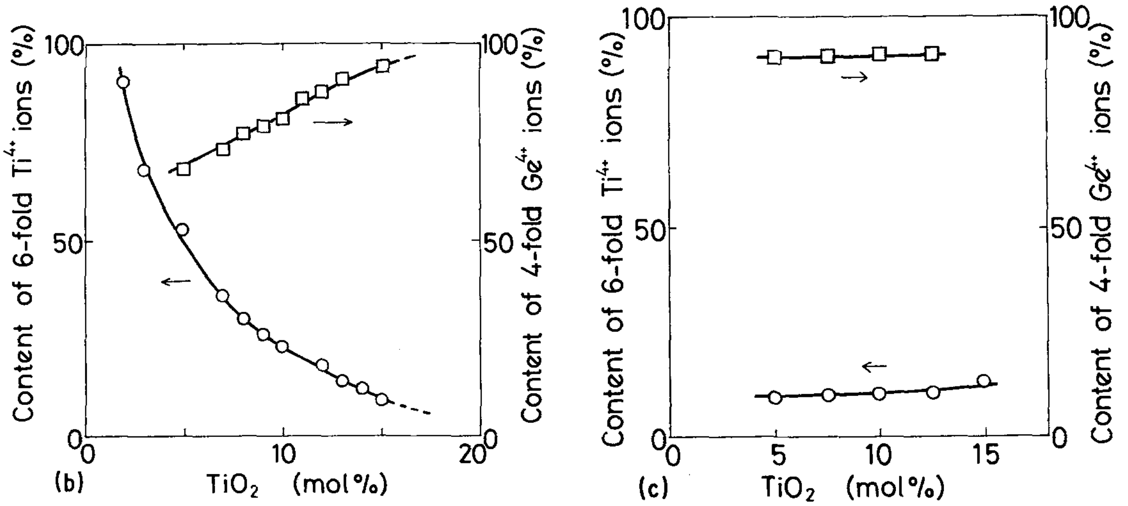


*Figure 4* Contents of 6-fold $Ti^{4+}$ ions and 4-fold $Ge^{4+}$ ions in the crystallized glasses of compositions (a) $(10\text{-}x)Na_2O \cdot xTiO_2 \cdot 90GeO_2$, (b) $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ and (c) $5Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$ determined from the crystallization behaviour.

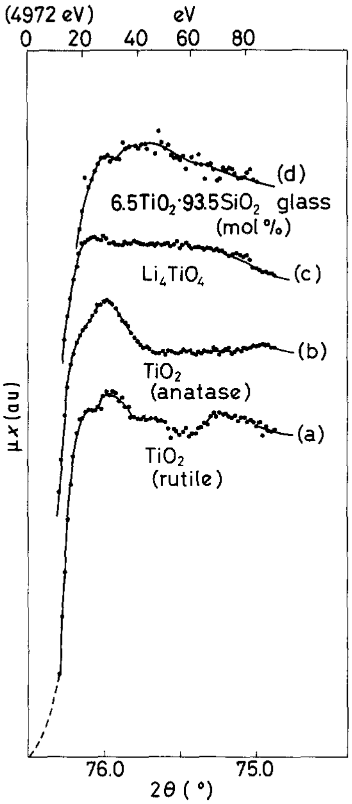


*Figure 5* X-ray absorption near *K* edge structure (XANES) spectra of $Ti^{4+}$ ions in (a) $TiO_2$ (rutile), (b) $TiO_2$ (anatase), (c) $Li_4TiO_4$ and (d) the $6.5TiO_2 \cdot 93.5SiO_2$ (mol %) glass.

