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The Si–O bonding in Na_2O–TiO–SiO_2 and K_2O–TiO_2 – SiO_2 glasses as studied by SiKβ X-ray fluorescence and infra-red absorption spectroscopy

SUMIO SAKKA, HITOSHI HOTTA
Faculty of Engineering, Mie University, Tsu, Mie-Ken, Japan

The SiKβ fluorescence X-ray and infra-red absorption spectra of Na_2O–TiO_2–SiO_2 and K_2O–TiO_2–SiO_2 glasses have been measured in order to study the Si–O bonding as a function of the composition of glass. The chemical shifts of the SiKβ peak relative to that of silica glass [$\Delta\lambda = \lambda(SiO_2) - \lambda(\text{specimen}) > 0$] and the wavenumbers of the infra-red absorption peaks around $950\,cm^{-1}$ and $1100\,cm^{-1}$ have been determined from the spectra. The SiKβ chemical shift in both series of glasses increased with increasing total content of R_2O and TiO_2 and with decreasing ratio of $TiO_2/(K_2O + TiO_2)$, where R_2O represents Na_2O or K_2O. The infra-red peaks around $950\,cm^{-1}$ and $1100\,cm^{-1}$ shifted towards lower wavenumbers with increasing total content of R_2O and TiO_2 and with decreasing ratio of $TiO_2/(R_2O + TiO_2)$. These experimental facts were interpreted as showing that the Si–O bond in glass was weakened as the total content of R_2O and TiO_2 increased and that the Si–O bond was weakened by R_2O more than by TiO_2.

1. Introduction

The structure of R_2O–TiO_2–SiO_2 glasses, where R_2O denoted an alkali oxide (Na_2O or K_2O) has attracted many authors [1–5] interested in the coordination number of Ti atoms in glass. In order to solve the problem of coordination of Ti atoms, more spectroscopic measurements are required. In addition, investigations on physico-chemical properties of glasses have been made [6–10] from the practical aspects. It is considered that the coordination of Ti atoms in glasses and their physico-chemical properties are related to the strength of Si–O bonds. Therefore, the Sikβ X-ray and infra-red spectra have been studied in this work with the purpose of obtaining information on the strength of Si–O bonds in glasses.

The chemical shift of the SiKβ X-ray emission spectra relative to quartz has been found by Gibbs and White [11, 12] to be related to the S–O bonding state in silicate crystals; it is larger for weaker, and accordingly longer, Si–O bonds. Dodd and Glen interpreted [13] the SiKβ spectra of silicon dioxide and silicates by molecular orbital theory and, in addition, assumed that the chemical shift of the SiKβ peak relative to silica glass represents destabilization (weakening) of the Si–O bonds. On the basis of the assumption made by Dodd and Glen, Sakka and Matusita [15], and Sakka and Senga [16] examined the effect of components other than SiO_2 on the strength of the Si–O bond in silicate and aluminosilicate glasses by measuring the chemical shift of the SiKβ line. Wiech *et al.* [17] correlated changes in SiKα and Kβ spectra with the OH and Na_2O contents of various silicate glasses.

Infra-red spectroscopy is one of the means for examining the strength of the Si–O bond. Toyuki [18] indicated that for Na_2O–SiO_2 glasses the peak wavenumbers in the region of 1100 to about $700\,cm^{-1}$, which are assigned to Si–O vibrations, shift to lower wavenumbers

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as the Na_2O content increases and that this corresponds to weakening of the Si–O bond with increasing Na_2O content. Manghnani *et al.* [19] and Takashashi *et al.* [3] measured infra-red spectra of several Na_2O–TiO_2–SiO_2 glasses.

2. Experimental

2.1. Preparation of glasses

Sixteen ternary glasses of the Na_2O–TiO_2–SiO_2 system with SiO_2 contents of 70, 60, 50 and 40 mol%, 4 binary glasses of the Na_2O–SiO_2 system, 23 ternary glasses of the K_2O–TiO_2–SiO_2 system with the K_2O contents of 70, 60, 50, 40 and 30 mol%, and 4 binary glasses of the K_2O–SiO_2 glasses were prepared. Commercially available silica glass was used as the reference. The compositions of the glasses used in the measurement are shown in Tables I and II. Eight of the K_2O-containing glasses, whose compositions are listed in Table II, were strongly hygroscopic, which made it impossible to obtain reliable data due to the formation of hydration products during measurement even with the specimens prepared in dry N_2 atmosphere.

