

Hydrogen Solubility in Cristobalite at High Pressure

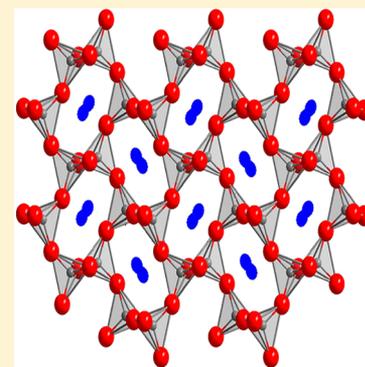
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ABSTRACT: Powder samples of cristobalite-I are loaded with hydrogen at pressures up to 90 kbar and $T = 250$ °C and quenched under pressure to the liquid N_2 temperature. The quenched samples are examined at ambient pressure by X-ray diffraction, Raman 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 °C.⁴ In cooling below 250 °C, this phase undergoes a reversible transition to the tetragonal phase cristobalite-I with the space group $P4_12_12$.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-transmit-

ting 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.

In the present work, an isotherm of the hydrogen solubility in cristobalite at a temperature of 250 °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 μm 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 $P4_12_12$, cell parameters $a = 4.9738$ Å and $c =$

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6.9373 Å) without any impurities. A batch of this silica powder weighing about 100 mg was placed into a copper capsule and covered with a disk of 0.01 mm Pd foil. The space remaining in the capsule was filled with aminoborane (NH_3BH_3), and the capsule was placed in the working zone of a toroid-type high-pressure chamber. The aminoborane was decomposed under a pressure of 10–15 kbar by heating it to 100–250 °C. The evolved hydrogen reacted with the cristobalite after permeating through the palladium foil, which prevented the cristobalite and aminoborane from mixing. The sample was exposed to an atmosphere of gaseous hydrogen at pressures from 14 to 90 kbar and $T = 250$ °C for 24 h. The hydrogen was always in excess. After the hydrogenation was complete, the high-pressure chamber was cooled to -196 °C to minimize the hydrogen losses in the course of further pressure release. When not in use, the samples thus prepared were stored in liquid nitrogen.

The hydrogen content of the $\text{SiO}_2\text{-H}_2$ samples was determined by hot extraction into a pre-evacuated volume in the course of heating to 500 °C at a rate of 20 °C/min. The sample was heated to 650 °C to complete the liberation of the gas and then cooled together with the released gas to the liquid nitrogen temperature to freeze out the gas components other than H_2 . The residue pressure in the measuring system was used to calculate the hydrogen content of the sample.

The Raman spectra from the quenched and initial samples were recorded in backscattering geometry using a micro-Raman setup composed of an Acton SpectraPro-2500i spectrograph and a CCD Pixis2K detector system cooled down to -70 °C. The measurements were performed near the liquid nitrogen temperature and in the spectral range from 140 to 4500 cm^{-1} . The 532 nm line of a single mode YAG CW diode pumped laser was focused on the sample by an Olympus 10× objective in an ~ 10 μm diameter spot that was slightly defocused due to light refraction in boiling nitrogen. Thus, the spatial resolution was about 10 μm whereas the spectral resolution varied between 2.1 and 3.7 cm^{-1} . The laser line was suppressed by a SuperNotch filter with the optical density $\text{OD} = 6$ and bandwidth ~ 160 cm^{-1} , while the beam intensity before the sample was ~ 20 mW.

The quenched samples were also studied by powder X-ray diffraction at ambient pressure and 85 K using a Siemens D500 diffractometer equipped with a home-designed nitrogen cryostat that permitted loading the powder samples without their intermediate warming.

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.² 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 N_2 temperature and its pressure proves to be slightly less than the value calculated from the pressure at 650 °C. The difference corresponds to $\Delta X \approx 0.005\text{--}0.015$. 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.