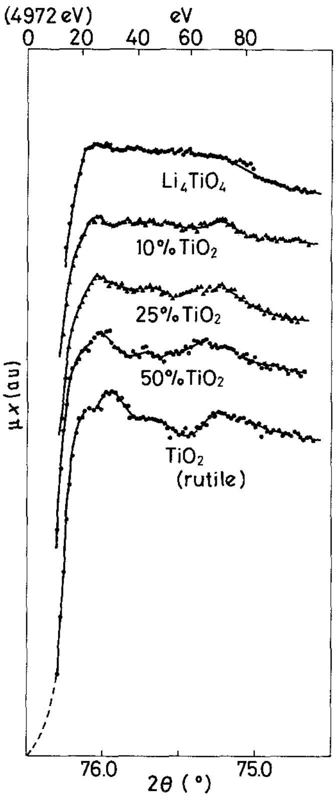


*Figure 6* XANES spectra of $Ti^{4+}$ ions in the $TiO_2$ (rutile)–$Li_4TiO_4$ crystal mixtures with different compositions. The attached number is the mol % of $TiO_2$ (rutile).

isolated in $Li_4TiO_4$, while they are linked with each other three-dimensionally via $SiO_4$ tetrahedra in $6.5TiO_2 \cdot 93.5SiO_2$ glass. The fine structure in the very small energy region (0 to 10 eV) which has been reported by Greegor *et al.* [9] could not be detected in the present work, because a weak emission line of tungsten (impurity element deposited on the copper target) was superimposed in that region. These differences in the present spectra from those of other authors, however, are not so serious for our purpose of determining the coordination state of $Ti^{4+}$ ions in the glasses because the difference in the spectrum between 4-fold and 6-fold coordinated $Ti^{4+}$ ions is remarkable. Fig. 6 shows XANES spectra of $Ti^{4+}$ ions in mixtures of $Li_4TiO_4$ and $TiO_2$ (rutile). The systematic change of the spectrum with the composition of the crystal mixture is observed. The peak at 20 to 30 eV, which is characteristic of 6-fold coordinated $Ti^{4+}$ ions, decreases in intensity with decreasing $TiO_2$ content. The peak can be discerned even if only 10% of $Ti^{4+}$ ions in the crystal mixture are in 6-fold coordination. This makes the semi quantitative analysis of the coordination state of $Ti^{4+}$ ions possible.

In Figs. 7a and b X-ray absorption spectra of $Ti^{4+}$ ions in $x TiO_2 \cdot (100\text{-}x) GeO_2$ glasses and $(20\text{-}x) Na_2O \cdot x TiO_2 \cdot 80GeO_2$ glasses are shown, respectively. A spectrum for $x TiO_2 \cdot (100\text{-}x) GeO_2$ glasses with $x$ of 9.5 is similar to $6.5TiO_2 \cdot 93.5SiO_2$ glass, indicating that the majority of $Ti^{4+}$ ions are in 4-fold coordination. The glass with $x = 12.7$ contains both 4- and 6-fold coordinated $Ti^{4+}$ ions. The $(20\text{-}x) Na_2O \cdot x TiO_2 \cdot 80GeO_2$ glasses with $x = 6$, 9, 11 and 14 give spectra similar to $Li_4TiO_4$ and $6.5TiO_2 \cdot 93.5SiO_2$ glass. Considering that the co-existence of just a small amount of 6-fold $Ti^{4+}$ ions with 4-fold $Ti^{4+}$ ions gives a hump at 20 to 30 eV as described above, it may be concluded that the majority of $Ti^{4+}$ ions in these glasses are in 4-fold coordination.

## 3.3. Infrared spectra of glasses

Figs. 8a, b and c, show IR spectra of glasses of series 1 to 3. The $TiO_2$ content of glass increases from the bottom curve to the top curve. The

