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X-Ray Fluorescence Spectroscopy of Inorganic Solids. III. Si K_α and K_β Spectra in Binary Silicates

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The Si K_α and K_β spectra of several silicates were measured. The K_α spectra showed negative energy shifts referred to SiO_2; these are consistent with the results for the binary silicate glasses. On the other hand, the K_β shifts were positive and the absolute values were about ten times as large as the K_α shifts in each compound. A linear relation was observed between K_α and K_β energy shifts. The Si 1s energy shift for the orthosilicate was estimated from the K_β spectral splitting of $Na_2Si_2O_5$. The stability of the silicon–oxygen bond was discussed with the aid of the shifts in K_β and the Si 1s. The above linear relation suggests that the silicon–oxygen bond strength is lowered (the K_β energy is increased) with decreasing Coulombic interaction (lowering K_α energy) between silicon and oxygen in the silicates.

Recently the chemical state analysis by means of X-ray fluorescence spectroscopy has been extensively developed. In the previous paper, we reported the variations of the Si K_α energy in binary silicate glasses as functions of the concentration and the kind of the basic oxides.[1] However, in order to discuss the nature of the silicon–oxygen bond, it is necessary to investigate further the K_β spectra in these materials. The Si K_β spectra correspond to the transition from Si 3p to 1s and they naturally bring out more valuable information about the electronic states in the silicon–oxygen bond than the K_α spectra do.

Dodd and Glen explained the origin of the Si K_β spectra in silicates by means of an MO theory and defined the destabilization energy of the silicon–oxygen bond.[2] Urch[3] and Tossell[4,5] extended this MO treatment by a more quantitative calculation and discussed the details of the nature of the silicon–oxygen bond. However, they were concerned mainly with SiO_2 and orthosilicates, whose spectra are simple and can be explained by assumming the tetrahedral cluster around silicon atoms. Sakka and Matusita measured the Si K_β spectra of simple binary silicate glasses of different compositions and discussed the chemical shifts and the changes of the band width in terms of the destabilization energy of the silicon–oxygen bond strength and the difference of the state of the silicon atoms, *i.e.* degree of the polymerization.[6] When we applied an improved two-crystal spectrometer to measure the Si K_β spectra of silicates, we found some appreciable changes of the spectral profile, as well as the spectrum width and the frequency, which have not been reported. The Si K_β energy shifts were also measured and discussed in terms of the destabilization of the Si–O bond caused by an introduction of the basic oxides to the silica network.

Experimental

Samples. Commercial α-quartz and other single oxides or carbonates were used to prepare the silicate glasses and crystals. Na_2SiO_3 was prepared by dehydrating a commercial $Na_2SiO_3 \cdot 9H_2O$. These synthesized samples were all checked by the X-ray powder diffraction method. Commercial Na_4SiO_4, $Al_2Si_3O_9$, $Mg_2Si_3O_8 \cdot 5H_2O$, and kaolinite were also used. The crystalline samples were ground and pressed into pellets within a polyvinyl chloride ring. The glassy samples were prepared by melting crystalline compounds or the mixtures of the component oxides and pouring them onto a stainless steel plate. The flat glasses were directly introduced into the spectrometer.

Apparatus. The spectrometer used in this experiment was of the two-crystal type. The analyzing crystal was ADP, and the Cr or Rh X-ray tubes were used for the primary X-ray source. The details of the apparatus were described in previous papers.[1,7]

K_α Chemical Shifts. In a previous paper we employed a fourth order equation for curve fitting to the upper part of the K_α spectra in order to evaluate the chemical shift. However, there is a better way to evaluate the shift than the curve fitting method when the K_α spectra of a series of compounds are different from each other only in absolute energy and are quite similar in their profiles. In this paper the following method was adopted. It consists of 4 steps. (See also Fig. 1.)

(i) The "standard" spectrum with a detailed profile of the reference material is obtained.

(ii) A sandwiched series of a "sample" and the "reference" spectra for the sample and for the reference materials respectively is obtained.

(iii) Both spectra are normalized.

(iv) Both spectra are displaced along the energy abscissa to fit the "standard" spectrum. The difference of the energy displacements evaluated with the least square method gives the chemical shift.