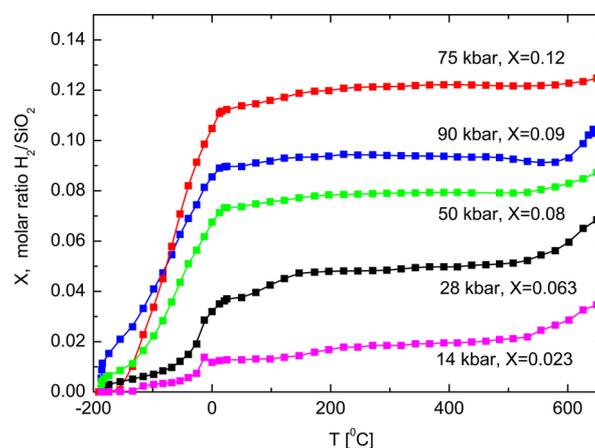


Figure 1. Thermal desorption curves of $\text{SiO}_2\text{-H}_2$ samples quenched from different synthesis pressures. The curves are labeled by the pressures of the sample synthesis and the H_2/SiO_2 molar ratio. The increase in the H_2/SiO_2 ratio at $T > 500$ °C is mostly due to the evolved water and other species (see text).

The open circles in Figure 2 show the mean hydrogen content $X = \text{H}_2/\text{SiO}_2$ of the cristobalite samples as a function of

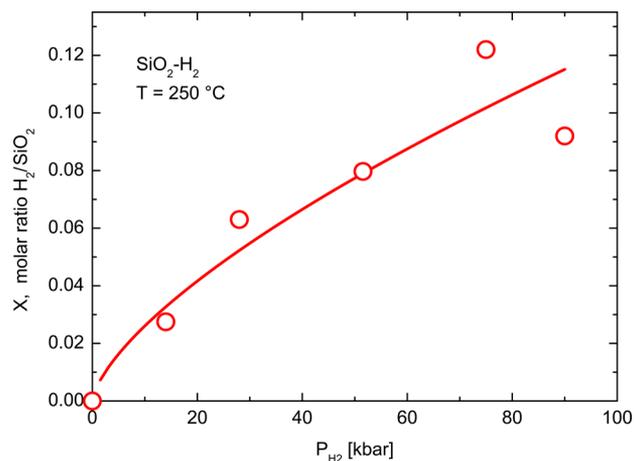


Figure 2. Pressure dependence of the mean hydrogen content of cristobalite at 250 °C. The open circles show the experimental data; the solid line is a guide for the eyes.

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

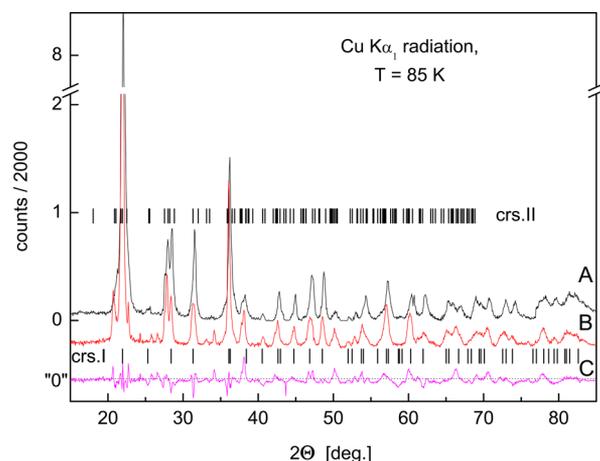


Figure 3. X-ray diffraction patterns of the cristobalite samples exposed to $P = 75$ kbar and $T = 250$ °C in a hydrogen atmosphere (B) and in Teflon (A). Cu $K\alpha_1$ radiation, ambient pressure, $T = 85$ K. Line C is the difference between B and the calculated profile fit.

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 the monoclinic high-pressure phase cristobalite-II^{7,8,10} with the lattice parameters reasonably increased due to the decrease in pressure. Three additional weak lines at 23° , 26° , and 34° in the diffraction pattern of the hydrogenated sample belong to the hexagonal ice Ih that condensed onto the sample surface while it was being loaded into the X-ray cryostat.