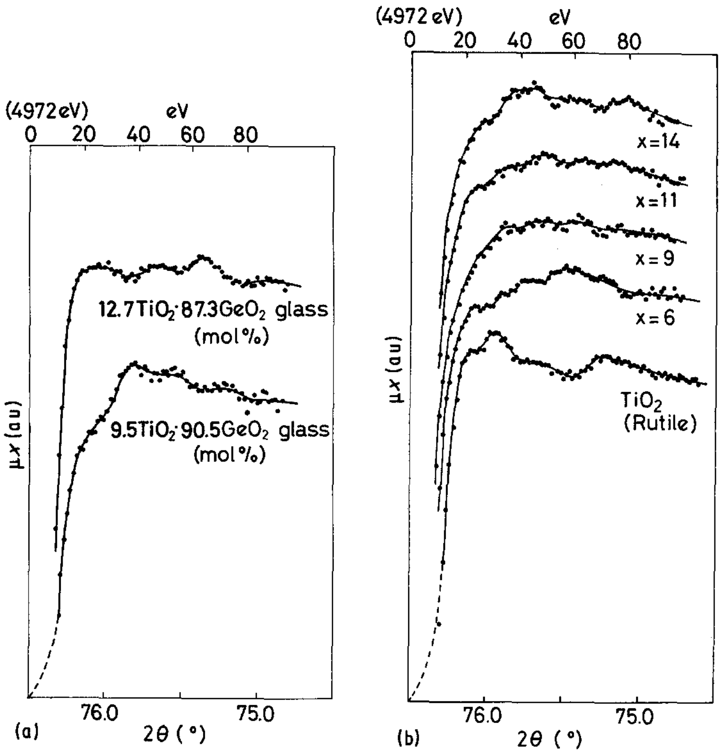


*Figure* 7 XANES spectra of $Ti^{4+}$ ions in (a) $x$TiO$_2$ · (100 $-x$)GeO$_2$ glasses and (b) (20 $-x$)Na$_2$O · $x$TiO$_2$ · 80GeO$_2$ glasses.

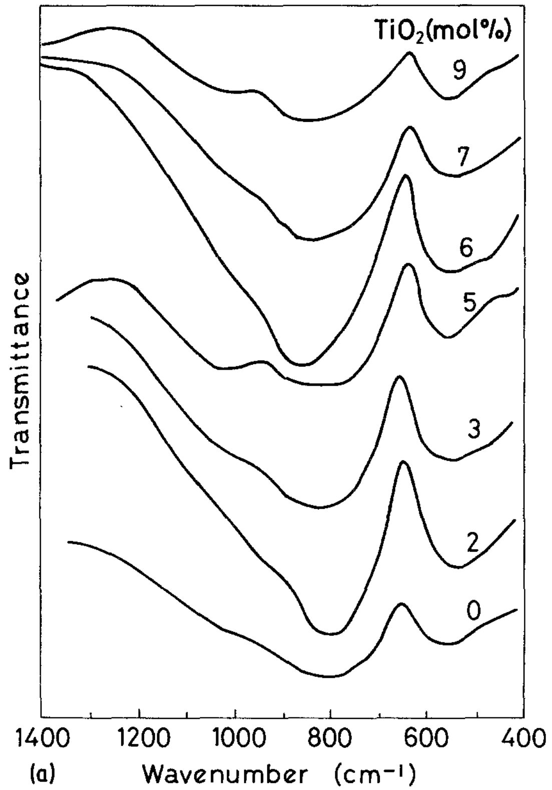
intense absorption peak at 800 to 850 cm$^{-1}$ is attributed to the Ge–O stretching vibration. In glasses of series 1 and 2, the absorption peak position is observed to shift toward the lower wavenumbers as the $TiO_2$ content decreases (or the $Na_2O$ content increases). In Fig. 9, the wavenumber of the peak is plotted as a function of $Na_2O$ content for glasses of series 1 and 2. The data for $Na_2O$–$GeO_2$ glasses are also shown for comparison. It is known that the shift of absorption peak is caused partly by the coordination change of some $Ge^{4+}$ ions from 4 to 6 and partly by mere addition of $Na_2O$ [10]. As can be seen in Fig. 9, the peak shift of $TiO_2$-containing glasses is slightly larger than that of binary $Na_2O$–$GeO_2$ glasses. The shift for glasses of series 3 and 4 is shown in Fig. 10 against the $TiO_2$ content. The shift of the absorption peak is relatively small in glasses of series 3, and it is scarcely observed in glasses of series 4.