Reagent grade chemicals of Na_2CO_3, K_2CO_3 and TiO_2 and silica powder for manufacturing optical glasses were used as starting materials. About 100 g batch placed in a platinum crucible was melted at 1200 to 1580° C for 2 h in an electric furnace with silicon carbide heating elements. The melt was poured into a round carbon mould, annealed at an appropriate temperature and cooled. The annealed glass was formed into a disc of 40 mm in diameter and 5 to 8 mm thick. The surfaces of the disc were ground and finished with 5 μm alumina powder for fluorescence X-ray measurements. For the measurement of infra-red spectra, a piece of glass was pulverized.

2.2. Fluorescence X-ray measurement

The X-ray emission spectra were taken with a Rigaku–Denki fluorescence X-ray spectrometer using Cr-target continuous X-ray as exciting radiation. The excitation voltage and current were 50 kV and 50 mA, respectively. The dispersion angle of the solar slit was 0.115°. An EDDT crystal was used as an analysing crystal, and a pulse height analyser was employed. A stepwise scan was made at intervals of 0.05° between 99.90° and 100.90° in 2θ with the fixed time method using the counting time of 40 seconds. The centre of the bandwidth at half peak intensity was taken as the peak position. The average of

TABLE I Chemical shifts of $SiK\beta$ and wavenumbers of Si–O stretching peaks in Na_2O–TiO_2–SiO_2 glasses

No.	Composition (mol%)			$TiO_2/(Na_2O + TiO_2)$	Chemical shift of $SiK\beta$*		Si–O stretching peaks (cm^{-1})	
	Na_2O	TiO_2	SiO_2		$\Delta\lambda \times 10^4$ (Å)	ΔE (eV)	950 cm^{-1} peak	1100 cm^{-1} peak
N 1	15	15	70	0.5	18.7	0.51	985	1130
N 2	15	25	60	0.625	28.1	0.76	955	1130
N 3	20	20	60	0.5	25.6	0.69	965	1130
N 4	25	15	60	0.375	26.1	0.71	960	1115
N 5	10	40	50	0.8	17.3	0.47	988	1160
N 6	15	35	50	0.7	23.7	0.64	975	1160
N 7	20	30	50	0.6	29.1	0.79	955	1120
N 8	25	25	50	0.5	32.5	0.88	940	1110
N 9	30	20	50	0.4	35.0	0.95	925	1100
N 10	35	15	50	0.3	38.9	1.05	915	1070
N 11	15	45	40	0.75	29.1	0.79	940	1120
N 12	20	40	40	0.67	39.9	1.08	940	1100
N 13	25	35	40	0.58	–	–	928	1080
N 14	30	30	40	0.5	40.4	1.09	910	1060
N 15	40	20	40	0.33	42.4	1.15	905	1040
N 16	45	15	40	0.25	43.4	1.17	905	1020
N 17	20	–	80				1000	1120
N 18	30	–	70				950	1080
N 19	40	–	60				925	1045
N 20	50	–	50				905	1020
S 1	–	–	100				(1100)	(1100)

*$\Delta\lambda = (SiO_2) - \lambda(\text{specimen})$, $\Delta E = (\text{specimen}) - E(SiO_2)$.

TABLE II Chemical shifts of SiKβ and wavenumbers of Si–O stretching peaks in K_2O–TiO_2–SiO_2 glasses

No.	Composition (mol %)			$TiO_2/(K_2O + TiO_2)$	Chemical shift of SiKβ†		Si–O stretching peaks (cm^{-1})	
	K_2O	TiO_2	SiO_2		$\Delta\lambda \times 10^4$ (Å)	ΔE (eV)	950 cm^{-1} peak	1100 cm^{-1} peak
K 1	15	15	70	0.5	19.7	0.54	986	1170
K 2	10	30	60	0.75	20.7	0.56	1000	1180
K 3	15	25	60	0.625	23.6	0.64	980	1160
K 4	20	20	60	0.5	25.1	0.68	985	1140
K 5	25	15	60	0.375	28.1	0.76	965	1140
K 6	30	10	60	0.25	30.5	0.83	965	1120
K 7	10	40	50	0.8	22.2	0.60	975	1180
K 8	15	35	50	0.7	27.1	0.74	955	1150
K 9	20	30	50	0.6	30.5	0.83	952	1130
K 10	25	25	50	0.5	32.0	0.87	940	1105
K 11	30	20	50	0.4	35.0	0.95	940	1080
(K 12)*	35	15	50	0.3				
(K 13)*	40	10	50	0.2				
K 14	15	45	40	0.75	32.5	0.88	945	1130
K 15	20	40	40	0.67	35.0	0.95	940	1090
K 16	30	30	40	0.5	39.4	1.07	930	1070
(K 16)*	40	20	40	0.33				
(K 18)*	50	10	40	0.17				
K 19	20	50	30	0.71	40.9	1.11	925	1065
K 20	30	40	30	0.57	44.8	1.22	900	1050
K 21	35	35	30	0.5	44.8	1.22	980	1040
(K 22)*	40	30	30	0.43				
(K 23)*	50	20	30	0.29				
K 24	20	–	80				1000	1140
K 25	30	–	70				980	1100
(K 26)*	40	–	60					
(K 27)*	50	–	50					

