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Studies on Si-O bonding in silicate and aluminosilicate glasses based on SiKβ emission X-rays

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The Si*Kβ* X-ray emission spectra of silicate and aluminosilicate glasses and crystals have been measured with an X-ray fluorescence spectrometer and the chemical shifts of the Si*Kβ* peak relative to that of SiO_2 glass have been determined. Trends in the chemical shift of the Si*Kβ* peak for $Na_2O–SiO_2$, $Li_2O–SiO_2$ and $Li_2O–Al_2O_3–SiO_2$ glasses were similar to those of their crystalline counterparts, indicating that the strength of the Si–O bond varies in the same way with composition in both glass and crystal. The chemical shift in alkali aluminosilicate glasses containing equal molar proportions of aluminium oxide and alkali oxide increased with decreasing SiO_2 content, indicating that the Si–O bond also weakened in aluminosilicate glasses. The same effect was also observed when zirconia was added. The Si*Kβ* bandwidths for $Na_2O–Al_2O_3–SiO_2$ and $Li_2O–Al_2O_3–SiO_2$ glasses with the Al_2O_3: M_2O ratio equal to one, remained almost the same as for SiO_2 glass, indicating that the addition of alkali does not result in the formation of non-bridging oxygens in the framework if accompanied by Al_2O_3.

1. Introduction

The effect of chemical composition on X-ray emission spectra is particularly useful for the study of glass structure since (1) it is largely controlled by the state of bonding of a particular ion to its immediate neighbours and is almost independent of the presence or absence of long-range order, and (2) it can be readily applied to study bonding of aluminium and silicon which are important constituents in industrial glasses [1]. The chemical shifts of the Al*Kα* line in Al_2O_3-containing glasses have been measured previously [2, 3] and these can be used to measure the coordination number of Al^{3+} ions in glass. Dodd and Glen [4] measured the Si*Kβ* spectra in $Li_2O–Al_2O_3–SiO_2$ glasses and used the chemical shift of the Si*Kβ* peak to calculate the Si–O bond energy, which decreased with lower SiO_2 contents. Wiech *et al.* [5] correlated changes in the Si*Kα* and *Kβ* spectra with the OH and Na_2O contents of various silicate glasses. Sakka and Matusita [6] measured chemical shifts of the Si*Kβ* line for several series of binary silicate glasses and obtained results indicating that the average Si–O bond weakened as alkali oxide was added to SiO_2. However, the Si–O bond strength remained relatively constant in $B_2O_3–SiO_2$ and $GeO_2–SiO_2$ glasses.

In this study the Si*Kβ* X-ray emission spectra were measured in polynary silicate glasses, including some with non-alkali network-modifiers or intermediates such as MgO, CaO, Al_2O_3 and ZrO_2. MgO and CaO, like alkali oxides, are typical network-modifiers, but the divalent cations may bond more strongly to the network than the alkali ions. Aluminium may replace silicon in the network.

2. Experimental methods

2.1. Preparation of glasses

$Na_2O–Al_2O_3–SiO_2$, $Li_2O–Al_2O_3–SiO_2$, CaO–MgO–SiO_2, CaO–Al_2O_3–SiO_2, $Na_2O–ZrO_2–SiO_2$, CaO–Al_2O_3–ZrO_2–SiO_2 and Na_2O–CaO–SiO_2 glasses were prepared by melting 100 g batches in platinum crucibles at 1300 to 1600° C for 2 to 4 h, depending on the glass composition. The melts were poured into round carbon moulds and an-

TABLE I Preparation of crystals

Crystals	Melting of glass	Crystallization of glass	X-ray data and references
$Na_2O–SiO_2$ system			
Na_2SiO_3	1400° C, 3 h	600° C, 3 h	ASTM Card 1-0836
$Na_2Si_2O_5$	1400° C, 2 h	600° C, 192 h	Reference 7
$Na_2Si_3O_7$	1450° C, 2 h	700° C, 28 h	
$Li_2O–SiO_2$ system			
Li_2SiO_3	1400° C, 2 h	650° C, 192 h	ASTM Card 4-0273
$Li_2Si_2O_5$	1400° C, 2 h	650° C, 192 h	ASTM Card 4-0436
$Li_2O–Al_2O_3–SiO_2$ system			
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ (β-quartz ss)*	1500° C, 3 h	750° C, 4 h	References 8 to 10 ASTM Card 15-27
(β-quartz ss)	1500° C, 3 h	1300° C, 4 h	
$Li_2O \cdot Al_2O_3 \cdot 3SiO_2$ (β-quartz ss)	1500° C, 3 h	750° C, 4 h	
(β-quartz ss)	1500° C, 3 h	1300° C, 4 h	
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ (β-quartz ss)	1500° C, 3 h	750° C, 4 h	
(β-spodumene ss)	1500° C, 3 h	1300° C, 4 h	
$Li_2O \cdot Al_2O_3 \cdot 6SiO_2$ (β-spodumene ss)	1550° C, 3 h	750° C, 4 h	
(β-spodumene ss)	1550° C, 3 h	1300° C, 4 h	
$Li_2O \cdot Al_2O_3 \cdot 8SiO_2$ (β-quartz ss)	1500° C, 3 h	750° C, 4 h	
(β-spodumene ss)	1500° C, 3 h	1300° C, 4 h	

*ss = solid solution

nealed at appropriate temperatures. After annealing, the glasses were formed into discs 40 mm in diameter and 5 to 8 mm thick. The surfaces of the disc were ground and finished with 5 μm alumina powder. Viscous melts which could not be poured out of the crucible were obtained as small pieces by quenching the melt in water. Specimens of such glasses were prepared by mixing powdered glass with about 20% cellulose powder and compressing discs of the mixture at 2000 kg cm^{-2}.