An energy discrepancy between the "standard" and "reference" spectra is usually found, partly because the former is obtained with a much greater number of scan

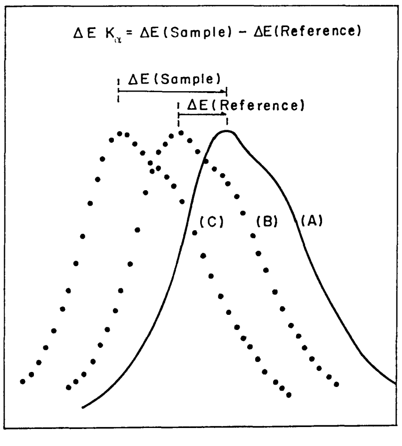

Fig. 1. Determination of the K_α energy shifts.
(A) "Standard" spectrum; (B) "reference" spectrum; (C) "sample" spectrum.

repeats than the "reference" and partly because the performance of the instrument changes from day to day.

K_β Energy Shifts. As the K_β spectra were complex in line shape the shift was evaluated from the energy of the center of gravity of the spectrum. Any complex spectrum was assumed to be composed of two to four Lorentzian curves of various positions and heights. The temperature fluctuation of the analysing crystal(ADP) causes errors of 0.04 eV/deg, which were corrected.

Results

The Si K_α energy shifts of silicates referred to α-quartz are listed in Table 1. All chemical shifts are negative. Generally the absolute values of the chemical shifts are large in samples with high alkali content whenever the comparison is possible. This tendency is in good agreement with the previous findings.[1] Table 1 also shows the K_β energy shifts referred to α-quartz. The shifts are positive and the absolute values are ten times as large as the corresponding K_α energy shifts. These values generally agree well with previous values.[6]

Figure 2 shows Si K_β spectra of several sodium silicates crystals as well as α-quartz and α-cristobalite. No difference between the latter two was detected. The profile becomes complex with Na_2O content and then returns to a single peak of different energy at Na_4SiO_4 composition. Similarly the $CaO-SiO_2$ system shows a complex profile at intermediate composition, followed by a single peak at the orthosilicate. Table 2 shows the results of Ca K_α, which were also measured for the discussion of ionic charges in silicates.

TABLE 1. CHEMICAL SHIFTS OF Si K_α AND K_β ENERGY OF SILICON COMPOUNDS

No.	Sample	ΔE K_α/eV	ΔE K_β/eV
1	α-Quartz	—	—
2	α-Cristobalite	−0.002	−0.11
3	SiO_2 (glass)	−0.010	0.0
4	α-$CaSiO_3$	−0.101	1.08
5	β-$CaSiO_3$	−0.066	0.93
6	β-Ca_2SiO_4	−0.107	1.17
7	γ-Ca_2SiO_4	−0.088	1.25
8	$Na_2Si_2O_5$	−0.050	0.56
9	$Na_2Si_2O_5$ (glass)	−0.061	0.68
10	Na_2SiO_3	−0.073	0.81
11	Na_2SiO_3 (glass)	−0.093	0.96
12	Na_4SiO_4	−0.109	1.56
13	$K_2Si_2O_5$ (glass)	−0.070	0.69
14	Mg_2SiO_4	−0.088	1.05
15	$ZrSiO_4$	−0.046	0.45
16	Mn_2SiO_4	−0.082	0.85
17	$Al_2Si_3O_9$	−0.026	0.24
18	$Mg_2Si_3O_8 \cdot 5H_2O$	−0.041	0.51
19	Kaolinite	−0.021	0.08
	Na_2SiF_6	0.364	0.70
	Si_3N_4	−0.161	1.70
	SiC	−0.379	2.60
	Si	−0.607	2.97
	Erros (average)	±0.01	±0.1

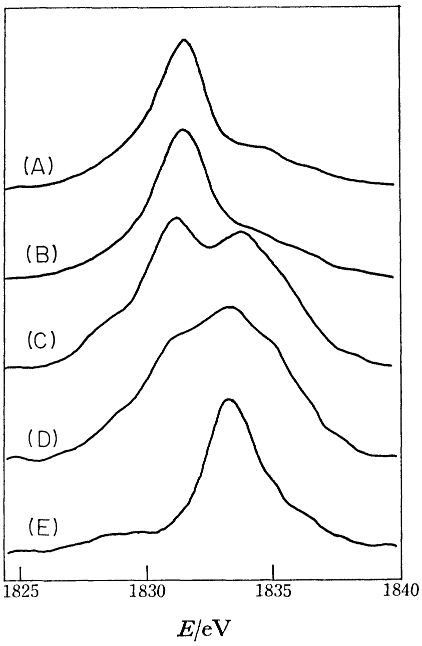

Fig. 2. Si K_β spectra of the Na_2O-SiO_2 system. (A) α-Cristobalite; (B) α-quartz; (C) $Na_2Si_2O_5$; (D) Na_2SiO_3; (E) Na_4SiO_4.