*Hygroscopic.

†$\Delta\lambda = \lambda\,(SiO_2) - \lambda$ (specimen), $\Delta E = E$ (specimen) $- E\,(SiO_2)$.

three measurements was adopted as the value for a particular sample. The peak shifts of the SiKβ line were measured with respect to the peaks of SiO_2 glass and quartz, which gave identical values, and represented in the units of wavelength (Å) and energy (eV). The following formulae were used so as to express the shifts:

$$\text{(wavelength)} \quad \Delta\lambda = \lambda\,(SiO_2) - \lambda\,(\text{specimen}) \quad (1)$$

$$\text{(energy)} \quad E = E\,(\text{specimen}) - E\,(SiO_2) \quad (2)$$

To reduce experimental errors arising from change in the interplanar spacing of the analysing crystal caused by the fluctuation in the ambient temperature, measurements on specimens were always accompanied by measurements of the standard.

2.3. Measurement of infra-red spectra

Infra-red spectra were measured using a grating infra-red spectrometer of Nihon–Bunko type IR-G. The wavenumber range between 4000 and 400 cm^{-1} was covered. The KBr pellet method was employed. The pellet was prepared by adding 2 mg glass powder to 200 mg spectroscopically pure, dried KBr, mixing well and pressing at the pressure of 400 kg cm^{-2} under evacuation. The pellet was 10 mm in diameter and 1 mm thick.

3. Results

3.1. X-ray spectra

The SiKβ spectra of $x Na_2O \cdot x TiO_2 \cdot (100 - 2x) SiO_2$ glasses, in which equal moles of Na_2O and TiO_2 are contained and their total contents vary, are shown in Fig. 1. The spectrum of silica glass is also shown for comparison. It is seen that the SiKβ peak shifts towards smaller 2θs (smaller wavelengths or larger energies) on simultaneous addition of Na_2O and TiO_2 and the chemical shift increases as the total content of Na_2O and TiO_2 increases. Some of the glasses containing Na_2O and TiO_2 seem to have a slight bump or a small shoulder on the side of the curve larger in 2θ than the peak.

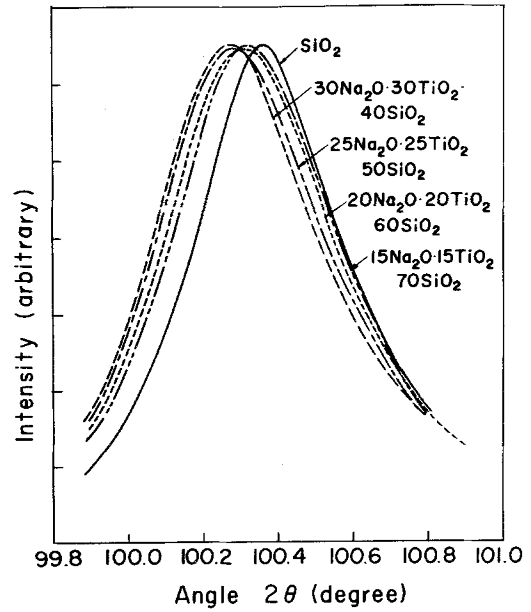

Figure 1 SiKβ spectra of SiO_2 and four $x Na_2O \cdot x TiO_2 \cdot (100-2x) SiO_2$ glasses.

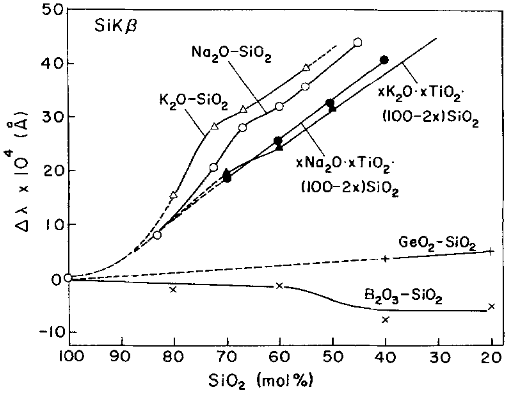

Figure 3 Chemical shifts of SiKβ bands of $x Na_2O \cdot x TiO_2 \cdot (100-2x) SiO_2$ and $x K_2O \cdot x TiO_2 \cdot (100-2x) SiO_2$ glasses. Those of other glasses [15] are also shown for comparison.

