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Structural and chemical effects on the SiKβ X-ray emission spectra for silicates and silico-phosphates

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The SiKβ X-ray emission spectra for several silicates and silico-phosphates were measured using a high-resolution X-ray fluorescence spectrometer with two InSb(III) analyser crystals. Molecular orbital calculation analysis for the obtained spectra was performed by a SCC-DV-Xα method and the energy positions and relative intensities of the spectral fine structures were calculated with Slater's transition-state method. The calculated results interpreted the spectral profiles successfully. The energy shifts of the SiKβ main peak were also discussed in terms of the electronegativity of the second-nearest-neighbour atoms. These shifts were attributed to the changes in the stability of the Si–O bonds due to the existence of second-nearest-neighbour P atoms.

1. Introduction

Chemical-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. This shift is very useful for the characterization of materials in solid–solution or glass systems [1–8].

In a previous study [8], we measured the chemical shifts of SiKα lines due to the difference of coordination states in several silicates and silico-phosphates by means of HRXFS. Using a SCC (self-consistent charge)–DV (discrete variational)–Xα molecular orbital (MO) theory [9], 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 Kα X-ray emissions and the coordination numbers around Si atoms.

On the other hand, Kβ emission spectra which correspond to the electronic transition from the 3p to 1s atomic orbital (AO) yield valuable information about the chemical states in materials. White and Gibbs [10] and later Dodd and Glen [11] interpreted the origin of the SiKβ spectra in silicates using MO theory and defined the destabilization energy of the Si–O bond. Urch [12] and Tossell [13–15] extended this MO treatment by more quantitative calculations and discussed the details of the nature of the Si–O bond. Sakka and Matusita measured the SiKβ spectra of binary silicate glasses, and they discussed the chemical shifts and the changes in the bandwidth in terms of the destabilization energy of the Si–O bond strength and the difference in the state of Si atoms [16]. Chelikowsky and Schlüter calculated the shape of the SiK-emission band and compared it with measured spectra [17, 18]. A comparison of the experimental results with the density of states of α-quartz was performed by Calabrese and Fowler [19], and earlier by Pantelides and Harrison [20], who compared the X-ray spectra with their theoretical results for β-cristobalite. Kikuchi *et al.* reported the variations of the SiKβ spectra of several silicates using a two-crystal spectrometer and found some changes of the spectral profiles as well as changes of width and line energy [21]. The valence band structure and the density of states of stishovite, a high-pressure SiO_2 polymorph which is octahedral in coordination, were calculated by Rudra and Fowler [22]. The experimental SiKβ spectrum of stishovite was presented by Wiech *et al.*, who reported that a quite different spectral shape was observed between stishovite and other tetrahedrally coordinated SiO_2 and also that subtle differences were observed according to the variations in the Si–O–Si bond angle [23, 24]. Cherlov *et al.* calculated the electronic structure of the $Si_2O_7^{6-}$ cluster and estimated the influence of the Si–O–Si bond angle for the spectra [25].

In this study we applied a high-resolution X-ray fluorescence spectrometer with two analyser crystals

TABLE I Samples studied

Crystals	
α-quartz	Si 4 coord.
Stishovite	Si 6 coord.
SiP_2O_7	Si 6 coord.
Glasses	
Batch composition	Analytical composition
$70SiO_2.30P_2O_5$	$73.9SiO_2.26.1P_2O_5$

TABLE II Conditions for the measurement of SiKβ spectra

Spectrometer	Rigaku, two-crystal spectrometer
Primary X-rays	Sc anode X-ray tube, 50 kV–50 mA
Analysing crystal	InSb(111) + InSb (111), 2d = 7.4806 A
X-ray path	Vacuum
Scan range (2θ)	128.010–132.300 (8–40 sec/ch)

to measure the SiKβ spectra for several silicates and silico-phosphates. In order to interpret the spectral profiles, MO calculation analysis was performed using the SCC–DV–Xα method and the energy positions and relative intensities of the fine structures for the spectra were calculated. The energy shifts were also discussed in terms of the electronegativity of the second-nearest-neighbour atoms.