TABLE 2. Ca K_α ENERGY OF SOME CALCIUM COMPOUNDS REFERRED TO CaF_2

Sample	ΔE K_α/eV
CaF_2	—
α-$CaSiO_3$	0.104
β-Ca_2SiO_4	0.121
CaO	0.161
CaS	0.233
Error (average)	0.008

Discussion

Si-O-Si and Si-O⁻ Bonds in Silicates and the Profiles of the K_β Spectra. The molecular orbital of SiO_4^{4-} ion has been constructed to assign the Si K_β spectra of silicates.[4] The Si K_β spectra involve the transition from Si 3p to Si 1s. According to the selection rule, however, the electrons in the molecular orbital of t_2 symmetry can take part in the transition if the tetrahedral geometry is considered. According to Tossell[4] the main bonding orbital $4t_2$ consists of Si 3p and O 2p atomic orbitals and the transition from this to Si 1s is the origin of the K_β main peak. The peak of higher energy than the main peak, which is shown as a shoulder in SiO_2, corresponds to the transition from $5t_2$ non-bonding orbital, which consists mainly of O 2p with a small mixing of Si 3p, to Si 1s. Further, the transition from $3t_2$ (O 2s+Si 3p) produces the spectrum on the energy side lower than the main peak. This has been called the K_β' satellite peak, but it is out of the spectral range covered by the present study.

It is understood that the silica network is modified by an introduction of a basic oxide, as expressed by the following chemical reaction.[8]

$$\equiv Si-O-Si\equiv + M_2O = 2\equiv Si-O^- + 2M^+$$

Thus there are two types of silicon–oxygen bonds: one is Si–O–Si and the other Si–O$^-$. The oxygen in the former type is called a bridging oxygen and in the latter is called a non-bridging oxygen; these are designated by O^0 and O$^-$ respectively. Considering only the nearest neighbor oxygens, the structure around the silicon atom can be considered as $Si[O^0]_4$ and $Si[O^-]_4$ for SiO_2 and orthosilicate respectively. In the compounds of intermediate composition, the general structure around a Si atom can be described as $Si[O^0]_n[O^-]_{4-n}$, when the chemical formula of the compounds is $M_{4-n}SiO_{4-n/2}$ (M; univalent cation).[†] The experimental spectra for Na_4SiO_4, Ca_2SiO_4 and SiO_2 can be well understood by the T_d symmetry, while in $Na_2Si_2O_5$ there are two intense peaks. The positions are located near the same positions as those of SiO_2 (Si–O–Si only) and Na_4SiO_4(Si–O$^-$ only). A complex profile is also seen in the spectrum of Na_2SiO_3, which consists of a peak and two or more shoulders. The fact that the higher energy peak increases with the concetration of the basic oxides also suggests that the shape of the K_β spectra could be resolved into two main components, one corresponding to the Si–O–Si type and the other to the Si–O$^-$ type bond.

Shifts of the Si 1s Energy. A discussion of the stability of the silicon–oxygen bond has been developed in terms of energy shifts of the K_β spectra.[2,6] The X-ray spectra do not give an absolute orbital energy, but give only a energy difference among levels. It is necessary to take the energy shift of the 1s level into consideration in order to discuss the stability of a bond from a K_β spectrum. In the following we will show one way of estimation of the 1s level shifts from the X-ray spectra.