The cristobalite-II phase has never been recovered to ambient pressure before. We refined its crystal structure under the constraint that the positional parameters of atoms in the unit cell were the same as those determined earlier for such a phase in the equilibrium state at pressures above 15 kbar.⁷ As seen from the difference spectrum at the bottom of Figure 3, this allows an overall satisfactory description of the experimental pattern for the mixed cristobalite-I and cristobalite-II phases. At the same time, the intensities of a few peaks and particularly those at 38° and 50° are not

reproduced. These peaks are likely to belong to the quenched cristobalite-II phase whose swelling at decreasing pressure should be accompanied by distortions of the complex crystal structure due to the pressure-induced changes in the positional parameters of atoms in the unit cell. The available X-ray data are not, however, sufficient to prove this conjecture because the fraction of the cristobalite-II phase in the samples is small (less than 20%) and its diffraction lines overlap with the lines of the cristobalite-I phase. To be on the safe side, we will further call this new phase a “cristobalite-II-like” phase.

Results of profile analysis of X-ray diffraction patterns of the quenched samples examined in the present paper are summarized in Table 1.

As seen from Table 1, the fraction of the cristobalite-II-like phase in all samples exposed to $P \geq 28$ kbar is about 20% and does not show clear pressure dependence. The unit cell volume of the cristobalite-I phase in the hydrogenated samples synthesized at 28 and 75 kbar is larger by 0.26 and 0.61 Å³, respectively, than that for the samples exposed to the same pressure and temperature in Teflon. These values considerably exceed the uncertainty ± 0.02 Å³ in the determination of the unit cell volume for cristobalite-I and therefore evidence the lattice expansion due to the penetration of hydrogen molecules in the cristobalite-I crystal structure.

It is also seen from Table 1 that the hydrogen-induced lattice expansion of the cristobalite-II-like phase is small and does not exceed the experimental error. At the same time, the results of Raman spectroscopy suggest that the lattices of the quenched cristobalite-I and cristobalite-II-like phases should be expanded similarly (see next section). Note in this connection that the Raman spectra are measured at 77 K (from the samples immersed in liquid nitrogen), whereas the X-ray patterns are collected at a higher temperature of 85 K = -188 °C. As seen from Figure 1, most quenched samples liberated a noticeable amount of hydrogen even on heating to this temperature at a rate of 20 °C/min and should therefore have lost much more hydrogen in the course of the X-ray measurements having taken a few hours. Being considered together, the Raman and X-ray data suggest that the quenched cristobalite-I and cristobalite-II-like phases should have had similar H_2 concentrations at 77 K,

Table 1. X-ray Results for the Quenched Samples

	28 ^a		75 ^a		90 ^a
	H_2 ^b	Teflon ^c	H_2	Teflon	H_2
molar ratio H_2/SiO_2	0.063		0.122		0.093
cristobalite-I $P4_12_12$					
a , Å	4.965(1)	4.957(1)	4.973(1)	4.958(2)	4.959(1)
c , Å	6.922(2)	6.902(2)	6.966(2)	6.908(4)	6.901(2)
V , Å ³ ^d	42.66(2)	42.40(2)	43.07(2)	42.46(4)	42.48(2)
$V_H - V_{Teflon}$, Å ³	0.26(3)		0.61(3)		
cristobalite-II-like phase $P2_1/c$					
a , Å	8.49(2)	8.32(2)	8.38(2)	8.38(2)	8.43(2)
b , Å	4.72(1)	5.01(1)	4.98(1)	5.02(1)	4.95(1)
c , Å	9.80(2)	9.77(2)	9.84(2)	9.89(2)	9.71(3)
β , deg	123.6	124.3	123.8	125.5	124.6
V , Å ³	42.4(2)	42.4(2)	42.7(2)	42.4(2)	41.7(2)
$V_H - V_{Teflon}$, Å ³	0.0(3)		0.3(3)		
phase ratio Cris I/Cris II	80/20	85/15	78/22	84/16	76/24

^a P , kbar. ^bSamples synthesized in a hydrogen atmosphere. ^cSamples exposed to the same pressure and temperature using Teflon as the pressure transmitting medium. ^d V is the volume per the formula unit (SiO_2) of cristobalite

but the less stable cristobalite-II-like phase further lost nearly all hydrogen at 85 K.