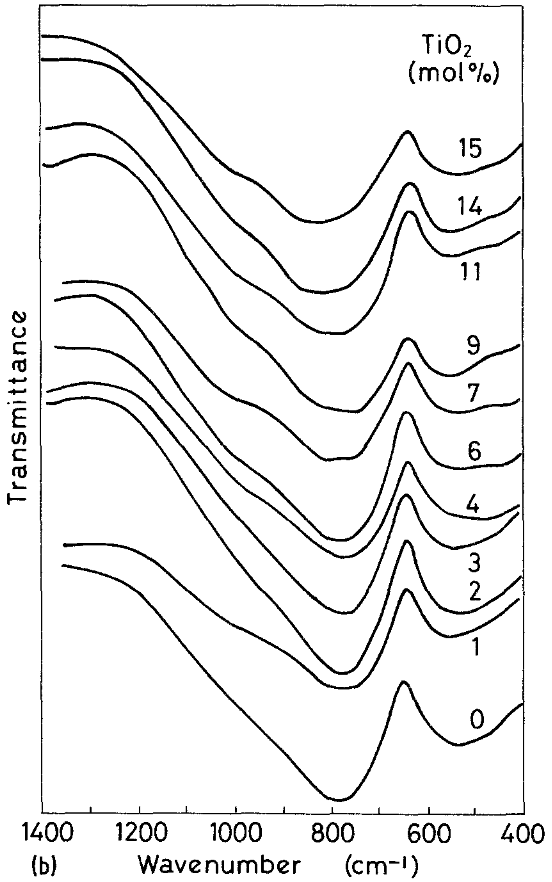
## 4. Discussion

### 4.1. Coordination state of $Ti^{4+}$ ions in germanate glasses

Crystallization of glasses is used as a preliminary approach to their structure. This technique may be useful especially when thermodynamically metastable crystals first precipitate in glasses. In that case the structure of glass is believed to be closely correlated with the precipitating metastable crystal. An example is fused $SiO_2$, which has a network structure similar to the first precipitating $\beta$-cristobalite. The addition of $TiO_2$ to $SiO_2$ glass does not change the fundamental structure. $Ti^{4+}$ ions merely substitute the tetrahedrally coordinated $Si^{4+}$ ions. The metastable, cristobalite type $SiO_2$ containing 4-fold coordinated $Ti^{4+}$ ions precipitates in the $TiO_2$–$SiO_2$ glasses [15].

It is assumed that crystallization of glasses can be used as a means for deducing the structure of the starting glass in the present $Na_2O$–$TiO_2$–$GeO_2$ systems, because metastable hexagonal $GeO_2$ crystals precipitate, although co-precipitating $Na_4Ge_9O_{20}$ crystal is thermodynamically stable. $\alpha$-quartz type hexagonal $GeO_2$ containing 4-fold coordinated $Ti^{4+}$ ions is metastable in the temperature range used in the present work. Actually, the precipitated hexagonal $GeO_2$ gradually transformed into the stable, tetragonal $GeO_2$ in which $Ge^{4+}$ ions are in 6-fold coordination on heating at higher temperatures or for longer times. In general, an ion tends to take a smaller coordination number at high temperatures. Considering that 6-fold coordinated $Ti^{4+}$ ions would not change to 4-fold





