Hydrogen Solubility in Cristobalite at High Pressure

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ABSTRACT: Powder samples of cristobalite-I are loaded with hydrogen at pressures up to 90 kbar and $T = 250 \degree C$ and quenched under pressure to the liquid N$_2$ temperature. The quenched samples are examined at ambient pressure by X-ray diffraction, Raman spectroscopy, and thermal desorption analysis. The hydrogen content of the samples is found to increase with pressure and reach a molecular ratio of $H_2/SiO_2 \sim 0.10$ at $P = 90$ kbar. At ambient pressure, the samples consist of a mixture of approximately 80% cristobalite-I phase and 20% cristobalite-II-like phase, the crystal lattices of both phases being slightly expanded due to the hydrogen uptake. According to Raman spectroscopy, the hydrogen is dissolved in these phases in the form of $H_2$ molecules.

INTRODUCTION

Silica is the most abundant compound in the Earth’s crust and mantle; therefore, studies on the pressure-induced phase transformations in silica play a key role in understanding the processes occurring in the Earth’s interior. However, this understanding will be incomplete in the absence of physical and chemical data concerning the interaction of silica with gases at high pressure because the Earth’s crust and upper mantle contain a lot of various gases, too. Recent studies revealed a high solubility of helium atoms (He/SiO$_2 = 1$ at $P = 5$ GPa)$^1$ and hydrogen molecules (H$_2$/SiO$_2 = 0.533$ at $P = 7.5$ GPa)$^2$ in the silica glass. The penetrations of the helium atoms and hydrogen molecules in the silica glass network lead to a decrease in its compressibility and prevent the collapse of large voids in it.$^{1,2}$

Among the crystalline phases of silica, cristobalite is the most likely candidate to absorb considerable amounts of hydrogen because its density is close to that of the amorphous phase and its structure has voids large enough to give room for guest atoms or molecules.$^3$ At ambient pressure, cristobalite is known to have two different crystal modifications. The high-temperature cubic phase (space group $Fd\bar{3}m$, $a = 7.166$ Å) can be produced from silica glass or quartz at temperatures above 1000 $\degree C$.$^4$ In cooling below 250 $\degree C$, this phase undergoes a reversible transition to the tetragonal phase cristobalite-I with the space group $P4_12_12_1$.$^5$ This tetragonal phase is metastable at room temperature and serves as the starting state in all studies of cristobalite under pressure.

A room-temperature investigation under hydrogen pressure has earlier shown the cristobalite-I phase to be stable at pressures up to 18 GPa.$^6$ This differs from the results of high-pressure experiments using nonhydrostatic pressure-transmitting media that showed cristobalite-I to transform to the high-pressure phase cristobalite-II at 1.5 GPa and further to cristobalite X-I at 10 GPa.$^7-10$ Reference 6 ascribes this contradiction to “the effect of non-hydrostaticity of pressure on the crystal lattice of minerals”. However, the pressurization of cristobalite in the helium atmosphere revealed a stepwise increase in its cell parameters at $P = 8$ GPa that was associated with the dissolved helium atoms.$^{11}$ Taking into account similar sizes of the helium atom and hydrogen molecule, we conclude that hydrogen is likely to dissolve in cristobalite, too.$^{12}$

In the present work, an isotherm of the hydrogen solubility in cristobalite at a temperature of 250 $\degree C$ and hydrogen pressures up to 90 kbar is constructed using a quenching technique. Each sample of cristobalite loaded with hydrogen at a given pressure was then rapidly cooled (quenched) to the N$_2$ boiling temperature and only warmed above this temperature when its hydrogen content was measured by hot extraction in vacuum. The hydrogenated cristobalite samples and, for comparison, samples exposed to the same pressure and temperature in Teflon as the pressure transmitting medium were studied by X-ray diffraction and Raman spectroscopy at ambient pressure and N$_2$ temperature.

EXPERIMENTAL METHODS

Powder of cristobalite with a grain size of 5–10 $\mu$m was prepared at the Institute of Silicate Chemistry RAS by annealing a silica glass. An X-ray examination showed that the powder consisted of the tetragonal cristobalite-I phase (space group $P4_12_12_1$, cell parameters $a = 4.9738$ Å and $c = 74.6973$ Å) without any impurities. A batch of this silica powder weighing about 100 mg was placed into a copper capsule and...
Figure 1. Thermal desorption curves of SiO$_2$–H$_2$ samples quenched from different synthesis pressures. The curves are labeled by the pressures of the sample synthesis and the H$_2$/SiO$_2$ molar ratio. The increase in the H$_2$/SiO$_2$ ratio at $T > 500$ °C is mostly due to the evolved water and other species (see text).

Figure 2. Pressure dependence of the mean hydrogen content of cristobalite at 250 °C. The open circles show the experimental data; the solid line is a guide for the eyes.

