LETTERS

High-resolution Si and P K- and L-edge XANES spectra of crystalline SiP$_2$O$_7$ and amorphous SiO$_2$-P$_2$O$_5$

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ABSTRACT

Si and P K- and L-edge XANES spectra of crystalline SiP$_2$O$_7$ (c-SiP$_2$O$_7$) and amorphous SiO$_2$-P$_2$O$_5$ (a-SiO$_2$-P$_2$O$_5$) are reported using synchrotron radiation and interpreted using molecular orbital considerations. The Si spectra are consistent with t6lsi in c-SiP$_2$O$_7$ and with t4tSi in a-SiO$_2$-P$_2$O$_5$ (25 mol% P$_2$O$_5$). The resolution of near-edge features in the Si L-edge spectrum of the crystalline material is unprecedented. These spectra show definitively that Si XANES spectroscopy is a powerful technique for determining t5osi and t6lsi in amorphous samples.

INTRODUCTION

Silicon diphosphate (c-SiP$_2$O$_7$) is one of several compounds in which Si has been shown to be sixfold coordinated with O at atmospheric pressure, and c-SiP$_2$O$_7$ has three different modifications: a cubic Pa3 phase and monoclinic P2$_1$/c and P2$_1$/n phases (Liebau, 1985). The IR and Raman spectra of cubic and monoclinic c-SiP$_2$O$_7$ were measured and interpreted by normal coordinate analyses using a modified valence force field (Chakraborty et al., 1987). The $^{29}$Si MAS NMR spectra of c-SiP$_2$O$_7$ have also been reported (Thomas et al., 1983; Mudrakovskyi et al., 1985; Grimmer et al., 1986; Stebbins and Kanzaki, 1991). The structure of glasses in the SiO$_2$-P$_2$O$_5$ system were studied using IR (Wong and Angell, 1976) and Raman spectra (Mysen et al., 1981; Shibata et al., 1981) and $^{29}$Si MAS NMR spectra (Weeding et al., 1985; Sekiya et al., 1988). The energy shifts of the SiK$\alpha$ X-ray emission lines in c-SiP$_2$O$_7$ and SiO$_2$-P$_2$O$_5$ glasses were calculated by a SSC-DV-X$\alpha$ MO method (Okura et al., 1990).

We report high-resolution Si and P K- and L-edge XANES spectra of c-SiP$_2$O$_7$ and SiO$_2$-P$_2$O$_5$ glass using synchrotron radiation. Our purposes are to interpret the XANES spectra within an MO framework and to show that XANES provides a sensitive probe for determining the Si coordination environment in amorphous materials such as a-SiO$_2$-P$_2$O$_5$.

EXPERIMENTAL METHODS

The c-SiP$_2$O$_7$ sample was synthesized by reacting high-purity SiO$_2$ and excess H$_3$PO$_4$ in an open silica-glass tube at about 950 °C and identified as a monoclinic P2$_1$/n phase by X-ray powder diffraction. SiO$_2$-P$_2$O$_5$ glasses were prepared by melting c-SiP$_2$O$_7$ at 1550 °C in a small Pt disk and quenching in air and H$_2$O. However, P$_2$O$_5$ was lost from our glass preparations during melting. Glass compositions were determined by electron microprobe analysis (EMPA). The spectra presently are from a glass with 75 mol% SiO$_2$ and 25 mol% P$_2$O$_5$ determined by EMPA.

The SiK- and PK-edge XANES spectra were measured using a double-crystal monochromator (DCM) of InSb (111) with synchrotron radiation. The energy resolution for the DCM is about 0.8 eV at 1840 eV. The SiL- and
RESULTS AND DISCUSSION

Figure 1 shows the SiK- and SiL-edge XANES spectra of c-SiP,O, and a-SiO,P,O,. The SiL-edge spectra are shown by the solid lines, and the SiK-edge spectra are shown by the solid lines with dots. The SiK- and SiL-edge spectra are aligned on a common scale by the SiKa, X-ray emission energy at 1740.0 eV, which corresponds to the Si 2p, - ls transition. The peak position and assignments are given in Table 1, in which ΔE for the SiK-edge spectra is the difference between each peak and the SiKa, X-ray emission energy at 1740 eV. SiK- and SiL-edge XANES spectra of c-SiP,O, are essentially similar to those for stishovite (Li et al., 1993), characteristic of 16Si. The line width of peak A in the SiL-edge spectrum is about 0.38 eV, which is the best resolution ever reported for solid state samples, to our knowledge. Peak A in the SiL-edge spectrum is assigned to the dipole-allowed transition of Si 2p electrons to a 3s-like a,s state (Tossell, 1975a; Iguchi, 1977). This state is split by about 0.65 eV due to the spin-orbit interaction of Si 2p orbitals. Peak C is attributable to the transition of Si 2p electrons to a 3p-like t,, state; it is weak because this transition is dipole-forbidden in an octahedral field. Peaks E and G are assigned to transitions of Si 2p electrons to empty Si 3d orbitals, the so-called shape resonance (Li et al., 1993). Because the t,, state is favored in energy over the e, state, and peak G to the e, state.

