X-Ray Fluorescence Spectroscopy of Binary Silicate Glasses

Takashi MAEKAWA, Niro KIKUCHI, Shigekazu SUMITA, and Toshio YOKOKAWA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The Si K_α emission lines of the several silicon compounds and binary silicate (Na, K, Rb, and B-silicates) glasses were measured. In the binary silicates, negative energy shifts from that of SiO_2 were observed. They were interpreted as indicating a relative decrease of the quantity of charge transfer from silicon to oxygen, when more electropositive elements like alkali metals are located on the next nearest neighbor positions of the silicon atoms. The Si K_α shifts of silicate glasses have a good correlation with the basicity of their melts.

As shown in the previous paper, the X-ray emission spectra provide important information about the chemical bonds in the compounds.[1] It is particularly useful to apply this technique to the study of non-crystalline materials, since the long range order disappears and the data on the bond character are quite limited. Among the many inorganic materials, the silicate glasses have drawn special attention in many fields. The network structure of these glasses has been confirmed from their thermodynamic as well as structural properties. However, the details of the Si–O bond, especially its relation to the chain or ring structures and their composition dependences are not satisfactorily understood. Recently, Sakka and Matusita reported Si K_α and K_β spectra of simple binary silicates.[2] Although they found some changes of the peaks of K_β spectra and their widths, no chemical shift of Si K_α was observed. On the other hand, Zopf *et al.* reported the chemical shifts of Si K_α for several silicates.[3] It has been implicitly assumed that Si–O–Si and Si–O^- bonds in silicates stay in the same energy values irrespective of the counter basic oxides. In the present work we applied an improved spectrometer to measure the chemical shifts of Si K_α, if any, and to look for a possible relation between the shifts and the basicity of the glasses.

Experimental

The apparatus used in this experiment is the same as that described in the previous paper.[1] The conditions of the measurement for the Si K_α are shown in Table 1. The features and the scanned ranges for the K_α spectra of silicon metal and SiO_2 are shown in Fig. 1. Because of the low reflecting power of the analyzing crystal (ADP) and the low concentration of silicon in the sample, the intensity of Si K_α was very weak compared with those of S K_α. The curve fit using a fourth order equation was applied to look for the maximum point of the spectrum. The chemical shifts were also obtained by the same procedure as noted in the previous paper.

Melts of M_2O+SiO_2 (M=Na, K, and Rb) were prepared by melting SiO_2 and M_2CO_3 in a platinum crucible. $PbO+SiO_2$ melts were prepared by heating the desired quantities of the two oxides in an alumina crucible. These melts were poured onto a stainless steel plate and quenched into flat glass samples. On the other hand, $B_2O_3+SiO_2$ has high viscosity and it is difficult to prepare flat glasses by such a procedure. In this case the melts were prepared and quenched in a platinum dish, which could be inserted directly into a sample holder of the spectrometer. The effects due to the surface roughness can be avoided by rotating the samples while the fluorescence spectrum was measured. SiC, Na_2SiF_6, and

Table 1. Conditions for the measurement of Si K_α spectra[a)]

X-Ray tube	Cr or Rh
voltage	50 kV (Cr) or 40 kV (Rh)
current	30 mA
Analyzing crystal	ADP ($2d=10.648$ Å)
Detector	PR Gas, proportional counter
PHA	differential
Scan speed (2θ)	0.02°/min
Storing time interval	2 s/channel, scan
Number of repeating scans	5—30
Energy interval	0.011 eV
Number of points used in the least square (fourth order)	70
σ_p (Si)[b)]	1.5%
σ_p (SiO_2)	1.7%

a) See Fig. 1 and Ref. 1. b) $\sigma_p=100\times[\Sigma(y_i/y_i(\text{calcd})-1)^2/(n-1)]^{1/2}$