2.2. Preparation of crystals

Crystals of the $Na_2O–SiO_2$, $Li_2O–SiO_2$ and $Li_2O–Al_2O_3–SiO_2$ systems shown in Table I were prepared. Appropriate compositions were melted in platinum crucibles and the resulting clear glasses were converted to crystals by heating at temperatures and times as shown in Table I. On reheating, $Li_2O–SiO_2$ and $Li_2O–Al_2O_3–SiO_2$ glasses crystallized easily in the bulk as well as at the surface. Bulk nucleation in these glasses has been studied previously [11, 12], however $Na_2O–SiO_2$ glasses crystallized slowly, so these were powdered before crystallization to promote surface nucleation. The crystalline phases were identified by X-ray diffraction. The conversion of most of the glass to crystals was confirmed by the absence of the diffuse X-ray scattering bands characteristic of glassy samples.

2.3. Measurement of the Si$K\beta$ spectra

The X-ray emission spectra were taken with a Rigaku–Denki fluorescence X-ray spectrometer using Cr-target continuous X-rays as exciting radiation. The excitation voltage and current were 50 kV and 50 mA, respectively. An EDDT crystal was used as an analysing crystal. A pulse height analyser was employed. A stepwise 2θ scan was made at intervals of 0.05°, and peak positions determined at half peak intensity. The average

TABLE II Chemical shifts of Si$K\beta$ for reference materials

Material	$\Delta 2\theta$ (EDDT) (deg)	$\Delta\lambda \times 10^4$ Å	ΔE (ev)
Silica glass, SiO_2 (Standard)	0	0	0
Orthoclase, $12.5\,K_2O \cdot 12.5\,Al_2O_3 \cdot 75\,SiO_2$	0.025	12.3	0.33
Mullite, $3\,Al_2O_3 \cdot 2\,SiO_2$	0.065	32	0.87
K_2SiF_6	0.065	32	0.87
Silicon metal, Si	0.218	106	2.9
SiP_2O_7	−0.013	−6.4	−0.17

$\Delta 2\theta = 2\theta_{(SiO_2)} - 2\theta_{(specimen)}$, $\Delta\lambda = \lambda_{(SiO_2)} - \lambda_{(specimen)}$, $\Delta E = E_{(specimen)} - E_{(SiO_2)}$.

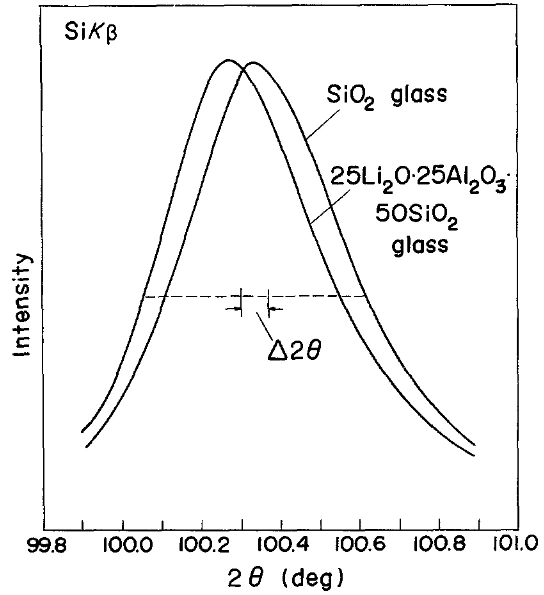

Figure 1 Examples of Si$K\beta$ bands. The chemical shift for the glass $25\,Li_2O \cdot 25\,Al_2O_3 \cdot 50\,SiO_2$ is shown by $\Delta 2\theta$.

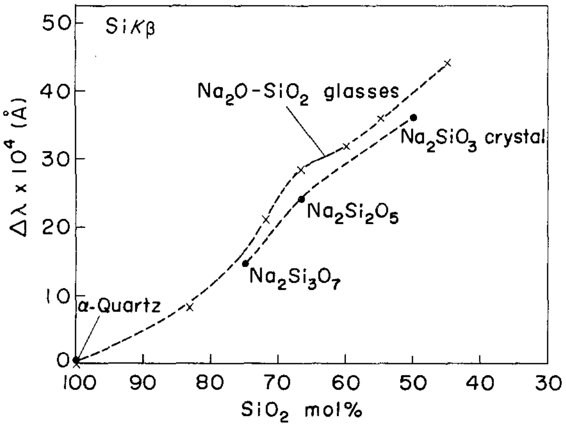

Figure 2 Comparison of the chemical shift $\Delta\lambda$ between glasses and crystals for the Na_2O–SiO_2 system. $\Delta\lambda = \lambda_{(SiO_2)} - \lambda_{(\text{specimen})}$.

of three measurements was adopted as the value for a particular sample. The peak shifts of the Si$K\beta$ line were measured with respect to the peaks of SiO_2 glass and quartz, which gave identical values. To reduce experimental errors arising from changes in the interplanar spacing of the analysing crystal caused by the fluctuation in the ambient temperature, measurements on samples were always accompanied by measurements of the standard.