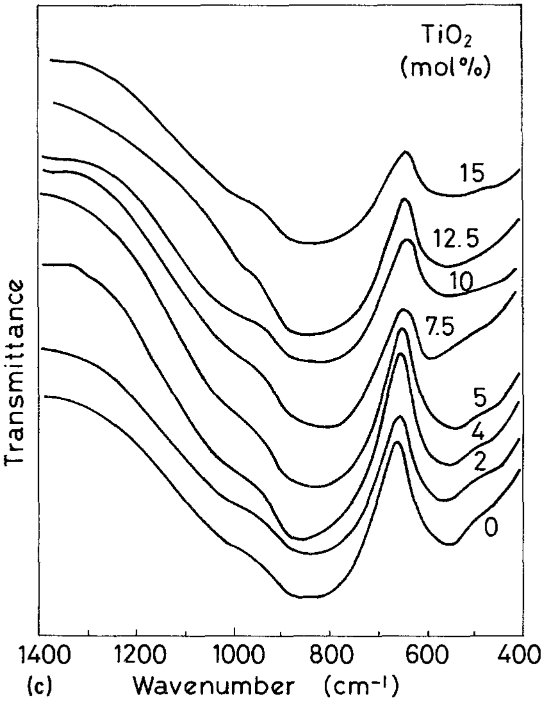


*Figure 8* Infrared absorption spectra of (a) $(10\text{-}x)\mathrm{Na_2O}\cdot x\mathrm{TiO_2}\cdot 90\mathrm{GeO_2}$ glasses, (b) $(20\text{-}x)\mathrm{Na_2O}\cdot x\mathrm{TiO_2}\cdot 80\mathrm{GeO_2}$ glasses and (c) $5\mathrm{Na_2O}\cdot x\mathrm{TiO_2}\cdot(95\text{-}x)\mathrm{GeO_2}$ glasses.

coordinated $\mathrm{Ti^{4+}}$ ions in the temperature range used in crystallizing the present glasses, the presence of 4-fold coordinated $\mathrm{Ti^{4+}}$ ions in the precipitated hexagonal $\mathrm{GeO_2}$ may be taken as showing that they are present in the starting glasses. Furthermore, one may conclude that the amount of 4-fold coordinated $\mathrm{Ti^{4+}}$ ions in the starting glass is not less than that in precipitated crystals.

The results deduced from the crystallization behaviour, that the majority of $\mathrm{Ti^{4+}}$ ions in $\mathrm{TiO_2}$–$\mathrm{GeO_2}$ and $\mathrm{Na_2O}$–$\mathrm{TiO_2}$–$\mathrm{GeO_2}$ glasses with large amounts of $\mathrm{TiO_2}$ are in 4-fold coordination, is confirmed by examining closely X-ray absorption spectra of $\mathrm{Ti^{4+}}$ ions in these glasses. The spectra of $\mathrm{Ti^{4+}}$ ions in the $\mathrm{TiO_2}$–$\mathrm{GeO_2}$ glasses indicated that the ions are in 4-fold coordination when the $\mathrm{TiO_2}$ content is kept at less than 9.5 mol%. The glass containing a large amount of $\mathrm{TiO_2}$ (12.7 mol%) gave the spectrum indicating the co-existence of 4-fold and 6-fold coordinated $\mathrm{Ti^{4+}}$ ions. Correspondingly, no crystals other than the hexagonal $\mathrm{GeO_2}$ containing 4-fold coordinated $\mathrm{Ti^{4+}}$ ions precipitated in the former glasses, while

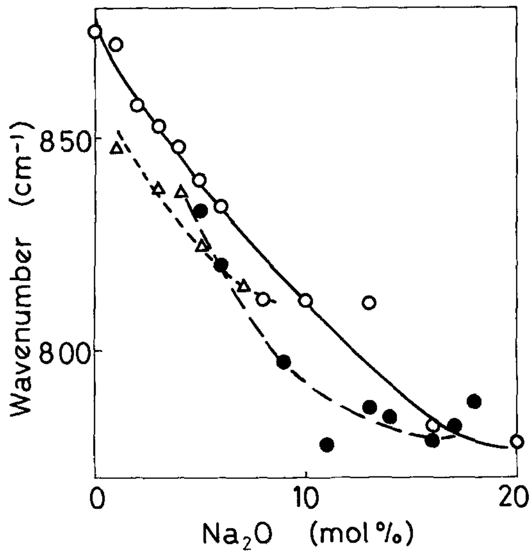


*Figure 9* Change of the wavenumber of the IR absorption peak due to Ge–O bonding with $Na_2O$ content: △, $(10\text{-}x)Na_2O \cdot xTiO_2 \cdot 90GeO_2$ glasses; ●, $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ glasses; ○, $xNa_2O \cdot (100\text{-}x)GeO_2$ glasses.

a small amount of the tetragonal $GeO_2$ containing 6-fold coordinated $Ti^{4+}$ ions co-precipitated with the hexagonal one in the latter glass.