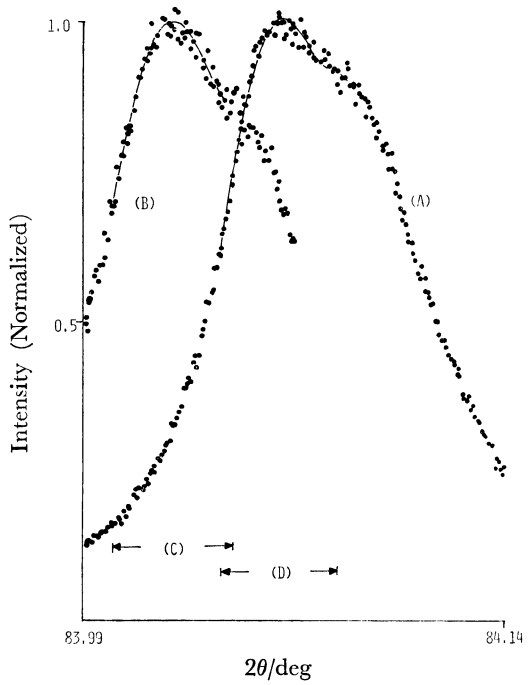


Fig. 1. Silicon K_α spectra of pure silicon and SiO_2 (upper part only). The solid line is obtained by a least square fit by a fourth order equation. (A): Si, (B): SiO_2, (C) and (D): ranges used in the least square. Maximum intensity; 5000 and 2800 counts for Si and SiO_2 respectively.

TABLE 2. SILICON K_α ENERGY SHIFTS FOR SOME SILICON COMPOUNDS

$\Delta E = E(\text{specimen}) - E(\text{Si})$

Compound	ΔE/eV		
	This work		Literature[a]
SiC	0.228±0.005[b]	(3)[c]	0.25
Si_3N_4	0.446±0.001	(5)	0.49
SiO_2 (α-quartz)	0.606±0.007	(6)	0.60
Na_2SiF_6	0.971±0.017	(3)	0.90

a) W. Nefedow, Ref. 4. b) Error limit: t-distribution, 95% certainty. c) Number of measurements.

TABLE 3. CHEMICAL SHIFTS OF Si K_α FOR BINARY SILICATE GLASSES

$\Delta E = E(\text{specimen}) - E(SiO_2)$

Specimen		ΔE/eV	
Na_2O	(33.3)[a] $-SiO_2$	−0.058±0.019[b]	(4)[c]
	(50.0) $-SiO_2$	−0.094±0.013	(5)
K_2O	(20.0) $-SiO_2$	−0.041±0.009	(7)
	(33.3) $-SiO_2$	−0.072±0.019	(5)
	(50.0) $-SiO_2$	−0.095±0.016	(6)
	(66.7) $-SiO_2$	−0.117±0.022	(6)
Rb_2O	(20.0) $-SiO_2$	−0.049±0.016	(6)
	(50.0) $-SiO_2$	−0.085±0.021	(5)
PbO	(33.3) $-SiO_2$	−0.064±0.022	(4)
	(50.0) $-SiO_2$	−0.067±0.014	(6)
	(60.0) $-SiO_2$	−0.072±0.039	(4)
	(66.7) $-SiO_2$	−0.093±0.012	(5)
	(80.0) $-SiO_2$	−0.081±0.026	(5)
B_2O_3	(50.0) $-SiO_2$	−0.002±0.010	(5)
	(66.7) $-SiO_2$	−0.006±0.021	(6)

a) Mole per cent for binary silicates. b) Error limit: t-distribution, 95% certainty. c) Number of measurements.

other crystalline samples were prepared in pellet forms of 34 mm diameter.

Results and Discussion

In Table 2 the results of the Si K_α energy shifts of some silicon compounds referred to the energy of metallic silicon are listed. The positive shift of Si K_α in Na_2SiF_6 is the largest among them. This result agrees well with that by a previous author.[4] The silicon K_α shifts of binary silicates from that of SiO_2 are shown in Table 3 and are plotted in Fig. 2. The chemical shifts are all negative, but depend on the composition and the kind of the counter oxides. The following points may be noted from the results.

i) In M_2O+SiO_2 (M=Na, K, and Rb) systems, the Si K_α energy goes more negative with increase of M_2O concentration. No differences among the three alkali oxides can be detected.

ii) In $PbO+SiO_2$, the shifts are similar to those of the above systems. But the absolute value is somewhat smaller than that of the former systems.

iii) In $B_2O_3+SiO_2$, the shifts are too small to give any composition dependence.