It is very likely that the cristobalite-I phase also lost a considerable amount of hydrogen on heating from 77 to 85 K. Particularly, as seen from Table 1, the unit cell volume 42.48 \AA^3 of this phase in the most unstable 90 kbar sample is less than that of 43.07 \AA^3 in the 75 kbar sample and even less than 42.66 \AA^3 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 $P = 75$

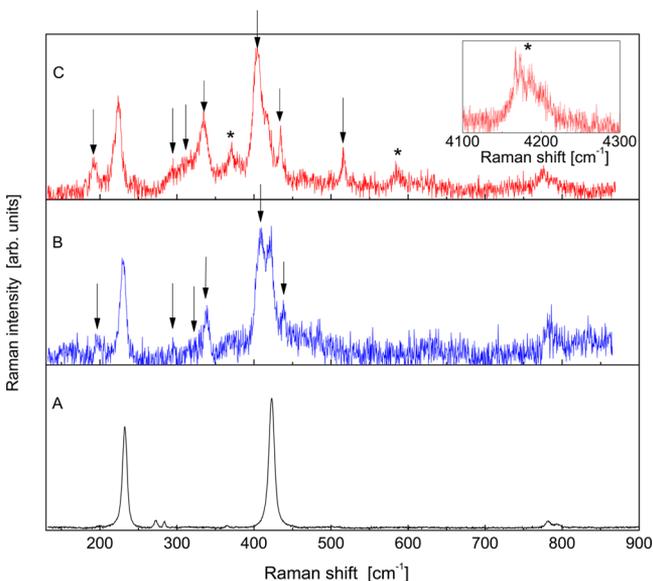


Figure 4. Raman spectra of the starting powder of cristobalite-I (A) and of the powder exposed to $P = 75$ kbar and $T = 250 \text{ }^\circ\text{C}$ in a hydrogen atmosphere (C) and in Teflon (B). The inset in panel C shows the peak of the stretching vibrations of the H_2 molecules dissolved in cristobalite. All measurements were performed at ambient pressure on the samples submerged in liquid nitrogen.

kbar and $T = 250 \text{ }^\circ\text{C}$ in a hydrogen atmosphere (Figure 4C) and in Teflon (Figure 4B). The lines at 232, 422.9, and 781.8 cm^{-1} in spectrum A correspond to vibration frequencies of the tetragonal cristobalite-I. The additional lines in spectra B and C indicated by the arrows can be attributed to the cristobalite-II phase studied earlier by Raman spectroscopy under high pressure.¹⁰ Table 2 lists the frequencies of the vibration modes observed in the present work and compares them with the earlier results.^{10,12}

As seen from Table 2, the lines at 232.0 and 422.9 cm^{-1} in the spectrum of the cristobalite-I phase in our initial sample (column 2) are shifted to higher frequencies compared to those measured in ref 10 (column 1), while the lines at 272.6 and 283.7 cm^{-1} are shifted to lower frequencies. This is because of the different measuring temperatures, 77 and 295 K, in these papers and the different temperature dependences of the frequencies of the lines. Namely, the Grüneisen parameter (γ) is positive for the first pair of lines and negative for the second pair,¹⁰ so the frequencies of the first two lines should increase with decreasing temperature, whereas the frequencies of the second two lines should decrease.

Positions of most other lines in the samples pressurized in Teflon (column 3) and in hydrogen (column 4) agree with

Table 2. Raman Shift Data (cm^{-1}) for the Quenched Samples

lit. ^a	initial sample ^b	pressurized sample ^c	hydrogenated sample ^d	phase
200		196	192.6	cristobalite-II-like
230.7	232.0	229.9	223.4	cristobalite-I
276.2	272.6			cristobalite-I
287.6	283.7			cristobalite-I
300		297	298	cristobalite-II-like
310		323	314	cristobalite-II-like
350		338.4	334.8	cristobalite-II-like
353			371.8	hydrogen
		408.6	404.06	cristobalite-II-like
419.9	422.9	421.5	417.6	cristobalite-I
430		437.9	434.7	cristobalite-II-like
470				cristobalite-II-like
			516	cristobalite-II-like
586			585.3	hydrogen
	781.8	784.8	777.1	cristobalite-I
	793.4			cristobalite-I