The X-ray absorption spectra of $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ glasses with the $TiO_2$ content, $x$, larger than 9 mol% suggest that the majority of $Ti^{4+}$ ions are in 4-fold coordination, semi-quantitatively agreeing with the results deduced from the crystallization behaviour. It is, then, concluded that the majority of $Ti^{4+}$ ions are in 4-fold coordination in glasses of series 2 when the $TiO_2$ content is large relative to the $Na_2O$ content. The XANES was not applied to glasses of series 2 containing $TiO_2$ smaller than 6 mol%, because of too small a content of $Ti^{4+}$ ions to obtain a clear spectrum with the conventional X-ray machine. On the basis of the crystallization behaviour, $Ti^{4+}$ ions are assumed to be in 6-fold coordination in the glasses of series 1 and 2 when the $TiO_2$ content is relatively small. For glasses of series 3, the conclusion that the majority of $Ti^{4+}$ ions are in 4-fold coordination may be deduced from the crystallization behaviour, as well. The glass composition region where $Ti^{4+}$ ions more than 90% should be in 4-fold coordination has been determined from the distribution of $Ti^{4+}$ ions between precipitated crystals, and is shown in Fig. 11. The coordination state of $Ti^{4+}$ ions in the alkali germanate glasses qualitatively agrees with that in the alkali silicate glasses [4, 5], namely, 4-fold coordinated $Ti^{4+}$ ions are incorporated into glasses when their content is large and 6-fold ones may preferably occur in glasses when their content is small.

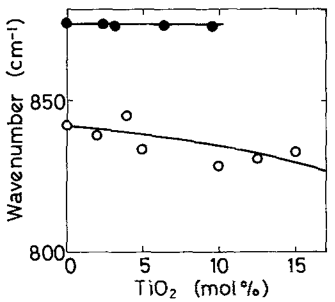


*Figure 10* Change of the wavenumber of the IR peak due to Ge–O bonding with $TiO_2$ content: ○, $5\,Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$ glasses; ●, $xTiO_2 \cdot (100\text{-}x)GeO_2$ glasses.

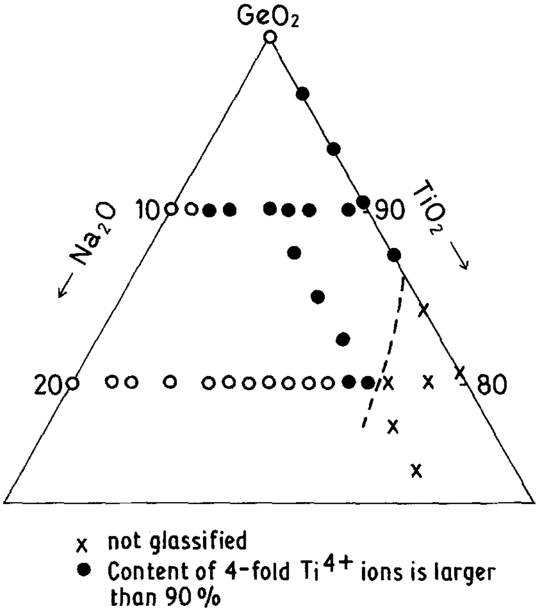


*Figure 11* Compositon region in $Na_2O–TiO_2–GeO_2$ glasses where the per cent of 4-fold coordinated $Ti^{4+}$ ions is over 90, determined based on the crystallization behaviour.

## 4.2. Coordination state of $Ge^{4+}$ ions in $TiO_2$-containing germanate glasses

The $Ge^{4+}$ ions in $Na_2O–TiO_2–GeO_2$ glasses are divided between the precipitating hexagonal $GeO_2$ and $Na_4Ge_9O_{20}$ on crystallization, as $Ti^{4+}$ ions are. This gives the semi-quantitative information on the coordination state of $Ge^{4+}$ ions in starting glasses. It has been found that the majority of $Ge^{4+}$ ions in these glasses take a 4-fold coordination number, and 6-fold $Ge^{4+}$ ions tend to increase with decreasing $TiO_2$ content (for increasing $Na_2O$ content). A more quantitative state analysis of

$Ge^{4+}$ ions in glasses will be made on the basis of IR spectroscopy in this section.

