

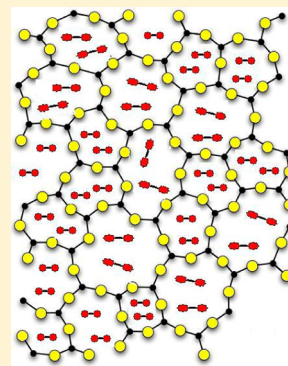
# Hydrogen Solubility in Amorphous Silica at Pressures up to 75 kbar

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**ABSTRACT:** The solubility of hydrogen in amorphous silica at a temperature of 250 °C and pressures up to 75 kbar is studied using a quenching technique. The molar ratio  $H_2/SiO_2$  is found to linearly increase with pressure from  $X = 0.16$  at  $P = 6$  kbar to  $X = 0.53$  at  $P = 75$  kbar. An investigation of a sample with  $X = 0.47$  by Raman spectroscopy demonstrated that hydrogen dissolves in silica in the form of  $H_2$  molecules, and these molecules occupy voids of, at least, two different types in the silica network. An X-ray diffraction study showed that the hydrogen molecules penetrating in the silica glass network prevented its irreversible densification occurring if the silica glass is compressed to the same pressure without hydrogen.



## INTRODUCTION

According to the most widely accepted model,<sup>1,2</sup> all planets of the solar system were formed and evolved from a presolar nebula containing silica dust and molecular hydrogen. In the course of formation of the planetesimals, the hydrogen and other nebula gases could be trapped by the silica and further play a key role in forming the terrestrial and giant planets.<sup>1,2</sup> In all cases, the  $SiO_2-H_2$  phases, if formed, could only exist at high pressures because the hydrogen solubility in silica is very low under ambient conditions. Despite the importance of the problem for geosciences and planetary science, very little is yet known about the high-pressure  $H_2$  solubility in any of the crystalline and amorphous modifications of silica. One of the first investigations of the  $SiO_2-H_2$  system at high pressure was performed by Hartwig in 1975.<sup>3</sup> Using Raman scattering, he determined the pressure dependence of the hydrogen and deuterium solubility in the vitreous silica at a temperature of 90 °C and pressures up to 850 bar. In 1977, Shelby<sup>4</sup> measured the hydrogen and deuterium solubility in different types of vitreous silica at pressures up to 850 bar and temperatures 0–800 °C using a volumetric technique. He also offered a model for calculating the solubility as a function of pressure and temperature. The experimental values of  $H_2/SiO_2 = 0.03$  at  $T = 90$  °C and the maximum pressure of  $P = 850$  bar were the same in both papers.<sup>3,4</sup>

FTIR studies of the reaction of silica with water at high pressures and temperatures ( $P = 10$ –30 kbar,  $T = 1100$ –1250 °C) by Tomozawa et al.<sup>5</sup> detected observable quantities of hydroxyl and hydride dissolved in the silica glass. The authors conjectured that the dissolved hydrogen was produced in the chemical reaction of water and graphite in the measuring cell and further diffused in the silica. Regrettably, the quantity of the dissolved hydrogen was not determined.

Recently, a high helium solubility in silica glass was discovered by two research groups at pressures up to 90 kbar<sup>6</sup> and 500 kbar.<sup>7</sup> The solubility of helium at  $P = 90$  kbar was estimated to be as high as  $He/SiO_2 = 1$  to 2.<sup>6</sup> Taking into account that the effective diameters of the helium atom and hydrogen molecule do not differ much (their so-called kinetic diameters are  $\sim 2.6$  and  $\sim 2.9$  Å,<sup>8</sup> respectively), one could expect that the hydrogen solubility in amorphous silica at 75 kbar should also be high.

In the present work, an isotherm of the hydrogen solubility in amorphous silica at a temperature of 250 °C and hydrogen pressures from 6 to 75 kbar is constructed using a quenching technique. Each sample of silica glass 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 quenched samples were studied by X-ray diffraction and Raman spectroscopy at ambient pressure and  $N_2$  temperature.

## EXPERIMENTAL METHODS

Powder of amorphous silica with a grain size of 5–10  $\mu m$  was purchased from Sigma-Aldrich. The powder was preliminary annealed at 900 °C for 4 h to remove hydroxyls and water. Batches of this silica powder weighing about 100 mg each were exposed to an atmosphere of gaseous hydrogen at  $P = 6$ –75 kbar and  $T = 250$  °C for 30 min. (Preliminary experiments at 75 kbar showed that an increase in the exposure time from 30 min to 1 and 2 h did not increase the hydrogen content of the

