Electron density distribution in stishovite, SiO$_2$: a new high energy synchrotron radiation study.

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Stishovite, SiO$_2$, is the high pressure polymorph of silica and crystallizes in the rutile structure, space group P4$_2$mm, $a_0 = 4.1773$ Å, $c_0 = 2.6655$ Å, $Z = 2$. It thus provides the rare opportunity to study Si 6-fold coordinated by oxygen. Since earlier electron density determinations were impeded by extinction [1, 2] we have carried out new single-crystal diffraction experiments at short wavelengths and extended our study to topological analysis. Crystals of irregular shape and maximum dimensions of 0.3 mm were kindly provided by J. Mosenfelder, Bayerisches Geoforschungsinstitut (synthesis conditions 14 GPa, 1300°C, 10 h). $\omega$-scan experiments were performed on two instruments:

- the conventional 4-circle diffractometer (D3), $\lambda = 0.400$ Å, $s_{\text{max}} = 1.539$ Å$^{-1}$, $N_{\text{Refl}} = 5951$, $N_{\text{uniq}} = 408$, $R_{\text{int}}(F^2) = 0.0398$,
- the triple-crystal diffractometer (BW5), $\lambda = 0.1235$ Å, $s_{\text{max}} = 1.350$ Å$^{-1}$, $N_{\text{Refl}} = 3795$, $N_{\text{uniq}} = 269$, $R_{\text{int}}(F^2) = 0.0117$.

The less satisfactory internal agreement factor of the first data collection is due to the fact that the chosen sample turned out to be a domain crystal. Structure refinements for neutral atoms were carried out with both independent atom (IAM) and generalized scattering factor models (GSF, multipoles up to 7th order) using the VALRAY system [3]. For the absorption and extinction free

Figure 1: Static deformation density $d\rho(r)$ in plane through SiO$_6$ coordination octahedron, contours at 0.05 e/Å$^3$. 
BW5-data, the GSF model converged at R(F) = 0.0038, GoF = 0.78, and even the more extended and less accurate D3-data reached R(F) = 0.0086, GoF = 0.99. Referring to the BW5-results, Figs. 1 and 2 show the static deformation density distributions in the plane through the SiO$_6$ coordination polyhedron (exhibiting two short equatorial and two long axial Si-O bonds) and in the plane containing the pseudo-trigonal arrangement of two equatorial and one axial bond each oxygen is engaged in, respectively. The ensuing topological analysis of the total model density distribution served to determine bond critical points (bcp) and the corresponding bcp-properties such as density, $\rho_c$, curvatures perpendicular ($\lambda_1, \lambda_2$) and parallel ($\lambda_3$) to the bond, and the Laplacian, $\nabla^2 \rho_c$, [4]. Averaged over the different data sets and models one obtains:

<table>
<thead>
<tr>
<th></th>
<th>$d$ [Å]</th>
<th>$\rho_c$ [e/Å$^3$]</th>
<th>$\lambda_1$ [e/Å$^4$]</th>
<th>$\lambda_2$ [e/Å$^4$]</th>
<th>$\lambda_3$ [e/Å$^4$]</th>
<th>$\nabla^2 \rho_c$ [e/Å$^4$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Si-O)$_{eq}$</td>
<td>1.759</td>
<td>0.772</td>
<td>-5.15</td>
<td>-4.79</td>
<td>19.16</td>
<td>9.12</td>
</tr>
<tr>
<td>(Si-O)$_{ax}$</td>
<td>1.809</td>
<td>0.629</td>
<td>-3.68</td>
<td>-3.42</td>
<td>13.89</td>
<td>6.64</td>
</tr>
</tbody>
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Thus, Si-O bonding in stishovite can be classified as a predominantly closed-shell interaction with a considerable shared interaction contribution, which decreases with increasing bond length. This result conforms with the expectation that the ionicity of the Si-O bond increases when the Si coordination changes from four to six.

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References