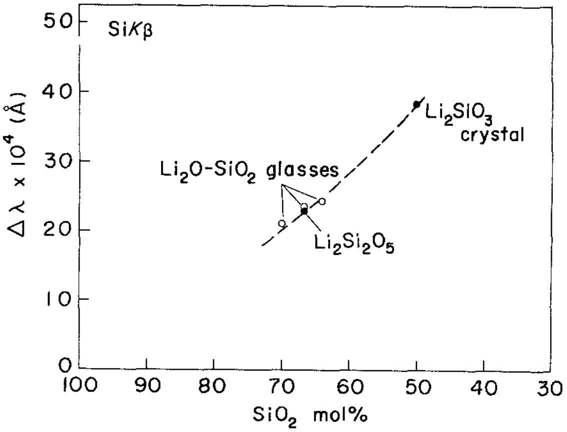

Figure 3 Comparison of the chemical shift between glasses and crystals for the Li_2O–SiO_2 system.

3. Results

3.1. Chemical shifts for alkali silicate and aluminosilicate crystals

Chemical shifts of the Si$K\beta$ line measured on reference materials are listed in Table II. Fig. 1 shows the examples of the Si$K\beta$ bands.

Figs. 2 to 4 compare chemical shifts, $\Delta\lambda$, of crystals and glasses. The data for Na_2O–SiO_2 and Li_2O–SiO_2 glasses were taken from reference [6]. Fig. 2 shows that the composition dependence of the chemical shift of Na_2O–SiO_2 crystals is similar to that for Na_2O–SiO_2 glasses, and that at the same composition the value for a crystal is slightly smaller than for glass. Only one point of comparison exists in the Li_2O–SiO_2 system (Fig. 3); at the $Li_2Si_2O_5$ composition the values are virtually identical. In Fig. 4, the composition

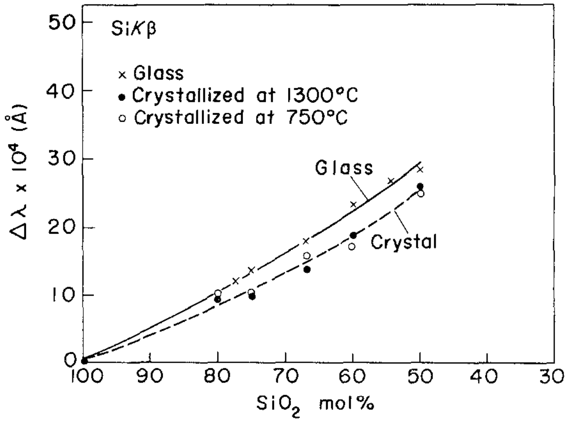

Figure 4 Chemical shifts of the Si$K\beta$ peak for $x\,Li_2O \cdot x\,Al_2O_3 \cdot (100 - 2x)\,SiO_2$ glasses and crystals.