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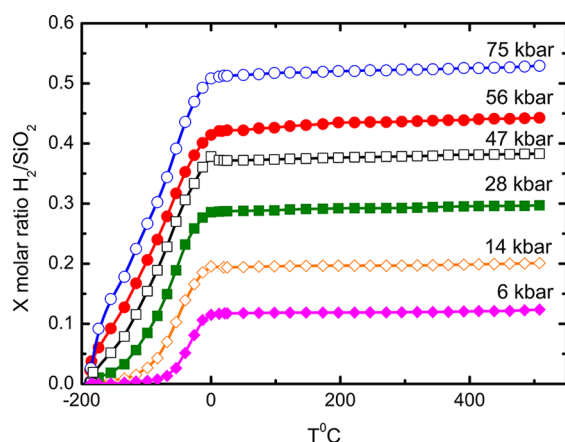
samples.) The hydrogen was produced by thermal decomposition of aminoborane ( $\text{NH}_3\text{BH}_3$ ) used as an internal  $\text{H}_2$  source in the high-pressure cell. After the hydrogenation was complete, the batch was cooled to  $-196^\circ\text{C}$  to prevent the hydrogen losses in the course 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  $500^\circ\text{C}$  at a rate of  $20^\circ\text{C}/\text{min}$ . Raman scattering studies of the initial silica and the  $\text{SiO}_2\text{-H}_2$  sample with an  $\text{H}_2/\text{SiO}_2$  ratio of  $X = 0.47$  were performed with an EnSpectr Raman microscope. The microscope collects the spectra in a wide range of Raman shifts from  $485$  to  $4770\text{ cm}^{-1}$  with a resolution of  $6\text{ cm}^{-1}$ , and therefore it is a convenient tool for detecting all known molecules, with a high vibration frequency, which can be dissolved in silica. The light source was a DPSS laser operated at  $532\text{ nm}$ . The beam with a nominal power of  $8\text{ mW}$  was polarized and directed normal to the face of the sample submerged in liquid nitrogen. The scattered light was collected with the same lens in backscattering geometry and resolved by an EnSpectr 532 spectrometer (EnSpectr microscope).

The obtained  $\text{SiO}_2\text{-H}_2$  samples were also studied by powder X-ray diffraction at ambient pressure and  $80\text{ K}$  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

**Hydrogen Solubility in Amorphous Silica.** Figure 1 depicts thermal desorption curves of  $\text{SiO}_2\text{-H}_2$  samples

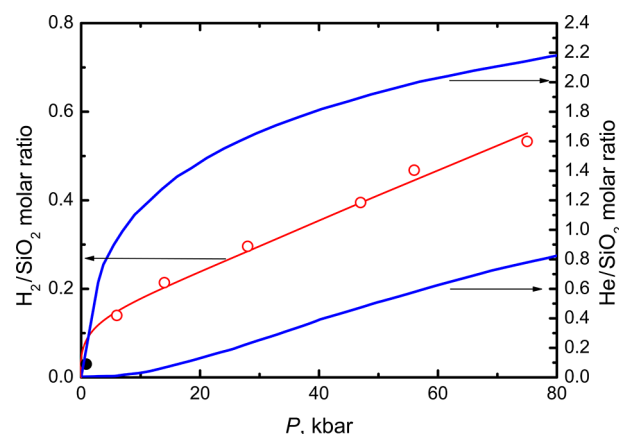


**Figure 1.** Thermal desorption curves of  $\text{SiO}_2\text{-H}_2$  samples quenched from different synthesis pressures. The curves are labeled by the pressures of the sample synthesis.

quenched from different synthesis pressures. The samples synthesized at minimal pressures (6 and 14 kbar) start evolving hydrogen at  $T = -174^\circ\text{C}$ . The desorption curves of these samples have a stepwise shape demonstrating the most intense hydrogen release at temperature from  $T = -116$  to  $-83^\circ\text{C}$  to  $+25^\circ\text{C}$ . The hydrogen release from the samples synthesized at maximal pressures (56 and 75 kbar) begins on heating above  $T = -187^\circ\text{C}$  and also ceases at room temperature. In whole, the curves in Figure 1 demonstrate a gradual decrease in the thermal stability of the  $\text{SiO}_2\text{-H}_2$  solid solutions with increasing

hydrogen concentration. Such an effect is typical of all metal hydrides and hydrogen clathrates.<sup>9,10</sup>

The open circles in Figure 2 show the hydrogen content  $X$  of the quenched  $\text{SiO}_2\text{-H}_2$  samples vs the pressure of synthesis. As