2. Experimental procedure

Samples used in this study are listed in Table I. The method of sample preparation has been already reported in a previous paper [8]. The crystals used as the reference standard were α-quartz (fourfold), stishovite (sixfold) and SiP_2O_7 (sixfold) [26]. The coordination number around Si atoms in the silico-phosphate glass samples was analysed using the high-resolution SiKα spectra, and was determined to be mainly fourfold by the authors [8].

High-resolution SiKβ spectra of the samples were measured by means of a two-crystal-type spectrometer (Rigaku Denki Kogyo Co., Ltd., Japan) [27] with two InSb(1 1 1) analyser crystals (2d = 7.4806 A) at room temperature. The conditions of measurement are summarized in Table II. 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 analyser (1 spectrum = 430 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. 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 present MO calculation was performed by the SCC–DV–Xα method. For the analysis of the electronic structure of solids by the Xα 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: R(Si–O) = 1.62 A) and SiO_6^{8-} (Oh: R(Si–O) = 1.75 Å) were adopted for fourfold and sixfold coordinated Si atoms, respectively. The values for interatomic distance were the reported mean Si–O distances for fourfold and sixfold coordinated substances [28]. The energy positions and relative intensities of the fine structures on the SiKβ spectra were calculated by Slater's transition-state method [29], which gives quite accurate results reflecting the relaxation effects of MOs caused by electron transitions by using a single numerical processing step. The relative intensity of X-ray emission by electron transitions between a valence MO and Si1s was evaluated by the flollowing equation;

$$I \propto E^3| < \phi_f|\mu|\phi_i > |^2 \qquad (1)$$

where I is intensity of emission, ϕ_f and ϕ_i are wave functions for 1s core orbital and one of valence MOs in Slater's transition-state model, respectively, and μ is a dipole moment. E is the energy of emission and corresponded with the energy distance between core level and valence MOs in this study. The only empirical parameter, α, in the Xα method was assumed to be 0.7 [9].

4. Results and discussion

4.1. Results of measurements

Measured SiKβ spectra of α-quartz, $73.9SiO_2.26.1P_2O_5$ glass, stishovite and SiP_2O_7 crystal are shown in Fig. 1. The following three transitions were

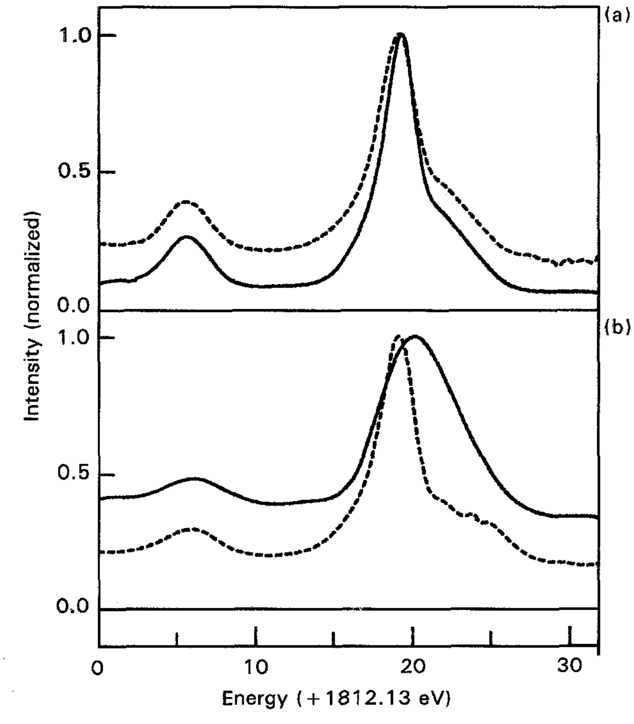

Figure 1 High-resolution SiKβ X-ray emission spectra of (a) α-quartz (—) and 73.9 $SiO_2 \cdot 26.1\ P_2O_5$ glass (- - -) and (b) stishovite (—) and SiP_2O_7 crystal (- - -).