TABLE III Chemical shifts of Si$K\beta$ line for glasses

Glass (mol%)		$\Delta 2\theta$ (EDDT) (deg)	$\Delta\lambda \times 10^4$ (Å)	ΔE (ev)
Alkali aluminosilicate glasses				
$15\,Na_2O \cdot 0.15\,Al_2O_3 \cdot 70\,SiO_2$		0.037	18.2	0.493
$20\,Na_2O \cdot 20\,Al_2O_3 \cdot 60\,SiO_2$		0.050	24.7	0.666
$11.2\,Li_2O \cdot 11.2\,Al_2O_3 \cdot 77.6\,SiO_2$	Al_2O_3/Li_2O = 1.0	0.025	12.5	0.330
$17.9\,Li_2O \cdot 4.5\,Al_2O_3 \cdot 77.6\,SiO_2$	0.25	0.027	13.3	0.360
$10\,Li_2O \cdot 15\,Al_2O_3 \cdot 75\,SiO_2$	1.5	0.033	16.3	0.440
$12.5\,Li_2O \cdot 12.5\,Al_2O_3 \cdot 75\,SiO_2$	1.0	0.028	13.8	0.373
$16.7\,Li_2O \cdot 8.3\,Al_2O_3 \cdot 75\,SiO_2$	0.5	0.033	16.3	0.440
$16.65\,Li_2O \cdot 16.65\,Al_2O_3 \cdot 66.7\,SiO_2$	1.0	0.037	18.2	0.493
$16\,Li_2O \cdot 24\,Al_2O_3 \cdot 60\,SiO_2$	1.5	0.046	22.7	0.613
$20\,Li_2O \cdot 20\,Al_2O_3 \cdot 60\,SiO_2$	1.0	0.048	23.7	0.693
$15.5\,Li_2O \cdot 30.4\,Al_2O_3 \cdot 54.1\,SiO_2$	1.97	0.050	24.7	0.666
$22.95\,Li_2O \cdot 22.95\,Al_2O_3 \cdot 54.1\,SiO_2$	1.0	0.054	26.6	0.719
$29.2\,Li_2O \cdot 16.7\,Al_2O_3 \cdot 54.1\,SiO_2$	0.57	0.061	30.1	0.813
$36.7\,Li_2O \cdot 9.2\,Al_2O_3 \cdot 54.1\,SiO_2$	0.25	0.065	32.0	0.866
$25\,Li_2O \cdot 25\,Al_2O_3 \cdot 50\,SiO_2$	1.0	0.058	28.6	0.773
Non-alkali glasses				
$16.7\,CaO \cdot 33.3\,MgO \cdot 50\,SiO_2$		0.078	38.5	1.04
$25\,CaO \cdot 25\,MgO \cdot 50\,SiO_2$		0.083	40.9	1.11
$37.5\,CaO \cdot 12.5\,MgO \cdot 50\,SiO_2$		0.097	47.8	1.29
$11.6\,CaO \cdot 12.7\,Al_2O_3 \cdot 75.7\,SiO_2$		0.031	15.3	0.413
$26.8\,CaO \cdot 8.6\,Al_2O_3 \cdot 64.6\,SiO_2$		0.054	26.6	0.719
$43.1\,CaO \cdot 12.5\,Al_2O_3 \cdot 44.4\,SiO_2$		0.093	45.8	1.24
$51.1\,CaO \cdot 7.2\,Al_2O_3 \cdot 41.7\,SiO_2$		0.105	51.8	1.40
Soda–lime–silica glass				
$15\,NaO \cdot 15\,CaO \cdot 70\,SiO_2$		0.055	27.1	0.733
Zirconia-containing glasses				
$28\,Na_2O \cdot 0.4\,ZrO_2 \cdot 68\,SiO_2$		0.050	24.7	0.666
$28\,Na_2O \cdot 0.8\,ZrO_2 \cdot 64\,SiO_2$		0.060	29.6	0.799
$28\,Na_2O \cdot 12\,ZrO_2 \cdot 60\,SiO_2$		0.064	31.6	0.852
$28.3\,CaO \cdot 9.1\,Al_2O_3 \cdot 5.4\,ZrO_2 \cdot 57.2\,SiO_2$		0.067	33.3	0.892
$45.6\,CaO \cdot 13.2\,Al_2O_3 \cdot 5.4\,ZrO_2 \cdot 35.8\,SiO_2$		0.111	54.7	1.48
$54.0\,CaO \cdot 7.6\,Al_2O_3 \cdot 5.2\,ZrO_2 \cdot 33.2\,SiO_2$		0.106	52.3	1.41

$\Delta 2\theta = 2\theta_{(SiO_2)} - 2\theta_{(specimen)}$, $\Delta\lambda = \lambda_{(SiO_2)} - \lambda_{(specimen)}$, $\Delta E = E_{(specimen)} - E_{(SiO_2)}$

dependence of the chemical shifts for crystalline phase ($\dot{s}$) precipitated at both 1300° C and 750° C is similar to that for glasses and the vlaues are again slightly smaller for crystals than for glasses of the same composition. The principal crystalline phase was mostly β-quartz solid solution at the crystallization temperature of 750° C, while for high-silica compositions it was β-spodumene at the crystallization temperature of 1300° C.

3.2. Chemical shifts for alkali aluminosilicate glasses

Chemical shifts of the Si$K\beta$ line for alkali aluminosilicate glasses are listed in Table III, together with those for other glasses. Fig. 5 compares $x\mathrm{Na_2O} \cdot x\mathrm{Al_2O_3} \cdot (100-2x)\,\mathrm{SiO_2}$ glasses with binary

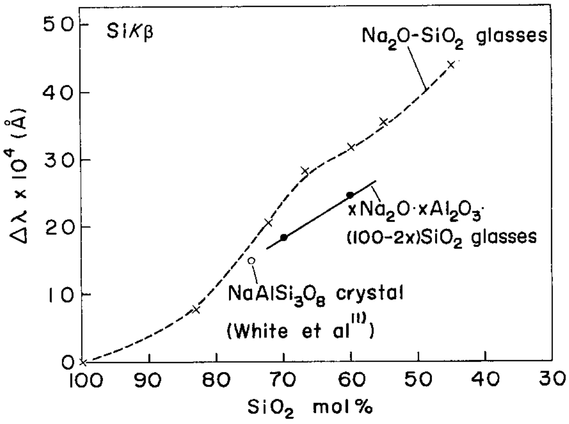

Figure 5 Chemical shifts of the Si$K\beta$ peak for $x\mathrm{Na_2O} \cdot x\mathrm{Al_2O_3} \cdot (100-2x)\,\mathrm{SiO_2}$ glasses.