### RESULTS AND DISCUSSION

The curves depicted in Figure 1 are calculated assuming that the gas evolved from the samples is molecular hydrogen. As seen from the figure, the most intense hydrogen release from all samples occurs at temperatures from $-187$ to $+25$ °C similar to the case of hydrogenated silica glass. The amount of the emitted gas nearly does not change on heating from 100–150 to 500 °C, and then the rate of the gas release increases again. After the samples are heated to 650 °C, the evolved gas is cooled to the liquid nitrogen temperature and its pressure proves to be slightly less than the value calculated from the pressure at 650 °C. The difference corresponds to $\Delta X \approx 0.005$–0.015.

This suggests that the gas evolved from the samples should contain some other species (presumably, water) along with the H$_2$ molecules and these species are frozen out at the N$_2$ temperature.

The open circles in Figure 2 show the mean hydrogen content $X = H_2/\text{SiO}_2$ of the cristobalite samples as a function of the pressure of synthesis. As seen from Figure 1, the hydrogen solubility in cristobalite increases from $X \approx 0.03$ at $P = 14$ kbar to $X \approx 0.1$ at $P = 90$ kbar.

It should be noted, however, that the results for higher pressures show the lower limit of the hydrogen solubility in the samples rather than the equilibrium solubility. As seen from Figure 1, the thermal stability of the quenched samples decreases with increasing synthesis pressure, and the samples synthesized at 50 and 90 kbar obviously start losing the hydrogen at temperatures below the quenching temperature of $-196$ °C. Particularly, due to these hydrogen losses, the amount of hydrogen that remained in the sample prepared at 90 kbar proved to be smaller than in the sample synthesized at 75 kbar.

Figure 3 shows diffraction patterns of the cristobalite sample loaded with hydrogen to $X = 0.122$ at a hydrogen pressure of 75 kbar and $T = 250$ °C and also the sample exposed to the same pressure and temperature without hydrogen (in Teflon as the pressure transmitting medium). Both these samples were quenched under pressure to the N$_2$ temperature and examined by X-ray diffraction at a somewhat higher temperature of 85 K = $-188$ °C. Most diffraction lines of these quenched samples are attributed to the initial tetragonal cristobalite-I phase and to...
180 structure due to the pressure-induced changes in the positional
178 cristobalite-II phase whose swelling at decreasing pressure
177 reproduced. These peaks are likely to belong to the quenched
176 few peaks and particularly those at 38°
175 cristobalite-II phases. At the same time, the intensities of a
174 experimental pattern for the mixed cristobalite-I and
173 Figure 3, this allows an overall satisfactory description of the
172 kbar.7 As seen from the di
171 such a phase in the equilibrium state at pressures above 15
170 in the unit cell were the same as those determined earlier for
169 under the constraint that the positional parameters of atoms
168 ambient pressure before. We re
167 The cristobalite-II phase has never been recovered to
166 it was being loaded into the X-ray cryostat.
164 di
163 pressure. Three additional weak lines at 23°
161 the monoclinic high-pressure phase cristobalite-II7,8,10 with the
160 lattice parameters reasonably increased due to the decrease in
159 pressure. Three additional weak lines at 23°, 26°, and 34° in the
158 di
157 the diffraction pattern of the hydrogenated sample belong to the
156 hexagonal ice Ih that condensed onto the sample surface while
155 it was being loaded into the X-ray cryostat.
154 The cristobalite-II phase has never been recovered to
153 ambient pressure before. We refined its crystal structure
152 under the constraint that the positional parameters of atoms
151 in the unit cell were the same as those determined earlier for
150 such a phase in the equilibrium state at pressures above 15
149 kbar.7 As seen from the difference spectrum at the bottom of
148 Figure 3, this allows an overall satisfactory description of the
147 experimental pattern for the mixed cristobalite-I and
146 cristobalite-II phases. At the same time, the intensities of a
145 few peaks and particularly those at 38° and 50° are not
144 reproduced. These peaks are likely to belong to the quenched
143 cristobalite-II phase whose swelling at decreasing pressure
142 should be accompanied by distortions of the complex crystal
141 structure due to the pressure-induced changes in the positional
140 parameters of atoms in the unit cell. The available X-ray data
139 are not, however, sufficient to prove this conjecture because the
138 fraction of the cristobalite-II phase in the samples is small (less
137 than 20%) and its diffraction lines overlap with the lines of the
136 cristobalite-I phase. To be on the safe side, we will further call
135 this new phase a “cristobalite-II-like” phase.
134 Results of profile analysis of X-ray diffraction patterns of the
133 quenched samples examined in the present paper are
132 summarized in Table 1.
131 As seen from Table 1, the fraction of the cristobalite-II-like
130 phase in all samples exposed to \( P \geq 28 \) kbar is about 20% and
129 does not show clear pressure dependence. The unit cell volume
128 of the cristobalite-I phase in the hydrogenated samples
127 synthesized at 28 and 75 kbar is larger by 0.26 and 0.61 \( \text{Å}^3 \)
126 respectively, than that for the samples exposed to the same
125 pressure and temperature in Teflon. These values considerably
124 exceed the uncertainty \( \pm 0.02 \text{Å}^3 \) in the determination of the
123 unit cell volume for cristobalite-I and therefore evidence the
122 lattice expansion due to the penetration of hydrogen molecules
121 in the cristobalite-I crystal structure.
120 It is also seen from Table 1 that the hydrogen-induced lattice
119 expansion of the cristobalite-II-like phase is small and does not
118 exceed the experimental error. At the same time, the results of
117 Raman spectroscopy suggest that the lattices of the quenched
116 cristobalite-I and cristobalite-II-like phases should be expanded
115 similarly (see next section). Note in this connection that the
114 Raman spectra are measured at 77 K (from the samples
113 immersed in liquid nitrogen), whereas the X-ray patterns are
112 collected at a higher temperature of 85 K = \( \lesssim 188 \) °C. As seen
111 from Figure 1, most quenched samples liberated a noticeable
110 amount of hydrogen even on heating to this temperature at a
109 rate of 20 °C/min and should therefore have lost much more
108 hydrogen in the course of the X-ray measurements having taken
107 a few hours. Being considered together, the Raman and X-ray
106 data suggest that the quenched cristobalite-I and cristobalite-II-
105 like phases should have had similar \( \text{H}_2 \) concentrations at 77 K, but the less stable cristobalite-II-like phase further lost nearly all
104 hydrogen at 85 K.
103 It is very likely that the cristobalite-I phase also lost a
102 considerable amount of hydrogen on heating from 77 to 85 K. Particularly, as seen from Table 1, the unit cell volume 42.48 \( \text{Å}^3 \)
101