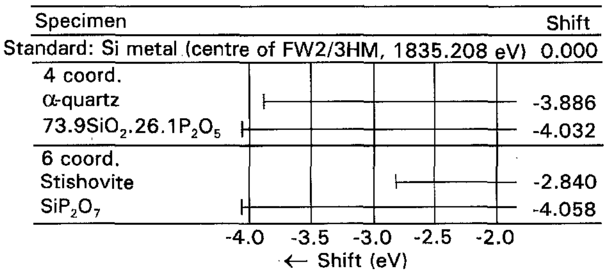

Figure 2 Shifts of SiKβ X-ray emission spectra. Peak position was defined as the centre of FW2/3M of the Kβ band.

observed on these spectra: (1) the main transition called the Kβ main peak; (2) a higher-energy transition than the main transition which appears as a shoulder; (3) a lower-energy transition than the main transition called the Kβ' satellite peak. The contribution from the second-nearest-neighbour P atoms were seen in the observed spectra.

The shifts of the SiKβ main peak for each sample referring to Si metal are shown in Fig. 2. The peak position was defined from the centre of full width at 2/3 maximum intensity (FW2/3M) of the Kβ band. In the fourfold coordinated samples, the emission from the silico-phosphate glass sample was located between stishovite and SiP_2O_7, and shifted slightly to the lower energy side from α-quartz with increasing content of P_2O_5. In the sixfold coordinated samples, the emission from SiP_2O_7 shifted to the lower energy side from stishovite. These results suggest that the Kβ main peak shifts to the lower energy side by the influence of the second-nearest-neighbour P atoms, and also that the coordination state of the materials in this system cannot be determined by such chemical shifts since the region of the energy shifts showed overlap between fourfold and sixfold coordination.

4.2. Molecular orbital calculation

The MOs for the SiO_4^{4-} and SiO_6^{8-} cluster models were constructed to assign the structures of observed SiKβ spectra. The energy positions and relative intensities of the fine structures on Kβ transition calculated with the transition-state approximation for above two geometries are shown in Fig. 3. The intensities of the fine structures were normalized on the basis of those of the fine structures $4t_2$ for the SiO_4^{4-} and $4t_{1u}$ for the SiO_6^{8-}, respectively. The calculated results reproduced the observed three transitions successfully.

The SiKβ spectra involve the transition from Si3p to Si1s AO. According to the selection rules for tetrahedral geometry, all MOs of t_2 symmetry can take part in the transition. The main bonding orbital σ $4t_2$ consists of Si3p and O2p AOs, and the transition from this to Si1s is the origin of the Kβ main peak. The Kβ shoulder corresponds to the transition from the $5t_2$ orbital, which consists mainly of O2p with a small mixing of Si3p, to Si1s. Further, the transition from $3t_2$ (Si3p + O2s) produces the Kβ' satellite peak. This assignment agreed with the results calculated by Tossell [14]. On the other hand, for octahedral geometry, all MOs of t_{1u} symmetry can take part in the transition. The Kβ main peak is assigned to the transition from the main bonding orbital $4t_{1u}$ (Si3p + O2p) to Si1s. The Kβ shoulder corresponds to the transition from the $5t_{1u}$ orbital (Si3p + O2p) to Si1s. The Kβ' satellite peak corresponds to the transition from $3t_{1u}$ (Si3p + O2s) to Si1s.

