

Molecular orbital calculation of SiK α chemical shift due to coordination in silicates and silico-phosphates

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Abstract—The energy shifts of SiK α due to coordination, tetrahedral and octahedral, in silicates and silico-phosphates were measured using a high-resolution X-ray fluorescence spectrometer with two InSb(111) analyzer crystals. It was found that sixfold oxygen coordinated Si atoms emit higher energy K α lines than fourfold coordinated Si atoms. Molecular orbital calculation analysis by a SCC-DV-X α method reproduced the effects of coordination. The calculations showed that these shifts were caused by changes in the effective charge of Si atoms due to the number of nearest-neighbor oxygen.

1. INTRODUCTION

COORDINATION-STATE analysis using the energy changes of characteristic X-ray lines, called chemical shifts, is one of the most widely used applications of high-resolution X-ray fluorescence spectroscopy (HRXFS) in the characterization of materials. Many studies on the coordination analysis of Al atoms in oxide compounds using the shifts of AlK α lines have been reported [1-4]. The AlK α line shows a clear shift between fourfold and sixfold coordination. This shift is very useful for the characterization of solid-solution or glass systems. Similar shifts in Mg and GeK α lines were found and applied to the determination of the coordination number of Mg and Ge atoms in various types of glasses [5-8].

A variety of molecular orbital (MO) calculations have become practicable. In our previous reports [9-11], using an SCC (self-consistent charge) - DV (discrete variational) - X α MO theory [12], we calculated the small change in the energy difference between the inner levels of the central atom by varying its coordination number, and succeeded in explaining the relation between the chemical shifts of K α X-ray emissions and the coordination numbers of Al, Mg and Ge atoms in their oxides.

The coordination state of Si atoms in silicon-containing oxide systems is fourfold, sixfold or mixed. Generally, a fourfold oxygen coordinated tetrahedral Si atom is the common building block in silicas and silicates. However, under the high-pressure condition, 17 crystallographically well-characterized inorganic silicates are known in which silicon exists in sixfold oxygen octahedral coordination [13]; the most notable is stishovite, a high-pressure SiO₂ polymorph [14,15]. On the other hand, one of the phases in the silico-phosphate system, SiP₂O₇, shows the presence of sixfold coordinated Si atoms only [16], and Si₅O(PO₄)₆ consists of isolated SiO₆ octahedra and Si₂O₇ groups which are linked by PO₄ tetrahedra [17], under atmospheric pressure. In the silico-phosphate glasses, the coordination state of Si atoms was reported to be fourfold [18-20], while papers pointing out the appearance of sixfold coordinated Si atoms with

Table 1 Samples studied

Crystals	
α -quartz	Si 4 coord
stishovite	Si 6 coord
SiP ₂ O ₇	Si 6 coord
Glasses	
Batch comp	Analytical comp.
90SiO ₂ .10P ₂ O ₅	92 6SiO ₂ 7 4P ₂ O ₅
85SiO ₂ 15P ₂ O ₅	89.1SiO ₂ .10 9P ₂ O ₅
80SiO ₂ 20P ₂ O ₅	87 5SiO ₂ 12.5P ₂ O ₅
75SiO ₂ .25P ₂ O ₅	80 5SiO ₂ 19 5P ₂ O ₅
70SiO ₂ 30P ₂ O ₅	73.9SiO ₂ .26.1P ₂ O ₅
60SiO ₂ 40P ₂ O ₅	71 2SiO ₂ 28 8P ₂ O ₅

increasing contents of P₂O₅ were also presented [21–24]. In the present paper, the chemical shifts of SiK α lines due to the coordination state were studied by means of HRXFS and a SCC–DV–X α MO method.