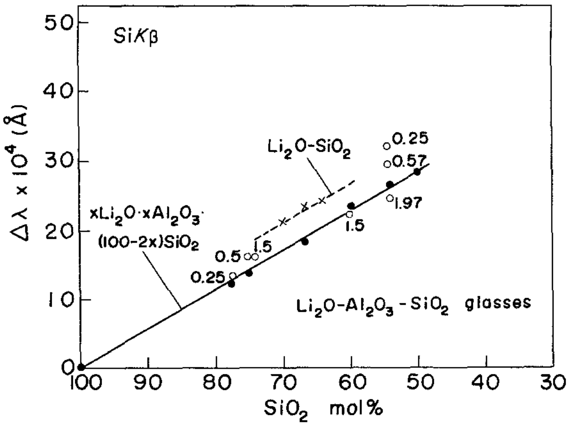

Figure 6 Chemical shifts of the Si$K\beta$ peak for Li_2O–Al_2O_3–SiO_2 glasses. ● $Al_2O_3:Li_2O = 1$ ○ $Al_2O_3:Li_2O \neq 1$ (Ratio given by the number).

Na_2O–SiO_2 glasses. The chemical shifts for the former are slightly smaller than those for the latter, demonstrating the effect of Al_2O_3 added in place of Na_2O. The $\Delta\lambda$ for the $NaAlSi_3O_8$ crystal measured by White and Gibbs [13] is shown in Fig. 5 for refefence. It is seen that the $\Delta\lambda$ value of the crystal is similar to that of the corresponding glass. Fig. 6 shows that the Li_2O–Al_2O_3–SiO_2 glasses exhibit similar, but slightly smaller, chemical shifts than Li_2O–SiO_2 glasses at identical SiO_2 contents. In the Li_2O–Al_2O_3–SiO_2 system, the effect of changing $Al_2O_3:Li_2O$ ratio is slight, slthough smaller $Al_2O_3:Li_2O$ ratios do tend to give larger chemical shifts.

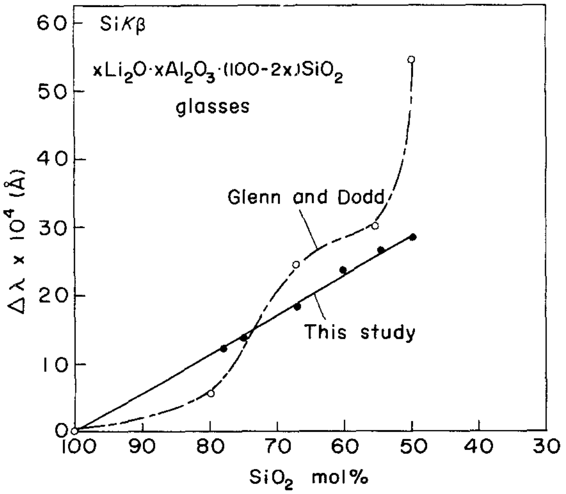

Figure 7 Comparison of the present data with those by Dodd and Glen [4] for $xLi_2O \cdot xAl_2O_3 \cdot (100-2x)$ SiO_2 glasses and β-eucryptite crystal. X Crystal (Dodd and Glen); ▫ Crystal (This study).

Fig. 7 compares data obtained in the $xLi_2O \cdot xAl_2O_3 \cdot (100-2x)$ SiO_2 glasses with those obtained by Dodd and Glen [4]. In both sets of measurements the chemical shift increases with decreasing SiO_2 content. The values of the chemical shift are similar except for the composition lowest in SiO_2, at $25\,Li_2O \cdot 25\,Al_2O_3 \cdot 50\,SiO_2$ for which Dodd and Glen gave a $\Delta\lambda$ value almost twice as large as that obtained by us. We repeated the preparation and remeasured the shift, but the same result was found. For crystallization products of the eucryptite composition our data gave good agreement with the data by Dodd and Glen, as shown in Fig. 7.

3.3. Chemical shifts for non-alkali and ZrO_2-containing glasses

Fig. 8 shows the chemical shifts for non-alkali silicate glasses. The data for a soda-lime glass and Na_2O–SiO_2 glasses are also shown for comparison. It can be seen that non-alkali glasses containing CaO and MgO and those containing CaO and Al_2O_3 show similar behaviour to Na_2O–SiO_2 glasses; the chemical shift increases as the SiO_2 content decreases, and the value of the chemical shift are close to those of Na_2O–SiO_2 glasses having the same SiO_2 content.