4.3. Chemical shifts of SiKβ main peak

It was reported that the Kβ energy of silicate was shifted to the higher energy side when basic oxide was introduced to the silica network [21]. The Kβ peak shifted to the lower energy side with increasing content of P_2O_5 in the case of the silico-phosphate system. As the main peak of SiKβ was caused by the electron transition from σ Si–O bonding to Si1s, the average electronegativity of the second-nearest-neighbour atoms of Si atoms dominated the change of SiKβ energy indirectly. The following mechanism for the negative energy shift in this system is assumed. If the second-nearest-neighbour atoms are more electronegative than Si atoms as P atoms, the valence electrons of Si atoms move to O atoms and the effective charge of Si atoms increases. Therefore the stabilization of the Si–O bond is caused and the relative

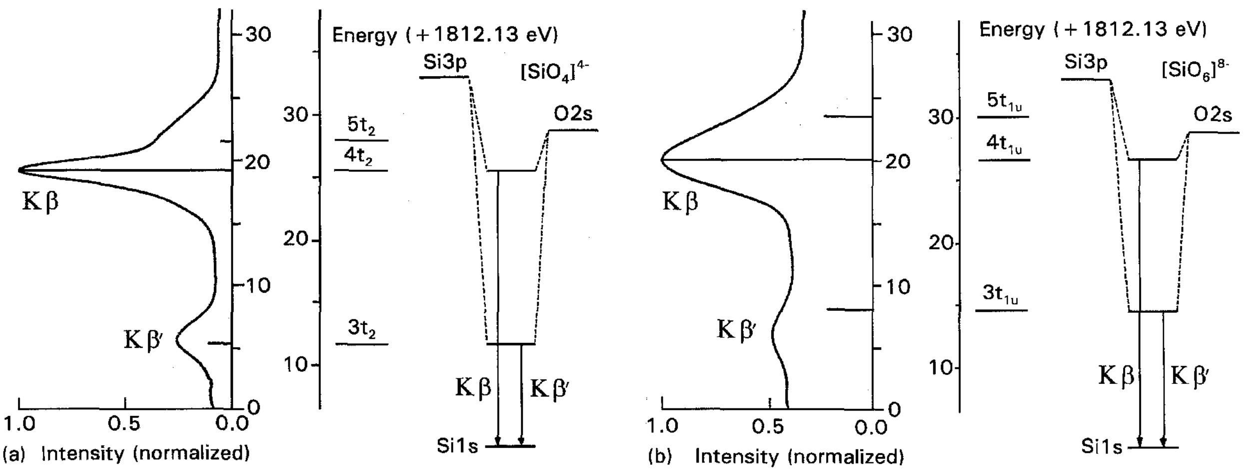

Figure 3 Calculated energy positions and relative intensities of fine structures on SiKβ transition for SiO_4^{4-} (α-quartz) (a) and SiO_6^{8-} (stishovite) (b) clusters.

position of the main bonding orbital σ $4t_2$ and $4t_{1u}$ for Si1s goes down, which makes Kβ shift to the lower energy side.

The shifts of the Kβ′ satellite and Kβ shoulder positions in the spectra were not observed with increasing content of P_2O_5. This fact is explained in terms of the orbital compositions. In the tetrahedral and octahedral geometries, Si3p AO participates primarily in $4t_2$ and $4t_{1u}$ MOs concerned with the Kβ main peak, respectively, and $3t_2$ and $3t_{1u}$ MOs concerned with the Kβ′ satellite consist of mostly O2s AO ($3t_2$; 94.0%, $3t_{1u}$; 97.8%), while $5t_2$ and $5t_{1u}$ MOs concerned with the Kβ shoulder consist of almost O2p AO ($5t_2$; 93.2%, $5t_{1u}$; 99.7%), respectively. Therefore the contribution from the second-nearest-neighbour P atoms is primarily given to the main bonding orbitals ($4t_2$ and $4t_{1u}$), and this leads to the shift of only the Kβ main peak.

5. Conclusion

Structural and chemical effects on the SiKβ X-ray emission spectra for several silicates and silico-phosphates were studied by means of HRXFS. The MO calculation analysis by a SCC–DV–Xα method interpreted the observed spectral profiles successfully. The energy shifts of SiKβ main peak were attributed to the changes in the stability of the Si–O bonds due to the existence of the second-nearest-neighbour P atoms. A theoretical basis for the chemical-state analysis of Si atoms in a silicon-containing oxide system using high-resolution SiKβ spectra was proposed.

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