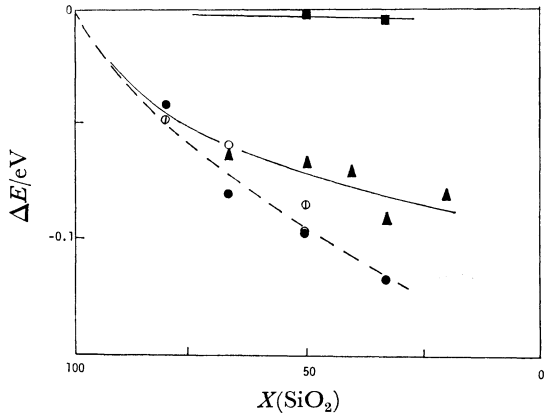
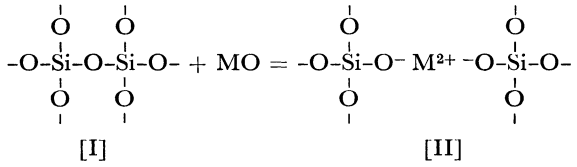


Fig. 2. Chemical shifts of Si K_α for binary silicates. $X(SiO_2)$ is the mole percent of SiO_2 in binary silicates.
○: Na_2O-SiO_2, ●: K_2O-SiO_2, ◐: Rb_2O-SiO_2, ▲: PbO-SiO_2, ■: B_2O_3-SiO_2.
Error limits are shown in Table 3.

K_α Shifts and the Effective Charges. It is known that the energy of X-ray emission spectrum from an atom in its compounds depends upon the chemical environment of the atom, *i.e.* partial charges, bond lengths, and coordination numbers.[5-8] Generally the positive shifts of X-ray energy in the third period elements in the periodic table correspond chiefly to cationic charges on the atom.[6] In the previous paper we observed the relation between S K_α energy shifts of sulfides and the electronegativity of the counter atoms. The present experimental results (Table 2) coincide with the general trend that the shifts go more positive with an increase of the electronegativity differences between silicon and the combined atoms. The silicon atom in Na_2SiF_6 coordinates six fluorine atoms and cannot be compared in a straightforward way with the others.

In the homogeneous mixtures of SiO_2 with other metal oxides, the three dimensional network structure of SiO_2 is modified by the following reaction.



The size and number of the resulting descrete anions depend on the composition as well as the kind of the metal oxides.[9] Although SiO_4 tetrahedra remains as a structural unit through the above reaction, the electronic density of an Si–O bond should change from [I] to [II]. The ionic structure of an O–M bond should cause some effects on the neighboring Si–O bond character. Thus we must compare the electronic structure between Si–O–Si and $Si-O^-$–M^{2+} instead of considering the Si–O bond only. The source of the charge transferred to oxygen is restricted to silicon atoms in SiO_2, while the main source of the electron is the electropositive element (M in the above equation) in silicates. Mixing SiO_2 with a M_2O results in a relative decrease of the positive charge on the silicon

atom compared with that of SiO_2. This idea coincides with the principle of the electronegativity equalization proposed by Sanderson.[10] The positive charge on silicon atoms will decrease with the increase of the concentration of the metal oxides. This is again in accord with the experimental findings.

K_α Shifts and the Basicity. The thermodynamic studies of these liquid silicates show that the activity of SiO_2 drastically decreases from that of pure SiO_2.[11] In these mixed oxide melts, an useful idea called the basicity of the melt is often employed. Basicity is defined by the oxygen ion activity in the melts.[12] It depends on the metal oxide solute and its concentration. Thus the basicity of the lead silicates is smaller than that of alkali silicates at the same SiO_2 content. Both components of $B_2O_3+SiO_2$, on the other hand, are considered to be acidic in nature. Addition of B_2O_3 to SiO_2 gives a negligible shift of Si K_α energy. Therefore, the basicity reflects the degree of the positive charges on the silicon atoms, although the former is directly determined by the activity of the metal oxide and the latter is primarily determined by the ionic potential (Coulombic force) of a metal ion. There will even be a possibility of finding the basicity scale of the silicate melts by measuring the Si K_α energy of their glassy samples. The significance of the X-ray energy shifts will be similar to the ultraviolet spectra of a probe ion (for example, $^3P_1 \leftarrow {}^1S_0$ of Pb^{2+} ion) under the presence of polarizing elements like Si, P, and others.[13]

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