^aData 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. ^bOur data for the initial sample of cristobalite-I. ^cSample exposed to $P = 75$ kbar and $T = 250 \text{ }^\circ\text{C}$ using Teflon as the pressure transmitting medium. ^dSample synthesized in a hydrogen atmosphere at $P = 75$ kbar and $T = 250 \text{ }^\circ\text{C}$.

results of ref 10 (column 1) for the cristobalite-II phase and can therefore be attributed to similar vibrational modes in the cristobalite-II-like phase. The exceptions are the new lines at 408.6 and 404.06 cm^{-1} (columns 3 and 4, respectively) and at 516 cm^{-1} (column 4), which have no analogues in the cristobalite-II spectrum measured at high pressure.¹⁰ These lines can nevertheless belong to the quenched cristobalite-II-like phase, because its crystal structure is likely to have lower symmetry than the structure of the high-pressure cristobalite-II phase (see the previous section), and the lower symmetry will give rise to additional vibrational modes.

All lines of the cristobalite-I and cristobalite-II-like phases in the spectrum of the hydrogenated sample (column 4) are shifted by a few cm^{-1} to lower frequencies compared with those for the sample pressurized in Teflon without hydrogen (column 3). These shifts are indicative of the hydrogen-induced expansion of the crystal lattices of both cristobalite-I and cristobalite-II-like phases in the hydrogenated sample. The lattice expansion of the cristobalite-I phase is confirmed by X-ray diffraction (see Table 1). In the case of the cristobalite-II-like phase, the accuracy of the X-ray data is insufficient to estimate the lattice expansion. Nevertheless, a similar lowering of the Raman frequencies in the cristobalite-I and cristobalite-II-like phase suggests a similar lattice expansion of these phases.

The Raman spectrum of the hydrogenated sample also contains lines at 371.8 , 585.3 , and 4167 cm^{-1} labeled by asterisks in Figure 4C. Figure 5 compares this spectrum with that of a H_2 gas.¹² As one can see, the lines at 371.8 and 585.3 cm^{-1} are close to the lines of two rotational modes ($S(0)$ at 353 cm^{-1} and $S(1)$ at 586 cm^{-1}) and one stretching mode ($Q(0)$ at

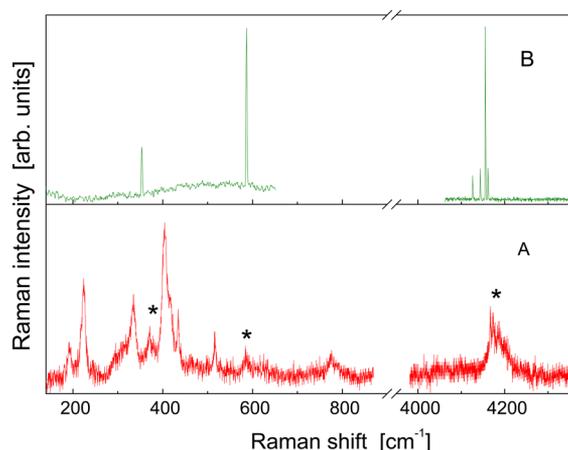


Figure 5. Raman spectrum of the cristobalite powder exposed to $P = 75$ kbar and $T = 250$ °C in a hydrogen atmosphere (A) and the spectrum of a hydrogen gas at $P = 30$ bar (B) measured in ref 12.

4155 cm^{-1}) of free H_2 molecules. This shows that hydrogen dissolves in cristobalite in the molecular form. It is noteworthy that the frequency of the S(1) mode is virtually the same for the H_2 molecules in cristobalite and in the gas, while the frequencies of the S(0) and Q(0) modes are higher for the H_2 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 $\text{H}_2/\text{SiO}_2 \sim 0.1$ 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 \AA^3 , 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 H_2 molecules weakly interacting with the silica structure.

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Notes

The authors declare no competing financial interest.

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