As already mentioned, it has been found that the shift of the IR absorption peak at 800 to 900 $cm^{-1}$ with $Na_2O$ content in the binary $Na_2O$–$GeO_2$ glasses is ascribed partly to the change in average coordination number of $Ge^{4+}$ ions. When $TiO_2$ is added to the $GeO_2$ glass, the situation is somewhat different. That is, the $Ti^{4+}$ ions give an additional broad band at 500 to 600 $cm^{-1}$, if they are incorporated in 6-fold coordination. A small hump on the lower wavenumber side of the intensive peak due to the Ge–O bonding appears if the incorporated $Ti^{4+}$ ions are in 4-fold coordination [7]. This hump is attributed to the desymmetrization of the $GeO_4$ tetrahedron due to the formation of mixed Ge–O–Ti bonds in the network. The hump, therefore, may not be placed at a constant wavenumber, but shifts along with the main peak due to Ge–O bonding. The hump is very small, and so the peak position for the Ge–O bonding is easily determined, making the state analysis of $Ge^{4+}$ ions possible irrespective of the presence of $Ti^{4+}$ ions.

As is clearly seen in Fig. 10, the wavenumbers of the Ge–O peak of the $TiO_2$-containing germanate glasses are smaller than those of binary $Na_2O$–$GeO_2$ glasses at the same $Na_2O$ content. The amount of 6-fold $Ge^{4+}$ ions, $N_6$, can be estimated from the shift of the IR peak relative to the $GeO_2$ glass ($\Delta\nu$) using the following equation [10]:

$$N_6 = \frac{(\Delta\nu - 3.0x) \times 100}{175} \qquad (1)$$

where the number, 3.0, in parentheses corresponds to the shift in $cm^{-1}$ due to the mere addition of 1.0 mol % alkali oxide and $x$ is mol % of the alkali oxide. The 175 in the denominator is the difference in peak position in $cm^{-1}$ between the hexagonal $GeO_2$ and rutile type $GeO_2$. In Fig. 12 $N_6$ is plotted against $Na_2O$ content for $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ glasses, and is compared with that for the binary $xNa_2O \cdot (100\text{-}x)GeO_2$ glasses. It is noticed that more 6-fold coordinated $Ge^{4+}$ ions occur in $Na_2O$–$TiO_2$–$GeO_2$ glasses than in $Na_2O$–$GeO_2$ glasses. As $TiO_2$ replaces $GeO_2$ in the $5Na_2O \cdot 95GeO_2$ glass, the wavenumber of Ge–O bonding slightly shifts towards the lower value, showing that $N_6$ slightly increases as the amount of substituting $Ti^{4+}$ ions increases. These suggest that in $Na_2O$–$TiO_2$–$GeO_2$ glasses the coordination change of $Ge^{4+}$ ions from 4-fold to 6-fold occurs more preferably than that of $Ti^{4+}$ ions does. In other words, $Na_2O$ reacts more readily with a $GeO_4$ tetrahedron to form a $GeO_6$ octahedron than with $TiO_4$ to form $TiO_6$ in $Na_2O$–$TiO_2$–$GeO_2$ glasses of relatively large $TiO_2$ contents.

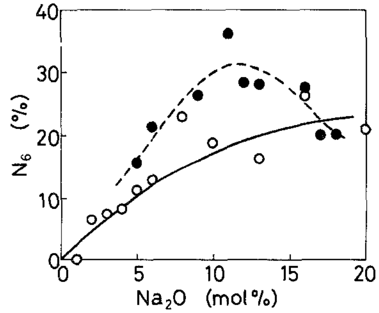


*Figure 12* Variation of the content of 6-fold coordinated $Ge^{4+}$ ions with $Na_2O$ content: ○, $xNa_2O \cdot (100\text{-}x)GeO_2$ glasses; ●, $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ glasses.