Peaks A, C, E, and G in the SiK-edge spectrum align reasonably well with the corresponding peaks in the SiL-edge spectrum and are also comparable with AlK-edge spectra of corundum (McKeown et al., 1985). Peak A is assigned to the transition of Si ls electrons to a 3s-like a,s state; it is weak because this transition is forbidden in the octahedral crystal field. Peak C is attributed to the dipole-allowed transition of Si ls electrons to the 3p-like t,, state. Peaks E and G are assigned to transitions of Si ls electrons to the 3p-like t,, state. Peaks A and C are assigned to multiple scattering in the

### Table 1. Assignments for SiK- and SiL-edge XANES spectra of c-SiP,O, and a-SiO,P,O,

<table>
<thead>
<tr>
<th>Peaks (eV)</th>
<th>ΔE (eV)</th>
<th>Assignments</th>
<th>Peaks (eV)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1846.2</td>
<td>106.2</td>
<td>A</td>
<td>1844.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 1s → 3s-like a,s</td>
<td></td>
<td>c-SiO,P,O,</td>
</tr>
<tr>
<td>C</td>
<td>1848.9</td>
<td>106.9</td>
<td>C</td>
<td>1846.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 1s → 3p-like t,,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1853.7</td>
<td>113.7</td>
<td>E</td>
<td>1854.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 1s → 3d-like e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1866.3</td>
<td>126.3</td>
<td>G</td>
<td>1863.7</td>
</tr>
</tbody>
</table>

* The reading error is ±0.1 eV.
stishovite K-edge spectrum (Li et al., 1993), disappears, probably indicating that peak E includes a significant contribution from the multiple scattering of the more distant atom shells. Other peaks, attributed to the multiple scattering in the stishovite spectra (Li et al., 1993), are weak in the c-SiP$_2$O$_5$ spectra.

Just as the SiK- and SiL-edge spectra of c-SiP$_2$O$_5$ are very similar to those of stishovite, the SiK- and SiL-edge spectra of a-Si$_2$O$_5$-P$_2$O$_5$ are very similar to the corresponding spectra of α quartz (Li et al., 1993). In particular, peak C in the SiK-edge spectra shifts by 2.0 eV, from 1848.9 eV for c-SiP$_2$O$_5$ to 1846.9 eV for a-Si$_2$O$_5$-P$_2$O$_5$. This is very convincing evidence for $^{29}$Si in a-Si$_2$O$_5$-P$_2$O$_5$, in good agreement with MAS NMR results from Weeding et al. (1985).

The SiK- and SiL-edge XANES spectra of a-Si$_2$O$_5$-P$_2$O$_5$, can be readily assigned according to the MO scheme for a tetrahedral crystal field. In the SiL-edge spectrum, peak A is assigned to the dipole-allowed transition of Si 2p electrons to a 3s-like $a_1$ state (Tossell, 1975b; Iguchi, 1977), and its splitting of about 0.61 eV is apparently due to the spin-orbit interaction of Si 2p orbitals. Peak C is attributed to the transition of Si 2p electrons to a 3p-like $t_2$ state; the $p \rightarrow p$ transition is dipole-allowed in the tetrahedral field (Hansen et al., 1992), and consequently, peak C is very strong. Peaks E and G are attributed to the transition of Si 2p electrons to empty Si 3d states (the shape resonances). In a tetrahedral field, the Si 3d orbitals are split into $t_2$ and $e$ sets, and the $e$ set is more favored in energy, so that peak E is assigned to the transition of Si 2p electrons to the $e$ states, and the peak G to the $t_2$. Peaks in the SiK-edge spectra of a-Si$_2$O$_5$-P$_2$O$_5$ are assigned as follows: peak A, due to the dipole-forbidden transition Si 1s $\rightarrow$ 3s-like $a_1$, is too weak to be observed; peak C is assigned to the dipole-allowed transition Si 1s $\rightarrow$ 3p-like $t_2$; and peaks E and G are assigned to transitions of Si 1s $\rightarrow$ 3d-like $e$ and $t_2$, respectively, the so-called symmetry-forbidden shape resonances. Also, the features due to the multiple scattering effect from the more distant atom shells in the α quartz spectra essentially disappear, partly related to the short-range structure in the vitreous sample.

Figure 2 shows PK- and PL-edge XANES spectra of c-SiP$_2$O$_5$ and a-Si$_2$O$_5$-P$_2$O$_5$. The PL-edge spectra are shown as solid lines, and the PK-edge spectra are shown as solid lines with dots. The PK- and PL-edge spectra are aligned on a common scale by the $PK_α$, X-ray emission energy at 2013.7 eV. The peak assignments are similar to SiK- and SiL-edge spectra of a-Si$_2$O$_5$-P$_2$O$_5$. PK- and PL-edge spectra indicate that the local structure of P in both c-SiP$_2$O$_5$ and a-Si$_2$O$_5$-P$_2$O$_5$ is tetrahedral. However, compared with the SiL-edge spectrum, peaks A and C are not resolved in the PL-edge spectra for c-SiP$_2$O$_5$, and peak G is very broad. For a-Si$_2$O$_5$-P$_2$O$_5$, peaks A and C (even the spin-orbit splitting of peak A) are very well resolved, and peak G is much sharper. These results indicate a marked change in the structural state of P in the a-Si$_2$O$_5$-P$_2$O$_5$, and these changes will be discussed at length elsewhere.

In general, as shown in Figures 1 and 2, XANES features are aligned very well in both K- and L-edge spectra, and the relative intensities are also in good agreement with those expected from the dipole selection rules. The small shift for the equivalent feature in the K- and L-edge spectra is probably related to the relaxation of inner-shell 1s and 2p holes, even though the shift due to the inner-shell 1s and 2p relaxation of Si 1s is < 1 eV (Bozek et al., 1987).

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**REFERENCES CITED**