2. EXPERIMENTAL

Samples used in this study are listed in Table 1. The crystals with known coordination state were α -quartz (fourfold), stishovite (sixfold) and SiP₂O₇ (sixfold). The α -quartz was reagent grade and stishovite was prepared at the Research Center for Extreme Materials, Osaka University, Japan. Synthesis of SiP₂O₇ was by direct reaction of H₃PO₄ with SiO₂; the mixture of these raw materials with the starting composition SiO₂ : P₂O₅ = 1 : 1.2 (in mole), in view of evaporation of the P₂O₅ ingredient, was heated for 24 h at 1000°C in a platinum crucible. These crystals were confirmed by the X-ray diffraction method. The SiO₂–P₂O₅ glass samples were prepared by melting H₃PO₄ and SiO₂ for 1 h at 1500–1600°C in platinum crucibles and dipping the crucible into water. Their compositions were analyzed quantitatively by chemical analysis. Compositional deviation of glass samples from starting batches is also indicated in the table.

High-resolution SiK α spectra of the samples were measured using a two-crystal type spectrometer (Rigaku Denki Co., Ltd., Japan) [25] with two InSb (111) analyzer crystals ($2d = 7.4806$ Å) at room temperature. The conditions of measurement are summarized in Table 2. The wavelength used for calibration was SiK α of metallic Si (wavelength = 7.1254 Å). Samples were excited with X-rays generated by a Sc target tube operated at 50 kV and 50 mA. Spectra were obtained by using a multichannel analyzer (1 spectrum = 600 channels). Fluorescent X-rays were detected with a gas flow proportional detector. The reference sample for the calculations of chemical shift and full width at half maximum intensity (FWHM) was metallic Si and the peak position was defined from the center of FWHM. The spectrum of metallic Si was measured just before and just after the measurement of each sample spectrum, in order to cancel the drift of the measurement system. The measurement of each sample was repeated three times independently.

3. MOLECULAR ORBITAL CALCULATIONS

The purpose of the present MO calculation is to show the effect of coordination on K α transition. Using the Hartree–Fock–Slater approximation [26], the accuracy of calculation is almost the same as that of the Hartree–Fock method and computation time is dramatically shortened. In this study, the SCC–DC–X α method was used.

Table 2 Conditions for the measurement of SiK α spectra

Spectrometer	Rigaku, two-crystal spectrometer
Primary X-rays	Sc anode X-ray tube, 50 kV–50 mA
Analyzing crystal	InSb(111) + InSb(111), $2d = 7.4806$ Å
X-ray path	Vacuum
Scan range (2 θ)	143.005 – 146.000 (4–10 sec/ch)

For the analysis of the electronic structure of solids by the X α method, a unit composed of several atoms, i.e. a cluster, is used to simplify the MO calculation process. The cluster models for the calculation were constructed with Si and O atoms. Both SiO $_4^{4-}$ (Td) and SiO $_6^{2-}$ (Oh) were adopted for fourfold and sixfold coordinated Si atoms, respectively. The interatomic distance was selected as the parameter of this calculation.

The X-ray transition energy can be calculated in two ways [27]: (i) ΔE_{SCF} method; and (ii) Slater's transition-state method. The K α energy is represented as

$$E(K\alpha) = E^{X\alpha}(n_{1s} = 2, n_{2p} = 5) - E^{X\alpha}(n_{1s} = 1, n_{2p} = 6) \quad (1)$$

$$= \epsilon_{2p}^{X\alpha}(n_{1s} = 1.5, n_{2p} = 5.5) - \epsilon_{1s}^{X\alpha}(n_{1s} = 1.5, n_{2p} = 5.5) \quad (2)$$

where $E^{X\alpha}$ is atomic total energy, n_i the occupation number of orbital i , $\epsilon_i^{X\alpha}$ the eigenvalue of orbital i . Equation (1) is the ΔE_{SCF} method and Eqn (2) is the Slater's transition-state method. The calculations of K α energy were performed by the Slater's transition-state method, which gave quite accurate results reflecting the relaxation effects of MOs caused by electron transitions by using a single numerical processing step. The only empirical parameter, α , in the X α method was assumed to be 0.7 [12].