These shoulders, if any, are not discussed here since they are very small. Fig. 2 shows the spectra of $x Na_2O \cdot (50-x) TiO_2 \cdot 50SiO_2$ glasses, in which the total content of Na_2O and TiO_2 is constant at 50 mol% and the ratio $TiO_2/(Na_2O + TiO_2)$ varies. It is seen that the smaller amount of TiO_2 leads to larger chemical shifts while the total content of Na_2O and TiO_2 is constant. The values of chemical shifts expressed by the wavelength and energy are summarized in Table I for sodium glasses and in Table II for potassium glasses.

Fig. 3 shows the chemical shifts of the SiKβ peak, $\Delta\lambda$, as a function of the SiO_2 content for $Na_2O–TiO_2–SiO_2$ and $K_2O–TiO_2–SiO_2$ glasses with equal moles of R_2O (Na_2O or K_2O) and TiO_2. It is seen that the chemical shift increases with decreasing SiO_2 content (increasing total content of R_2O and TiO_2) for both sodium and potassium glasses. The $\Delta\lambda$s of a number of binary silicate glasses [15] are also shown in the figure for comparison. It can be seen that at constant SiO_2

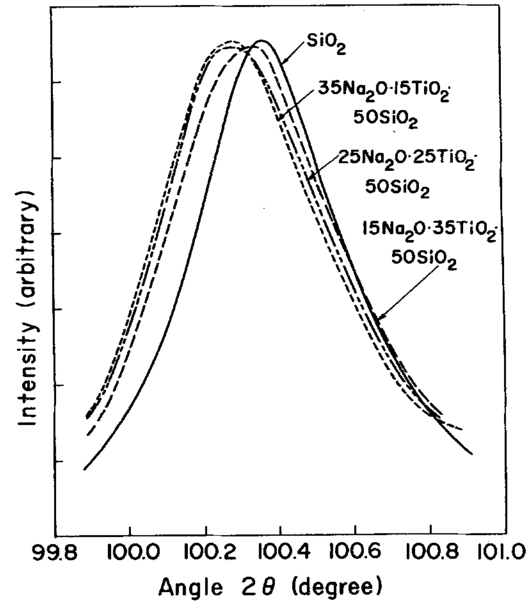

Figure 2 SiKβ spectra of SiO_2 and three $Na_2O \cdot (50-x) TiO_2 \cdot 50SiO_2$ glasses

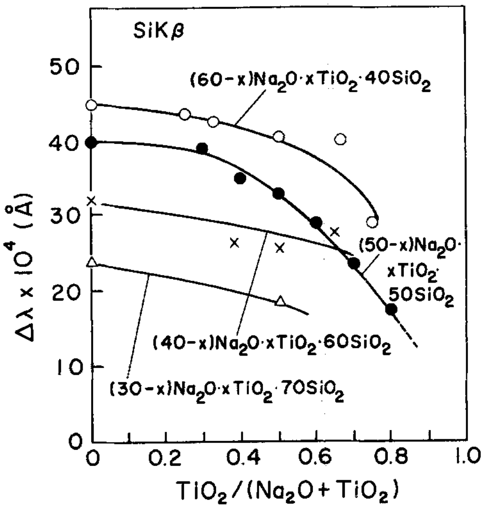

Figure 4 Chemical shifts of SiKβ bands of $Na_2O–TiO_2–SiO_2$ glasses, in which the total content of Na_2O and TiO_2 is constant, as a function of the mole ratio $TiO_2/(Na_2O + TiO_2)$.

contents the $\Delta\lambda$ is smaller for R_2O–TiO_2–SiO_2 glasses than for R_2O–SiO_2 glasses.

Figs. 4 and 5 show the $\Delta\lambda$s of SiKβ as functions of the ratio $TiO_2/(R_2O + TiO_2)$. It can be seen that the $\Delta\lambda$ markedly increases with decreasing $TiO_2/(R_2O + TiO_2)$ ratio for both sodium and potassium glasses.