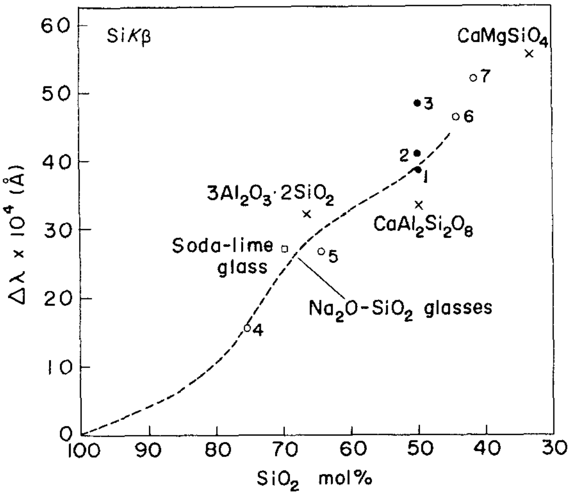

Figure 8 Chemical shifts of the Si$K\beta$ peak for non-alkali glasses. (1) $16.7\,CaO \cdot 33.3\,MgO \cdot 50\,SiO_2$, (2) $25\,CaO \cdot 25\,MgO \cdot 50\,SiO_2$, (3) $37.5\,CaO \cdot 12.5\,MgO \cdot 50\,SiO_2$, (4) $11.6\,CaO \cdot 12.7\,Al_2O_3 \cdot 75.7\,SiO_2$, (5) $26.8\,CaO \cdot 8.6\,Al_2O_3 \cdot 64.6\,SiO_2$, (6) $43.1\,CaO \cdot 12.5\,Al_2O_3 \cdot 44.4\,SiO_2$, (7) $51.1\,CaO \cdot 7.2\,Al_2O_3 \cdot 41.7\,SiO_2$; $3\,Al_2O_3 \cdot 2\,SiO_2$: Mullite, $CaAl_2Si_2O_8$: Anorthite, $CaMgSiO_4$; Monticellite, Soda-lime : $15\,Na_2O \cdot 15\,CaO \cdot 70\,SiO_2$.

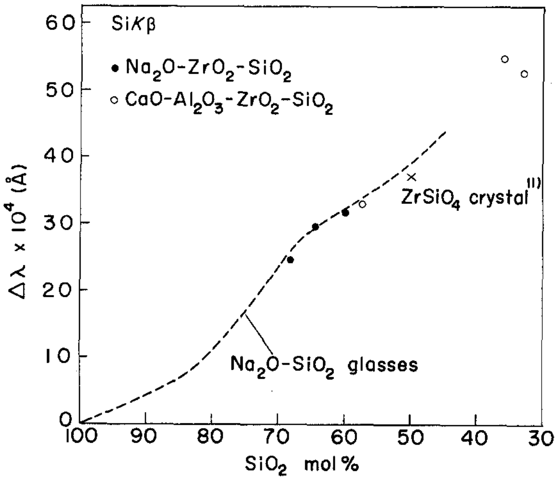

Figure 9 Chemical shifts of the Si*K*β peak for ZrO_2-containing glasses.

Fig. 9 shows the chemical shifts for zirconia-containing glasses. It can be seen that variation of the chemical shift with the SiO_2 content is similar to that for Na_2O–SiO_2 binary glasses.

3.4. Bandwidths of the Si*K*β line

Figs. 10 and 11 show the Si*K*β bandwidths at the half-peak intensity for Na_2O–Al_2O_3–SiO_2 and Li_2O–Al_2O_3–SiO_2 glasses, respectively, as a function of the SiO_2 content. The data for Na_2O–SiO_2 and Li_2O–SiO_2 glasses are also shown for comparison. It is seen that the width of the Si*K*β band for sodium aluminosilicate and lithium aluminosilicate glasses is similar to that of SiO_2 glass.

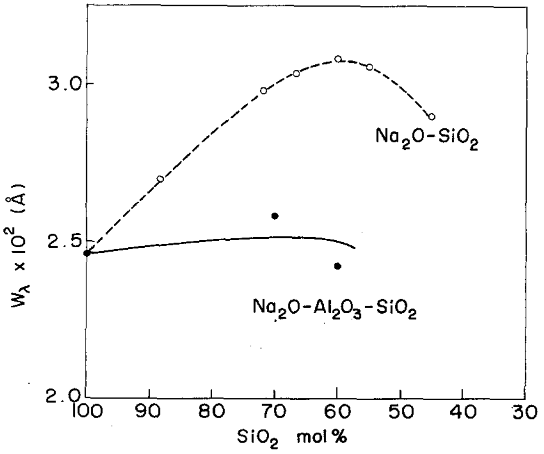

Figure 10 Peak widths of the Si*K*β band for Na_2O–Al_2O_3–SiO_2 glasses.

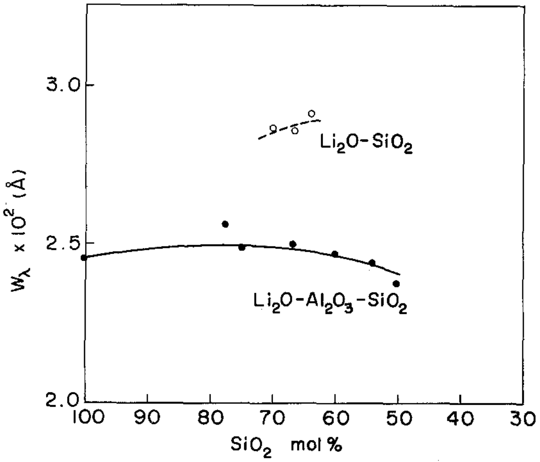

Figure 11 Peak widths of the Si*K*β band for Li_2O–Al_2O_3–SiO_2 glasses with the Al_2O_3 : Li_2O ratio equaling unity.