Table 1. X-ray Results for the Quenched Samples

<table>
<thead>
<tr>
<th></th>
<th>28°</th>
<th>75°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{H}_2 )</td>
<td>Teflon</td>
<td>( \text{H}_2 )</td>
</tr>
<tr>
<td>molar ratio ( \text{H}_2/\text{SiO}_2 )</td>
<td>0.063</td>
<td>0.122</td>
<td>0.093</td>
</tr>
<tr>
<td>cristobalite-I ( \text{P}_4\text{I}_2/2\text{c} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a, \text{Å} )</td>
<td>4.965(1)</td>
<td>4.957(1)</td>
<td>4.973(1)</td>
</tr>
<tr>
<td>( c, \text{Å} )</td>
<td>6.922(2)</td>
<td>6.902(2)</td>
<td>6.966(2)</td>
</tr>
<tr>
<td>( V, \text{Å}^3 )</td>
<td>42.66(2)</td>
<td>42.40(2)</td>
<td>43.07(2)</td>
</tr>
<tr>
<td>( V_{\text{cristobalite-II}} - V_{\text{Teflon}} \text{Å}^3 )</td>
<td>0.26(3)</td>
<td>0.61(3)</td>
<td></td>
</tr>
<tr>
<td>cristobalite-II-like phase ( \text{P}_2_1/c )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a, \text{Å} )</td>
<td>8.49(2)</td>
<td>8.32(2)</td>
<td>8.38(2)</td>
</tr>
<tr>
<td>( b, \text{Å} )</td>
<td>4.72(1)</td>
<td>5.01(1)</td>
<td>4.98(1)</td>
</tr>
<tr>
<td>( c, \text{Å} )</td>
<td>9.80(2)</td>
<td>9.77(2)</td>
<td>9.84(2)</td>
</tr>
<tr>
<td>( \beta, \degree )</td>
<td>123.6</td>
<td>124.3</td>
<td>123.8</td>
</tr>
<tr>
<td>( V, \text{Å}^3 )</td>
<td>42.4(2)</td>
<td>42.4(2)</td>
<td>42.7(2)</td>
</tr>
<tr>
<td>( V_{\text{cristobalite-II}} - V_{\text{Teflon}} \text{Å}^3 )</td>
<td>0.0(3)</td>
<td>0.3(3)</td>
<td></td>
</tr>
<tr>
<td>phase ratio Cris I/Cris II</td>
<td>80/20</td>
<td>85/15</td>
<td>78/22</td>
</tr>
</tbody>
</table>

\( ^{\text{a}}P, \text{kbar.} \) \( ^{\text{b}}\text{Samples synthesized in a hydrogen atmosphere.} \) \( ^{\text{c}}\text{Samples exposed to the same pressure and temperature using Teflon as the pressure transmitting medium.} \) \( ^{\text{d}}V \) is the volume per the formula unit (\text{SiO}_2) of cristobalite
of this phase in the most unstable 90 kbar sample is less than that of 43.07 Å³ in the 75 kbar sample and even less than 42.66 Å³ in the 28 kbar sample.