## 5. Summary

The coordination state of $Ti^{4+}$ and $Ge^{4+}$ ions in glasses of compositions of $(10\text{-}x)Na_2O \cdot xTiO_2 \cdot 90GeO_2$, $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$, $5Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$ and $xTiO_2 \cdot (100\text{-}x)GeO_2$ has been investigated by using techniques based on the crystallization, X-ray absorption and IR absorption spectrometry. The following results have been obtained.

1. Upon crystallization of glasses, $Ti^{4+}$ ions were incorporated into both metastable hexagonal $GeO_2$ and stable $Na_4Ge_9O_{20}$ type crystals. In the hexagonal $GeO_2$ and the $Na_4Ge_9O_{20}$ type crystals, $Ti^{4+}$ ions replace 4-fold and 6-fold coordinated $Ge^{4+}$ ions, respectively.

2. The fraction of 4-fold and 6-fold coordinated $Ti^{4+}$ ions in the crystallized glasses has been determined from (i) the content of the precipitated hexagonal $GeO_2$ and $Na_4Ge_9O_{20}$ type crystals and (ii) the amount of $Ti^{4+}$ ions incorporated into each crystal determined from the lattice constant of the corresponding crystal. The fraction of 4-fold $Ti^{4+}$ ions in the crystallized glasses of compositions $(10\text{-}x)Na_2O \cdot xTiO_2 \cdot 90GeO_2$ and $5Na_2O \cdot xTiO_2 \cdot (95\text{-}x)GeO_2$ was 80 to 90%, independent of the $TiO_2$ content. For $(20\text{-}x)Na_2O \cdot xTiO_2 \cdot 80GeO_2$ glasses, the majority of $Ti^{4+}$ ions were assumed to be in 6-fold coordination at small $TiO_2$ contents, and the fraction of 4-fold $Ti^{4+}$ ions gradually increased up to over 90% as the $TiO_2$ content was increased.

3. The distribution of $Ti^{4+}$ ions into two

coordination states in the crystallized glasses was regarded as a reflection of the starting glass from the viewpoint of stability of precipitating crystals in the temperature range used in the experiment.

4. It was confirmed by the X-ray absorption spectrum near the *K*-edge that 4-fold coordinated $Ti^{4+}$ ions are abundant in glasses at large $TiO_2/Na_2O$ ratios.

5. It has been found by IR spectroscopy that the amount of 6-fold coordinated $Ge^{4+}$ ions was larger in $Na_2O–TiO_2–GeO_2$ glasses than in binary $Na_2O–GeO_2$ glasses for the identical $Na_2O$ content, suggesting that 4-fold coordinated $Ge^{4+}$ ions change their coordination state to 6-fold more preferentially than 4-fold $Ti^{4+}$ ions do when the $TiO_2$ content is large relative to the $Na_2O$ content.

6. It is concluded that $Ti^{4+}$ ions are incorporated as 6-fold coordinated $Ti^{4+}$ ions into $Na_2O–GeO_2$ glasses at small $TiO_2/Na_2O$ ratios. At high $TiO_2/Na_2O$ ratios, they may take a 4-fold coordination state, replacing 4-fold coordinated $Ge^{4+}$ ions than in binary $Na_2O–GeO_2$ glasses. The following scheme may be obtained. The constituent $Na_2O$ reacts more readily with $TiO_4$ tetrahedra to form $TiO_6$ octahedra than it does with $GeO_4$ tetrahedra to form $GeO_6$ octahedra at small $TiO_2/Na_2O$ ratios. On the contrary, $Na_2O$ reacts more preferentially with $GeO_4$ tetrahedra to form $GeO_6$ octahedra instead of making $TiO_6$ octahedra from $TiO_4$ tetrahedra at large $TiO_2/Na_2O$ ratios. This scheme of change in coordination state of $Ti^{4+}$ ions is consistent with that for $Na_2O–TiO_2–SiO_2$ glasses.

## Acknowledgements

This work has supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. The authors wish to thank Mr N. Nishihama and Mr Y. Miki for their assistance in the experiment.

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*Received 20 March*
*and accepted 12 April 1984*