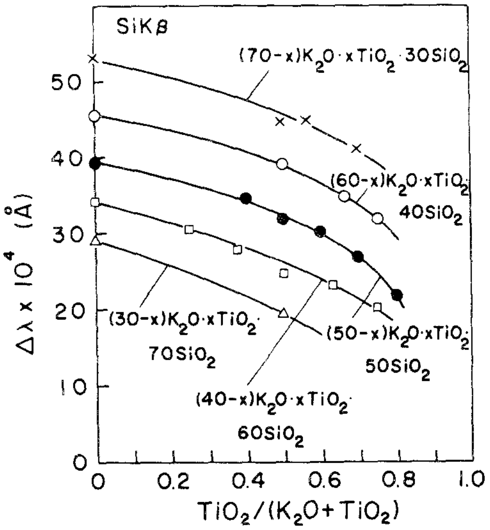

Figure 5 Chemical shifts of SiKβ bands of K_2O–TiO_2–SiO_2 glasses, in which the total content of K_2O and TiO_2 is constant, as a function of the mole ratio $TiO_2/(K_2O + TiO_2)$.

3.2. Infra-red spectra

The measured infra-red spectra are shown in Figs. 6 and 7. The figures indicate that there are strong absorptions in 1180 to 900 cm^{-1}, weak absorptions in 790 to 700 cm^{-1} and at ~ 600 cm^{-1}, and relatively sharp absorptions in 500 to 450 cm^{-1}. These absorption bands were discussed for Na_2O–SiO_2 glasses by Toyuki [18], who assigned them to vibrations of infra-red active Si–O stretching, inactive Si–O–Si bending, and active Si–O–Si bending, respectively. In this study attention will be paid to the absorptions in the frequency range

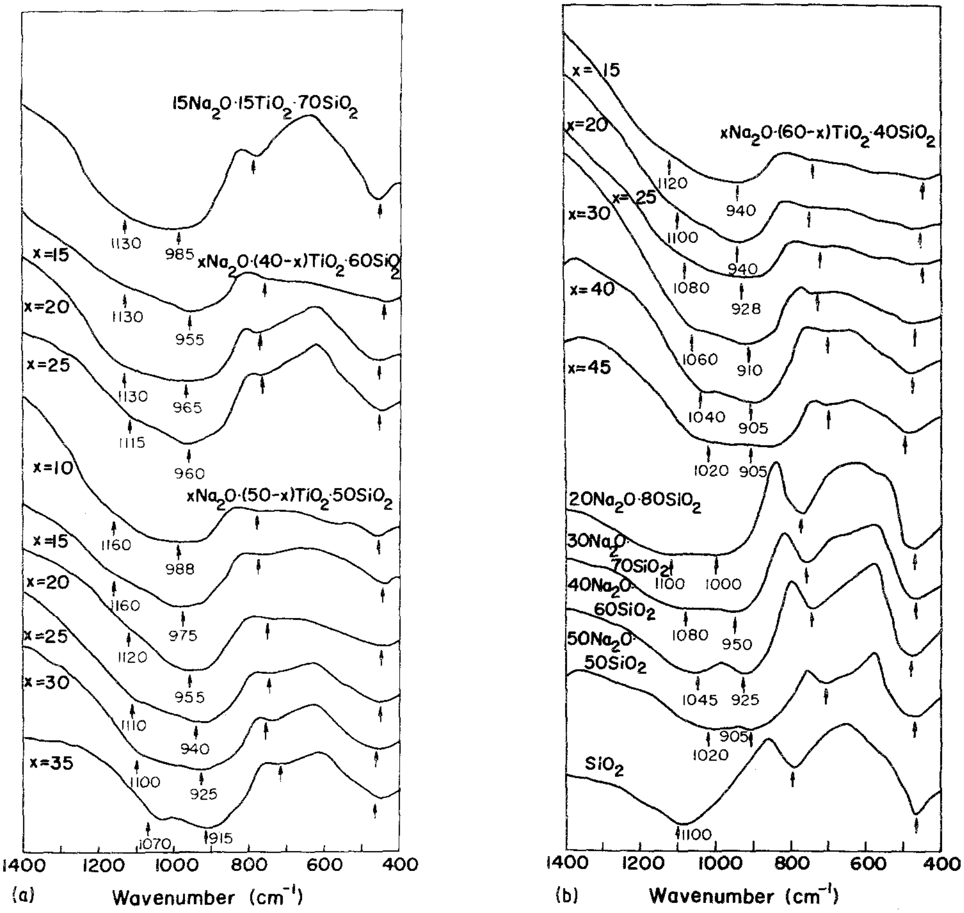

Figure 6 (a) and (b) Infra-red absorption spectra of Na_2O–TiO_2–SiO_2 glasses.