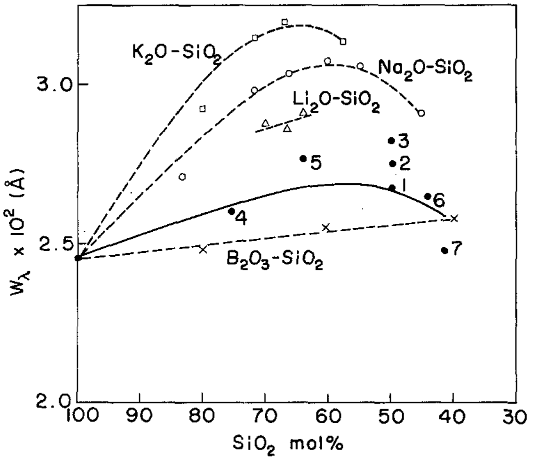

Figure 12 Peak widths of the Si*K*β band for non-alkali silicate glasses. (1) $16.7\,CaO \cdot 33.3\,MgO \cdot 50\,SiO_2$, (2) $25\,CaO \cdot 25\,MgO \cdot 50\,SiO_2$, (3) $37.5\,CaO \cdot 12.5\,MgO \cdot 50\,SiO_2$, (4) $11.6\,CaO \cdot 12.7\,Al_2O_3 \cdot 75.7\,SiO_2$, (5) $26.8\,CaO \cdot 8.6\,Al_2O_3 \cdot 64.6\,SiO_2$, (6) $43.1\,CaO \cdot 12.5\,Al_2O_3 \cdot 44.4\,SiO_2$, (7) $51.1\,CaO \cdot 7.2\,Al_2O_3 \cdot 41.7\,SiO_2$.

Fig. 12 shows bandwidths of the Si*K*β line for CaO–MgO–SiO_2 and CaO–Al_2O_3–SiO_2 glasses. Bandwidths for alkali silicate glasses and B_2O_3–SiO_2 glasses are also shown for comparison. It is seen that bandwidths for non-alkali glasses are smaller than those of alkali silicate glasses.

4. Discussion

4.1. Chemical shift of the Si*K*β line

White and Gibbs [13] found a linear relationship between the Si*K*β peak shift and the Si–O distances in silicate minerals. This parameter, the bond length, is considered to be related to energy levels of bonded Si and O atoms and therefore to the strength of the Si–O bonds. Using MO theory, Dodd and Glen [4] attributed the Si$K\beta$ peak to a $3p(\sigma^b)$ to $1s$ transition. Furthermore, they interpreted the shift of the Si$K\beta$ peak to higher energies, relative to that for quartz, as destabilization; that is, weakening of the Si–O bond [14]. This concept, applied previously by the present authors to binary glasses [6], is also applicable to the results of the present study.

It was noted that the $\Delta\lambda$ values of the Si$K\beta$ line amongst crystals in the Na_2O–SiO_2, Li_2O–SiO_2 and Li_2O–Al_2O_3–SiO_2 systems are similar to or slightly smaller than those of the corresponding glass. This indicates that the average Si–O bond strength in crystals is slightly larger than that in glasses, which might be understood from the fact that generally the atomic arrangement is more regular and the molar volume is smaller in crystals than in glasses.

Apart from the slight difference in the bond strength between glasses and crystals, from Figs. 2 and 3 and [6] it appears that the average strength of the Si–O bonds in both glasses and crystals decreases with increasing alkali oxide content (or with decreasing SiO_2 content) in binary alkali silicates. The strengths of Si–O bonds in silicate glasses containing network-formers (B_2O_3 and GeO_2) are similar to those in SiO_2 itself. It was therefore interesting to see if an "intermediate" oxide, Al_2O_3, would weaken the Si–O bond. It can be seen in Figs. 5 and 6 that the addition of Al^{3+} does weaken the average Si–O bond strength.

Comparison of $\Delta\lambda$ for Na_2O–Al_2O_3–SiO_2 glasses containing equal $Al_2O_3 : Na_2O$ ratios with those of Na_2O–SiO_2 glasses (Fig. 5) indicates that the strength of the Si–O bond also weakens in Na_2O–Al_2O_3–SiO_2 glasses as the SiO_2 content decreases, but to a lesser degree than in Na_2O–SiO_2 glasses. For instance, at 60% SiO_2, $\Delta\lambda$ is 31.5×10^{-4} Å for Na_2O–SiO_2 glass, but is 24.5×10^{-4} Å for Na_2O–Al_2O_3–SiO_2 glass. The composition of the latter is $20\,Na_2O \cdot 20\,Al_2O_3 \cdot 60\,SiO_2$ and we have to take into account the contribution of the 20 mol% Na_2O in causing the chemical shift. This can be tentatively estimated as 11.5×10^{-4} Å by using the value for the 20:80 glass taken from Fig. 5. This is much smaller than the $\Delta\lambda$ for $20\,Na_2O \cdot 20\,Al_2O_3 \cdot 60\,SiO_2$, indicating that the Al^{3+} ions contribute to the chemical shift, and therefore to the weakening of the Si–O bond strength, although the contribution may be somewhat smaller than that of alkali ions. Similar comparisons can be made between Li_2O–SiO_2 and Li_2O–Al_2O_3–SiO_2 glasses (Fig. 6). In fact, Al^{3+} ions are believed [15, 16] to share the network structure with Si^{4+} ions in these glasses, just as B^{3+} and Ge^{4+} ions do in B_2O_3–SiO_2 and GeO_2–SiO_2 glasses. Nevertheless, it has been shown in this work that Al^{3+} affects the Si–O bond more than B^{3+} and Ge^{4+}.