In the proceeding section we assummed that the double peaks of Si K_β in $Na_2Si_2O_5$ could be assigned to the transition from Si–O–Si and Si–O$^-$ type bonding orbitals. All silicon atoms in the crystalline materials are identical and they are bound to one non-bridging oxygen and three bridging oxygens in a first coordination shell. The 1s electron of the silicon atom is under the average shielding effects of Si 3p (+O 2s and O 2p) electrons. This implies that the separation of two peaks of K_β spectrum of $Na_2Si_2O_5$ corresponds to the difference of the orbital energies of Si–O–Si and Si–O$^-$ bonds, since the two peaks correspond to the transitions to the same Si 1s level. This energy difference is evaluated to be 2.4 eV.
Thus,

$$E_\sigma(\text{Si-O}^-, Na_2Si_2O_5) - E_\sigma(\text{Si-O-Si}, Na_2Si_2O_5) = 2.4\,\text{eV}. \tag{1}$$

E_σ's are the orbital energies of the bonding orbitals of the two types of Si–O bonds. On the other hand, the K_β energies of SiO_2 and Na_4SiO_4 are given by

$$E_{K_\beta}(\text{Si-O-Si}, SiO_2) = E_\sigma(\text{Si-O-Si}, SiO_2) - E_{1s}(SiO_2) \tag{2}$$

$$E_{K_\beta}(\text{Si-O}^-, Na_4SiO_4) = E_\sigma(\text{Si-O}^-, Na_4SiO_4) - E_{1s}(Na_4SiO_4) \tag{3}$$

respectively. If ΔE_{1s} is defined by

$$\Delta E_{1s} \equiv E_{1s}(Na_4SiO_4) - E_{1s}(SiO_2), \tag{4}$$

ΔE_{1s} is the energy difference of the 1s level between SiO_2 and Na_4SiO_4. From Eqs. 2 to 4,

$$\begin{aligned}\Delta E_{K_\beta}(\text{Si-O}^-, Na_4SiO) &\equiv E_{K_\beta}(\text{Si-O}^-, Na_4SiO_4) \\ &\quad - E_{K_\beta}(\text{Si-O-Si}, SiO_2) \\ &= E_\sigma(\text{Si-O}^-, Na_4Si_4) \\ &\quad - E_\sigma(\text{Si-O-Si}, SiO_2) - \Delta E_{1s}.\end{aligned} \tag{5}$$

If the first two terms of the right hand side in Eq. 5 are replaced by Eq. 1,

$$\begin{aligned}\Delta E_{K_\beta}(\text{Si-O}^-, Na_4SiO_4) &= 2.4 - \Delta E_{1s} \\ &= 1.6 \text{ (see Table 1)}.\end{aligned} \tag{6}$$

Thus the energy shift of Si 1s of Na_4SiO_4 referred to SiO_2 can be estimated to be about 0.8 eV. In this argument the energies of Si–O in Si–O–Si and Si–O$^-$ are assumed to be constant irrespective of the molecular symmetry. Nefedov *et al.* obtained the binding energy of 2p electrons of silicon of many silicon compounds from ESCA measurement.[9] In the SiO_4^{4-} type silicates, the 2p level is destabilized about 0.5—1.1 eV from that of SiO_2. By combining the X-ray K_α energy shifts of these materials (about −0.1 eV), the 1s level energy shifts are calculated to be 0.6—1.2 eV. The present value of 0.8 eV agrees well with these experimental findings.

Heat of Formation of the Silicates and the Silicon–Oxygen Bond Strength. In alkali silicates and silicate minerals, the Si K_β energy is larger than that of SiO_2. This is interpreted in terms of the destabilization of the silicon–oxygen bond in these materials. White and Gibbs observed a linear relation between K_β energy shifts and the silicon–oxygen bond length.[10] Dodd

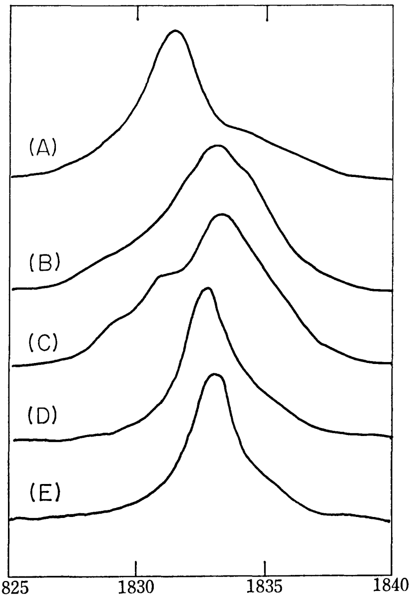

Fig. 3. Si K_β spectra of the CaO-SiO_2 system.
(A) α-Quartz; (B) β-$CaSiO_3$; (C) α-$CaSiO_3$; (D) β-Ca_2SiO_4; (E) γ-Ca_2SiO_4.