4. RESULTS AND DISCUSSION

4.1. Results of measurements

In Fig. 1 the SiK α spectra profiles of three crystalline samples are shown. The results of the SiK α energy shifts of each sample referred to the energy of metallic Si are shown in Fig. 2. All chemical shifts are positive. The energy shifts of stishovite and SiP $_2$ O $_7$ from that of α -quartz were 0.142 and 0.259 eV, respectively. It was found that the SiK α line shows a clear shift between fourfold and sixfold coordination. The sixfold coordinated Si atoms emit higher energy K α than the fourfold coordinated Si atoms, this effect is similar to that observed in Al, Mg and Ge atoms. It was observed that all the emissions from the silico-phosphate glasses are located in the vicinity of that of α -quartz and that the line shape and the FWHM (≈ 1.415 eV) are found to be almost identical for all the glasses and α -quartz. These suggest that fourfold coordinated Si atoms are predominant for the glasses presented in this study.

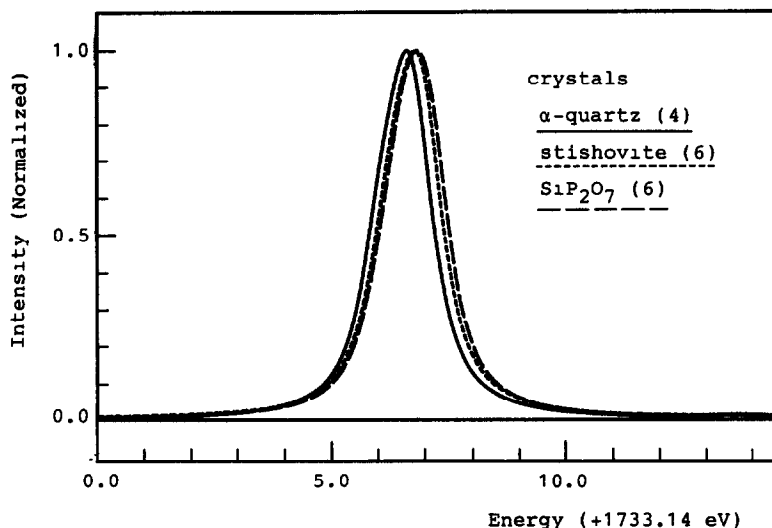
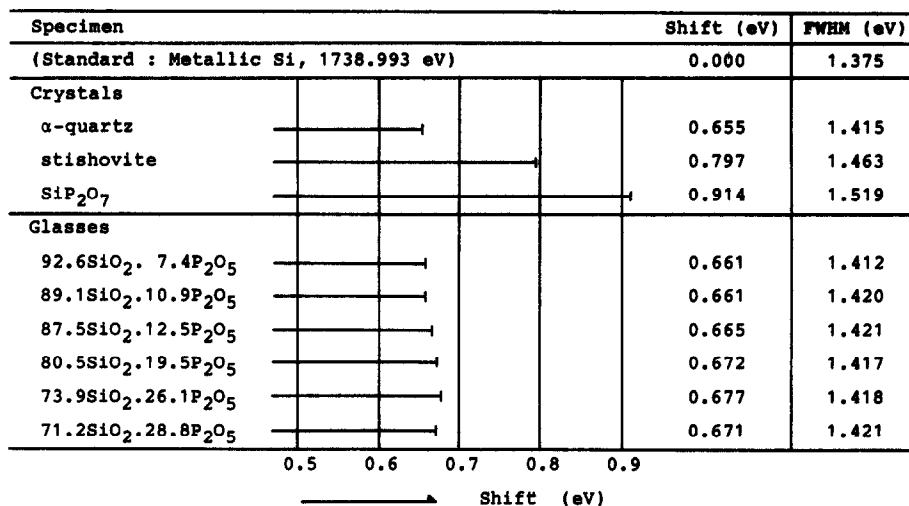


Fig 1 High-resolution SiK α X-ray emission spectra of α -quartz (—), stishovite (---) and SiP $_2$ O $_7$ crystal (- - -) The figures in parentheses denote known coordination number of Si atoms in their samples

Fig 2 Shifts of SiK α X-ray emission spectra due to coordination states.Table 3 Results of DV-X α calculations (ground state)