RAMAN SPECTROSCOPY

Figure 4 shows Raman spectra of the initial powder of cristobalite-I (Figure 4A) and the samples exposed to $P = 75$ kbar and $T = 250$ °C in a hydrogen atmosphere (C) and in Teflon (B). The inset in panel C shows the peak of the stretching vibrations of the H₂ molecules dissolved in cristobalite. All measurements were performed at ambient pressure on the samples submerged in liquid nitrogen.

Table 2. Raman Shift Data (cm⁻¹) for the Quenched Samples

<table>
<thead>
<tr>
<th>$\text{cm}^{-1}$</th>
<th>initial sample</th>
<th>pressurized sample</th>
<th>hydrogenated sample</th>
<th>phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>196</td>
<td>192.6</td>
<td>cristobalite-II-like</td>
<td></td>
</tr>
<tr>
<td>230.7</td>
<td>232.0</td>
<td>229.9</td>
<td>cristobalite-I</td>
<td></td>
</tr>
<tr>
<td>276.2</td>
<td>272.6</td>
<td>223.4</td>
<td>cristobalite-I</td>
<td></td>
</tr>
<tr>
<td>287.6</td>
<td>283.7</td>
<td>223.4</td>
<td>cristobalite-I</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>297</td>
<td>298</td>
<td>cristobalite-II-like</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>323</td>
<td>314</td>
<td>cristobalite-II-like</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>338.4</td>
<td>334.8</td>
<td>cristobalite-II-like</td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>408.6</td>
<td>404.06</td>
<td>hydrogen</td>
<td></td>
</tr>
<tr>
<td>419.9</td>
<td>422.9</td>
<td>421.5</td>
<td>cristobalite-I</td>
<td></td>
</tr>
<tr>
<td>430</td>
<td>437.9</td>
<td>434.7</td>
<td>cristobalite-II-like</td>
<td></td>
</tr>
<tr>
<td>470</td>
<td></td>
<td></td>
<td>cristobalite-II-like</td>
<td></td>
</tr>
<tr>
<td>586</td>
<td>781.8</td>
<td>585.3</td>
<td>hydrogen</td>
<td></td>
</tr>
<tr>
<td>793.4</td>
<td>794.8</td>
<td>777.1</td>
<td>cristobalite-I</td>
<td></td>
</tr>
</tbody>
</table>

*Data for cristobalite-II and cristobalite-I extrapolated from $P = 2$ kbar to ambient pressure in ref 10 and data of ref 12 for gaseous hydrogen at $P = 30$ bar and room temperature. *Our data for the initial sample of cristobalite-I. *Sample exposed to $P = 75$ kbar and $T = 250$ °C using Teflon as the pressure transmitting medium. *Sample synthesized in a hydrogen atmosphere at $P = 75$ kbar and $T = 250$ °C.

Figure 4. Raman spectra of the starting powder of cristobalite-I (A) and of the powder exposed to $P = 75$ kbar and $T = 250$ °C in a hydrogen atmosphere (C) and in Teflon (B). The inset in panel C shows the peak of the stretching vibrations of the H₂ molecules dissolved in cristobalite. All measurements were performed at ambient pressure on the samples submerged in liquid nitrogen.
H₂ molecules in cristobalite. This can be understood assuming that the hydrogen molecules occupying voids in the cristobalite lattice are squeezed in one direction. No lines attributable to O−H or Si−H stretching vibrations are observed in the measured Raman spectra. This suggests that the concentration of these species in the quenched samples should not exceed the detection limit of 2−3 mol % of the spectroscopic technique used. Such an estimate agrees with results of our thermal desorption experiments described above.

## CONCLUSIONS

Our investigations thus demonstrated that hydrogen can dissolve in cristobalite under high pressure and its solubility reaches a molar ratio of H₂/SiO₂ ~ 0.1 at P = 90 kbar. The X-ray diffraction study showed that the quenched samples were composed of approximately 80% cristobalite-I and 20% cristobalite-II-like phases. Also, the X-ray diffraction revealed a hydrogen-induced expansion of the cristobalite-I phase unit cell volume by 0.26 and 0.61 Å³, respectively, in the samples hydrogenated at P = 28 and 75 kbar. The Raman spectroscopy showed that the hydrogen-induced lattice expansion occurred in both cristobalite-I and cristobalite-II-like phases and that hydrogen is dissolved in these phases mostly in the form of H₂ molecules weakly interacting with the silica structure.

## REFERENCES


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### Notes

The authors declare no competing financial interest.

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