[†] $n/2+(4-n)=4-n/2=$(Total number of oxygen atoms per silicon atom in the compound); for example, $n=2$ and 3 for Na_2SiO_3 and $Na_2Si_2O_5$ respectively.

and Glen defined the relative destabilization energy of silicon–oxygen bonds from the X-ray K_β energy shifts.[2)] However, according to the above argument, the relative destabilization energy of a bonding orbital is better redefined as

$$\Delta \equiv \Delta E_{K_\beta} + \Delta E_{1s}. \tag{7}$$

One obtains a larger destabilization energy for silicates than the previous value deduced only from the K_β chemical shifts.

It is worthwhile to note that when SiO_2 reacts with a basic oxide MO, the Si–O bond becomes weak in spite of the observation that the reaction is usually exothermic. Tossell explained this by an increase of the M–O bond strength.[11)] As seen from the Ca K_α sequence measured in the present study (Table 2), the K_α energy shifts to a lower value when the counter F atom is replaced by a less electronegative O and S. In other words, Ca K_α decreases with the decrease of the positive charge on that atom. This means the charge of Ca in silicates $CaSiO_3$ and Ca_2SiO_4 is higher than that of CaO. Therefore the destabilization of the Si–O bond will possibly be counterbalanced by stabilization of the Ca–silicate anion coulombic energy.

Relation between K_α Shifts and K_β Shifts. From the argument that Si K_α energy shifts reflect the degree of the cationic charge on silicon atoms, a relation between Si K_α and K_β energy shifts is expected among silicon compounds. The two quantities are plotted in Fig. 4, whose reference is silicon metal. Except for Na_2SiF_6, which is octahedral in coordination, a quadratic relation was obtained. A linear relation was obtained among silicates where the nearest neighbors are always 4 oxygen atoms and the charges on Si do not change much; this result was independent of the next nearest neighbor cations. (See Fig. 5.)

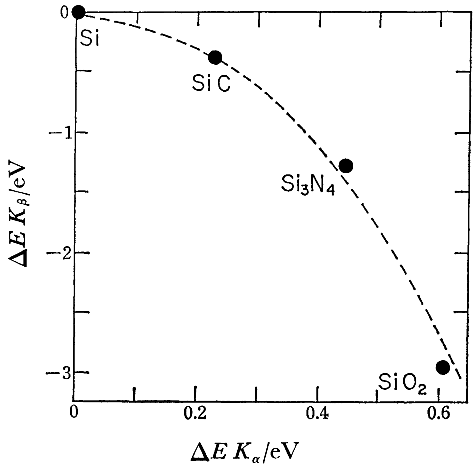

Fig. 4. Relation between Si K_α and K_β energy shifts for the several silicon compounds. The reference material is Si metal.

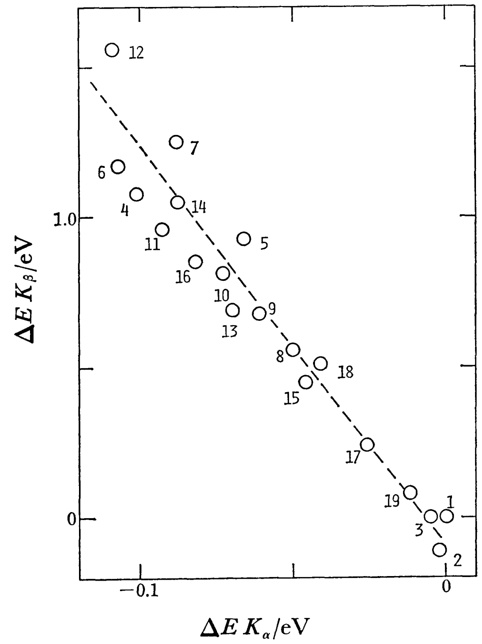

Fig. 5. Relation between Si K_α and K_β energy shifts for the silicates. The reference material is α-quartz. Numbers indicated in the figure correspond to the compounds in Table 1.

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