[SiO ₄] ⁴⁻ R(Si-O) 1 60 Å			[SiO ₆] ⁿ⁻ R(Si-O) 1 76 Å		
Level	Eigenvalue (eV)	Population	Level	Eigenvalue (eV)	Population
1a ₁	-1753 83450	2 0 (Si1s)	1a _{1g}	-1730 96193	2.0 (Si1s)
1t ₂	-484 09719	6 0 (O1s)	2a _{1g}	-460 43561	2.0 (O1s)
2a ₁	-484 09708	2 0 (O1s)	1t _{1u}	-460 43553	6.0 (O1s)
			1e _g	-460.43550	4 0 (O1s)
3a ₁	-114 39948	2 0 (Si2s)	3a _{1g}	-90 89829	2.0 (Si2s)
2t ₂	-71.97954	6 0 (Si2p)	2t _{1u}	-48 52372	6 0 (Si2p)

Effective charge Si^{+2.66}Effective charge Si^{+3.58}Table 4 Results of DV-X α calculations (transition state)

[SiO ₄] ⁴⁻ R(Si-O) 1 60 Å			[SiO ₆] ⁿ⁻ R(Si-O) 1 76 Å		
Level	Eigenvalue (eV)	Population	Level	Eigenvalue (eV)	Population
1a ₁	-1848 48903	1 5 (Si1s)	1a _{1g}	-1824 75256	1 5 (Si1s)
1t ₂	-496 88508	6 0 (O1s)	2a _{1g}	-466 43280	2 0 (O1s)
2a ₁	-496 88500	2 0 (O1s)	1t _{1u}	-466 43272	6 0 (O1s)
			1e _g	-466 43264	4 0 (O1s)
3a ₁	-145 99741	2 0 (Si2s)	3a _{1g}	-121 48222	2 0 (Si2s)
2t ₂	-105 80461	5 5 (Si2p)	2t _{1u}	-81 37471	5 5 (Si2p)

Effective charge Si^{+1.40}
(include hole)Effective charge Si^{+2.31}
(include hole)

4.2. Molecular orbital calculation

The results of the calculations for the clusters with the about mean Si-O distances in fourfold and sixfold coordinated substances [13] are shown in Tables 3 (ground state) and 4 (transition state), together with electronic structures of inner shells. The

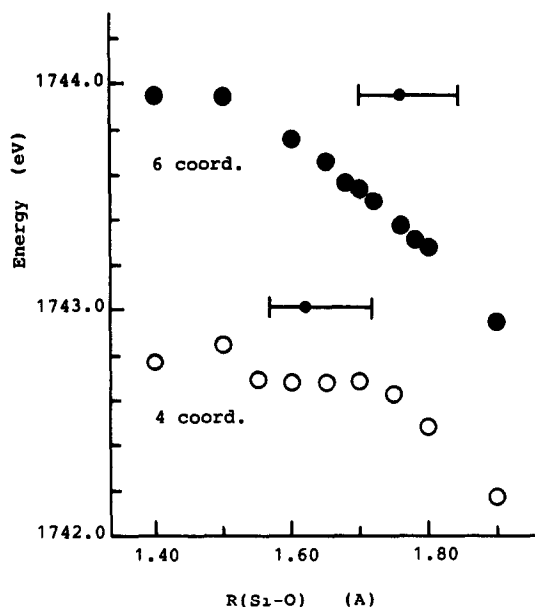


Fig 3 Calculated SiK α energy vs Si-O interatomic distance. Open circles and filled circles represent the results for SiO $_4^{4-}$ and SiO $_6^{8-}$, respectively. The horizontal section in this figure corresponds to the range of the reported possible Si-O interatomic distance, and the plotted point on the section indicates the mean Si-O interatomic distance, for fourfold and sixfold coordinated substances [13].

orbital eigenvalues in the transition state calculated by the Slater's transition-state method are lower than those in the ground state because of the relaxation effects of MOs caused by electron transitions. In the SiO $_4^{4-}$ model, Si 1s and 2p correspond to $1a_1$ and $2t_2$, respectively. The K $\alpha(1s-2p)$ energy is calculated to be 1742.69 eV (1848.49 eV-105.80 eV) from Table 4. In SiO $_6^{8-}$, 1s and 2p correspond to $1a_{1g}$ and $2t_{1u}$, respectively. The K $\alpha(1s-2p)$ energy is calculated to be 1743.38 eV (1824.75 eV-81.37 eV) from Table 4.