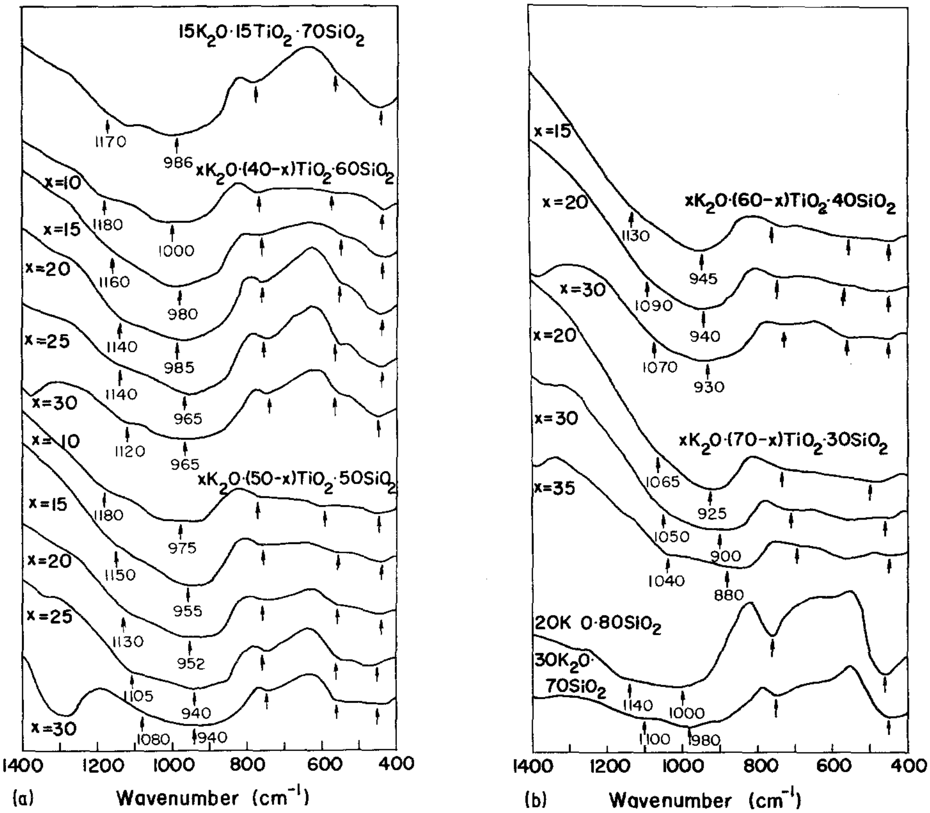

Figure 7 (a) and (b) Infra-red absorption spectra of K_2O–TiO_2–SiO_2 glasses.

of ~1180 to 900 cm^{-1}, since the peak wavenumbers of the absorptions at ~600 cm^{-1} and at 500 to 450 cm^{-1} show complicated dependence on glass composition [19] and the peaks in ~790 to 700 cm^{-1} may be mixed with those attributed to TiO_4 and TiO_6 groups [4].

It is seen from Figs. 6 and 7 that the absorptions in 1180 to 900 cm^{-1} consist of the weak band with a peak or a shoulder in ~1180 to 1020 cm^{-1} and the strong band with a peak in ~1000 to 900 cm^{-1}. The former will be called the 1100 cm^{-1} absorption and the latter the 950 cm^{-1} absorption. The peak wavenumbers of both the absorptions are given in Tables I and II. It should be noted that the dependence of the 1100 cm^{-1} peak exhibits a similar tendency as that of the 950 cm^{-1} peak, although the former is weak and less clear.

Figs. 8 and 9 show the plots of the wavenumbers of the 950 cm^{-1} absorption versus the ratio $TiO_2/(R_2O + TiO_2)$ with the parameters of SiO_2 content for Na_2O–TiO_2–SiO_2 and K_2O–TiO_2–SiO_2 glasses. For both sodium and potassium glasses, the peak shifts towards low