The effect of alkaline earth ions, which, like alkali ions, are classified as network-modifiers, was also interesting. It can be seen that the alkaline earth ions cause large chemical shifts (Fig. 8), that is, they decrease the strength of the Si–O bonds considerably, just as the Na^+ ions do.

It is interesting to note that Zr^{4+} ions (Fig. 9) also decrease the strength of the Si–O bond in spite of their high valency. The large chemical shift exhibited by $ZrSiO_4$ crystals (the value in Fig 9 is from [13]) seems to confirm this conclusion.

4.2. Bandwidth and glass structure

In the previous paper [6] on the Si$K\beta$ emission X-rays of binary silicate glasses, we interpreted peak widths of the Si$K\beta$ band on the assumption that larger widths, compared with those for SiO_2 glass, could be attributed to a wider distribution in the strength of the Si–O bond. Furthermore, the increase in width on adding an alkali oxide to SiO_2 glass was attributed to formation of non-bridging oxygens, which should result in a wider distribution in the Si–O bond strengths.

In the alkali aluminosilicate glasses studied it is believed [15, 16] that when an Al^{3+} ion enters the network replacing a Si^{4+} ion, it is surrounded by four oxygen ions. An alkali ion is required to neutralize the excess negative charge. This occurs without formation of non-bridging oxygen ions. Therefore, the distribution in the Si–O bond strength in alkali aluminosilicate glasses should be narrow compared with that for binary alkali silicate glasses, although the average bond strength in the aluminosilicate glasses is different from that in SiO_2 glass. Such features can be seen in Figs. 10 and 11. The bandwidth remains almost the same as that for SiO_2 glass when ($Na_2O + Al_2O_3$) and ($Li_2O + Al_2O_3$) are added.

Alkali silicate glasses show relatively large bandwidths [6] depending upon the type of alkali ion. Alkaline earth silicate glasses should show also somewhat larger widths than SiO_2 glass, as can be seen in Fig. 12 (note Glasses 1 to 3). Such an increase in bandwidth is attributed to the formation of non-bridging oxygen ions. It is expected that calcium aluminosilicate glasses would show smaller widths than the alkali silicate glasses, and Fig. 12 (Glasses 4 to 7) shows that this is found.

5. Summary

(1) The Si$K\beta$ X-ray emission spectra of glasses and crystals of the Na_2O–SiO_2, Li_2O–SiO_2, Na_2O–Al_2O_3–SiO_2, Li_2O–Al_2O_3–SiO_2, CaO–MgO–SiO_2, CaO–Al_2O_3–SiO_2, Na_2O–ZrO_2–SiO_2 and some other systems were measured with an X-ray fluorescence spectrometer to determine the chemical shift with respect to SiO_2 glass.

(2) The Si$K\beta$ peak wavelengths for the glasses of the Na_2O–SiO_2, Li_2O–SiO_2 and Li_2O–Al_2O_3–SiO_2 systems were slightly lower than or equal to those for crystallized products of the corresponding compositions, indicating that the strength of the Si–O bond in glasses is similar to or slighlty smaller than that in crystals.

(3) In aluminosilicate glasses of the Na_2O–Al_2O_3–SiO_2 and Li_2O–Al_2O_3–SiO_2 systems, the chemical shift of the Si$K\beta$ peak increases with decreasing SiO_2 content, similarly to those for Na_2O–SiO_2 and Li_2O–SiO_2 glasses, although the extent of the decrease for the aluminosilicate glasses was slightly lower compared with those for the binary alkali silicate glasses. It is suggested that the addition of Al^{3+} ions also causes the average Si–O bond strength in glass to decrease.

(4) The chemical shift of the Si$K\beta$ peak also increased with decreasing SiO_2 content in alkali-free CaO–MgO–SiO_2 glasses, the magnitude of the chemical shift being almost equal to that for Na_2O–SiO_2 glass of the same SiO_2 content.

(5) ZrO_2 was found to contribute to the increase in the chemical shift.

(6) The Si$K\beta$ bandwidths for Na_2O–Al_2O_3–SiO_2 and Li_2O–Al_2O_3–SiO_2 glasses containing equal moles of Al_2O_3 and alkali oxide remained almost the same as that for SiO_2 glass, in contrast with Na_2O–SiO_2 and Li_2O–SiO_2 glasses, which showed considerably larger widths. This was interpreted as resulting from the fact that replacement of Si^{4+} ions in the network by Al^{3+} with concomitant substitution of alkali ion neutralizes the negative charge and does not result in the formation of non-bridging oxygens.

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