The behavior of calculated SiK α energy vs. interatomic distance between Si and O atoms ($R(\text{Si-O})$) is shown in Fig. 3. The horizontal section in this figure corresponds to the range of the reported possible Si-O interatomic distance and the plotted point on the section indicates the mean Si-O interatomic distance, in fourfold and sixfold coordinated substances [13]. It was found that the calculated SiK α energy shows a clear shift between fourfold and sixfold coordination models and that the sixfold coordinated Si atom emits higher energy K α than the fourfold coordinated Si atom.

Although the calculated values for K α transition are higher than the observed K α energies, the results of the calculations reproduce the tendency of the SiK α shifts observed. This result supports the theory that the observed SiK α shifts are caused by a change of coordination and that it is possible to determine the coordination state of Si atoms by measuring SiK α shift.

The effective charge of the Si atom in each model was also calculated by Mulliken's population analysis [28], and the results are shown in Tables 3 and 4. The effective charge of the Si atom in SiO $_4^{4-}$ (ground state: 1.46; transition state: 1.40) is smaller than that in SiO $_6^{8-}$ (ground state: 2.33; transition state: 2.31). This result shows that the Si-O bond of SiO $_4^{4-}$ is more covalent than that of SiO $_6^{8-}$. The change in the effective charge due to the number of nearest-neighbor atoms is the cause of the K α shifts. This result agrees with that of our previous study on the cause of GeK α shift [10].

The effective charge also may be affected by the nature of the second-nearest-neighbor atoms, especially their electronegativity. If the second-nearest-neighbor atoms are highly electronegative, the valence electrons of Si atoms move to O atoms and the effective charge of Si atoms increases. These changes make SiK α shift to the higher

energy side. The phosphorus atom in pyrophosphoric acid is highly electronegative. In Fig. 2 Si atoms in SiP_2O_7 emit higher energy $K\alpha$ than those in stishovite and this shift (0.117 eV) is not due to coordination as the coordination state of Si atoms in these samples is equally sixfold. This result is similar to that observed for GeP_2O_7 , i.e. Ge atoms in GeP_2O_7 emit higher energy $K\alpha$ than those in tetragonal GeO_2 , and the coordination state of Ge atoms in their samples is equally sixfold [10].

MAEKAWA *et al.* measured the $\text{Si}K\alpha$ spectra in silicate and borate glasses, in which the coordination state of Si atoms is fourfold, and reported that all spectra showed negative energy shifts referred to α -quartz and that the $\text{Si}K\alpha$ energy increases with increasing contents of SiO_2 and B_2O_3 in glasses [29–32]. In this study, all the $\text{Si}K\alpha$ emissions from the silico-phosphate glass samples are slightly shifted to the positive energy side from α -quartz with increasing content of P_2O_5 , as shown in Fig. 2. These facts can be interpreted as follows; as the P atom is more electronegative than Si and B atoms, the contribution for the effective charge from the P atom is larger than that from Si and B atoms, therefore the $\text{Si}K\alpha$ emissions from the silico-phosphate glasses are shifted to the higher energy side.

5. CONCLUSION

It was found experimentally and theoretically that the $\text{Si}K\alpha$ line shows a clear shift due to coordination. Molecular orbital calculation analysis by the SCC–DV– $X\alpha$ method reproduced the effects of coordination. The analysis leads to the following conclusion; sixfold oxygen coordinated Si atoms emit higher energy $K\alpha$ than fourfold coordinated Si atoms, and the energy shifts are caused by changes in the effective charge of Si atoms due to the number of nearest-neighbor oxygen.

All of above results gave a theoretical basis for the method of determination of the coordination state of Si atoms in several materials by measurement of $\text{Si}K\alpha$ energy shifts.

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