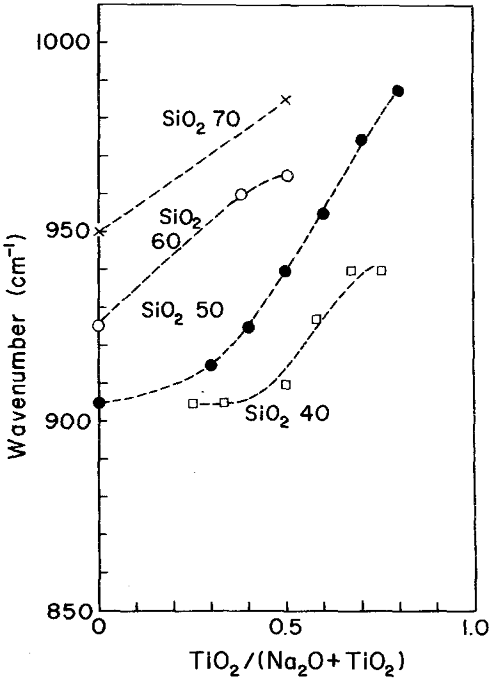

Figure 8 Wavenumbers of 950 cm^{-1} infra-red peaks plotted against the mole ratio $TiO_2/(Na_2O + TiO_2)$ for Na_2O–TiO_2–SiO_2 glasses.

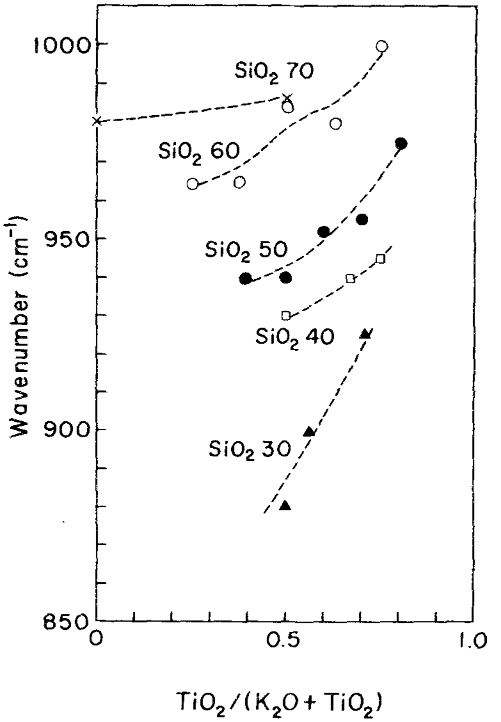

Figure 9 Wavenumbers of 950 cm^{-1} infra-red peaks plotted against the mole ratio $TiO_2/(K_2O + TiO_2)$ for $K_2O–TiO_2–SiO_2$ glasses.

wavenumbers as the SiO_2 content decreases with constant $TiO_2/(R_2O + TiO_2)$. With the constant SiO_2 content, that is, constant total content of R_2O and TiO_2, the peak shifts toward low wavenumbers as the ratio $TiO_2/(R_2O + TiO_2)$ decreases. The dependence of the peak wavenumber on the composition is not illustrated for the 1100 cm^{-1} absorption, but it is stressed again that the composition dependence of the 1100 cm^{-1} absorption is similar to that of the 950 cm^{-1} absorption.

4. Discussion

4.1. Chemical shift of SiKβ

White and Gibbs [11, 12] found that the chemical shift of the SiKβ peak relative to SiO_2 increased linearly with the Si–O distance for silicate minerals. This indicates that the larger chemical shift corresponds to a weaker Si–O bond, since the bond distance should be related to the strength of the Si–O bond. Dodd and Glen [14] suggested on the basis of molecular orbital theory that the SiKβ peak corresponds to the $3p(\sigma^b)$–1s transition of the electron and that the shift of the SiKβ peak towards high energies (small wavelengths) relative to SiO_2 corresponds to the weakening of the Si–O bond compared with that in SiO_2. The latter concept that the larger the chemical shift of SiKβ, the weaker the Si–O bond, will be applied to the result of this study.

It can be deduced from Fig. 3 that both R_2O (Na_2O or K_2O) and TiO_2 weaken the Si–O bond when added to SiO_2. On the other hand, it is remarkable that the glass-forming oxides such as GeO_2 and B_2O_3 do not affect the strength of the Si–O bond so much (Fig. 3). According to Figs. 4 and 5, the effect of TiO_2 in weakening the Si–O bond is smaller than that of the alkali oxides. For instance, $\Delta\lambda$ is 40×10^{-4} Å in $50Na_2O\cdot50SiO_2$ glass (Fig. 4), but as Na_2O is replaced by TiO_2, it markedly decreases, lowering to 24×10^{-4} Å and 17×10^{-4} Å, respectively, for the $TiO_2/(Na_2O + TiO_2)$ ratios 0.7 and 0.8. This tendency is true also for the series of glasses containing 40, 60 and 70 mol% of SiO_2 (Fig. 4). This tendency for the degree of weakening of the Si–O bond to decrease as the TiO_2 content increases, keeping a constant total content of $R_2O + TiO_2$, can be also found in the $K_2O–TiO_2–SiO_2$ glasses (Fig. 4).

4.2. Infra-red spectra

Toyuki [18] calculated the force constant of the Si–O stretching vibration from the wavenumbers of infra-red spectra for $Na_2O–SiO_2$ binary glasses. The result indicated that the decrease of the peak wavenumbers in the region 1100 to 900 cm^{-1} corresponds to the decrease of the force constant. On this basis it is assumed that also for $R_2O–TiO_2–SiO_2$ glasses the shift of the 1100 cm^{-1} and 950 cm^{-1} absorptions towards lower wavenumbers represents decrease of the force constant, that is, weakening of the Si–O bond.

It has been pointed out (Fig. 8) that the peak wavenumbers of the 1100 and 950 cm^{-1} absorptions pronouncedly decrease with the decrease in the SiO_2 content for $Na_2O–TiO_2–SiO_2$ glasses with constant ratio $TiO_2/(Na_2O + TiO_2)$. This would indicate that the Si–O bonds weaken as the SiO_2 content decreases. For glasses with constant total contents of Na_2O and TiO_2, the peak wavenumber is smaller with the glasses having a smaller $TiO_2/(Na_2O + TiO_2)$ ratio. This would indicate that Na_2O is more effective than TiO_2 in weakening the Si–O bond.

The situation is similar for $K_2O–TiO_2–SiO_2$ glasses (Fig. 9). The Si–O bonds become weak as the SiO_2 content decreases and K_2O is more effective than TiO_2 in weakening the Si–O bond.

4.3. Weakening of the Si–O bond

As to the strength of the Si–O bond, infra-red spectra gave a similar result to the SiKβ fluorescence X-ray spectra as described above. The relation of the weakening of the Si–O bond to the glass structure is not necessarily clear, but the following explanation seems possible.

The larger chemical shift of the SiKβ peak corresponds to the general weakening of the Si–O bonds.

As for the infra-red spectra, the 1100 cm^{-1} peaks are attributed to the stretching vibration of the Si–O bonds within the tetrahedra containing only bridging oxygens, and the 950 cm^{-1} peaks to the stretching vibration within the tetrahedra containing non-bridging oxygens [21, 22]. With this assumption, it can be stated that the Si–O bonds become weak with increasing total content of R_2O and TiO_2 and increasing ratio of R_2O to $(R_2O + TiO_2)$ in the SiO_4 tetrahedra containing one or more non-bridging oxygens as well as in those containing no non-bridging oxygen.

Toyuki [18] gave an electronic explanation for the weakening of the Si–O bond with increasing Na_2O content in Na_2O–SiO_2 glasses. The weakening was attributed to the lowering of the bond order caused by the localization of π electrons belonging to the Si–O network on the oxygens.

The coordination of titanium has not been discussed here, since further data are required for elucidating it.

5. Summary

The chemical shifts of the SiKβ peak relative to that of silica glass [$\Delta\lambda = \lambda(SiO_2) - \lambda(\text{specimen}) > 0$] and the wavenumbers of the infra-red absorption peaks around 950 cm^{-1} and 1100 cm^{-1} have been determined for Na_2O–TiO_2–SiO_2 and K_2O–TiO_2–SiO_2 glasses and the following results have been obtained:

(1) In both series of glasses the SiKβ chemical shift increased with increasing total content of R_2O and TiO_2 and with decreasing ratio of $TiO_2/(R_2O + TiO_2)$, where R_2O represents Na_2O or K_2O. This was interpreted as indicating that the Si–O bond becomes weaker as the total content of R_2O and TiO_2 increases and the ratio $TiO_2/(R_2O + TiO_2)$ decreases.

(2) The infra-red peaks around 950 cm^{-1} and 1100 cm^{-1} shifted towards lower wavenumbers with increasing total content of R_2O and TiO_2 and with decreasing ratio of $TiO_2/(R_2O + TiO_2)$. This was interpreted as indicating that the Si–O bond becomes weaker as the total content of R_2O and TiO_2 increases and the ratio $TiO_2/(R_2O + TiO_2)$ decreases, as in the case of the SiKβ chemical shift.

(3) It was suggested that the decrease of the average Si–O bond strength occurred in SiO_4 tetrahedra containing no non-bridging oxygens as well as in SiO_4 tetrahedra containing one or more non-bridging oxygens.

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