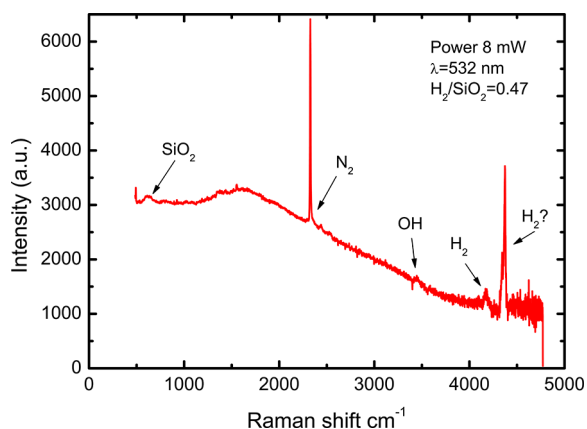
**Figure 2.** Pressure dependence of the hydrogen and helium solubility in silica glass. The red solid line fits the experimental points of hydrogen solubility (open circles) at a temperature of  $250^\circ\text{C}$ . The solid black circle indicates the hydrogen solubility at  $90^\circ\text{C}$  determined in ref 3. The solid blue lines show the upper and low boundaries of the helium solubility in silica glass estimated in ref 6.

seen from Figure 2, the hydrogen content of the samples approximately linearly increases with pressure from  $X = 0.16$  at  $P = 6\text{ kbar}$  to  $X = 0.53$  at  $P = 75\text{ kbar}$ . To meet the requirement that  $X = 0$  at  $P = 0$ , the red solid straight line fitting the experimental dependence at pressures from 6 to 75 kbar is smoothly turned downward at lower pressures. The solubility  $X = 0.05$  at a pressure of  $0.85\text{ kbar}$  read from this line is consistent with the maximal molar ratio  $X = 0.03$  at  $P = 0.85\text{ kbar}$  and  $T = 90^\circ\text{C}$  obtained by Hartwig<sup>3</sup> and shown by the solid circle.

The solid blue curves in Figure 2 represent the pressure dependences of the upper and lower limits on the helium solubility in silica glass estimated in ref 6 (the solubility was not measured experimentally). As one can see, the  $\text{He}/\text{SiO}_2$  ratio can reach as much as 0.8 to 2.2 at a helium pressure of 75 kbar. The conventional model of void-size distribution<sup>11</sup> predicts that in silica glass there are only about 0.1 voids per  $\text{SiO}_2$  formula unit accessible for He atoms with the kinetic diameter of  $\sim 2.6\text{ \AA}$ .<sup>12</sup> According to ref 6, a much larger number of He atoms can be "...continuously stacked in three-dimensionally connected voids, because voids in  $\text{SiO}_2$  glass may not be isolated...". The kinetic diameter of a  $\text{H}_2$  molecule equals  $\sim 2.9\text{ \AA}$ .<sup>8</sup> It is larger than the diameter of a He atom, and the hydrogen molecules can occupy a smaller number of about 0.05 voids per  $\text{SiO}_2$  unit (these are the voids inside the six-membered rings of silica).<sup>4</sup> Similar to the He atoms, most  $\text{H}_2$  molecules dissolved in silica glass under high pressure should therefore occupy the "connected voids" proposed in ref 6. This suggests that the  $\text{H}_2$  molecules in our  $\text{SiO}_2\text{-H}_2$  samples should have occupied the sites of, at least, two different types.

**Raman Spectroscopy.** A Raman spectrum collected from the sample synthesized at  $P = 56\text{ kbar}$  and  $T = 250^\circ\text{C}$  and having a molar ratio of  $\text{H}_2/\text{SiO}_2 = 0.47$  is shown in Figure 3. In the range of Raman shifts below  $\sim 4000\text{ cm}^{-1}$ , this spectrum virtually coincides with the spectrum of the initial silica glass:

- The peak at  $\sim 600\text{ cm}^{-1}$  labeled  $\text{D}_2$  is due to the breathing modes of the three-membered  $\text{SiO}_2$  rings;



**Figure 3.** Raman spectra of the  $\text{SiO}_2\text{-H}_2$  sample synthesized at  $P = 56$  kbar and  $T = 250$  °C.

other vibrational bands of  $\text{SiO}_2$  are not seen because of the strong background luminescence arising at the low measuring temperature of  $-196$  °C.

- The strong peak at  $2329\text{ cm}^{-1}$  is due to the stretching modes of  $\text{N}_2$  molecules in the  $\sim 50\text{ }\mu\text{m}$  layer of liquid nitrogen adjacent to the sample surface and located inside the focal spot of the laser beam.
- The weak peak at  $3442\text{ cm}^{-1}$  results from the OH stretching vibration modes. Such a peak was also observed in the Raman spectra of the initial  $\text{SiO}_2$  powder. The presence of this peak in the Raman spectra of the hydrogenated sample is therefore due to the incomplete removal of the hydroxyls and water from the initial silica glass by its preliminary annealing at  $650$  °C in air.

The peaks at  $4168$  and  $4374\text{ cm}^{-1}$  are only intrinsic to the spectrum of the hydrogenated silica. The peak at  $4168\text{ cm}^{-1}$  is close to the  $\text{Q}_1(0)$  peak at  $4161\text{ cm}^{-1}$  of the stretching modes of  $\text{H}_2$  molecules in a hydrogen gas.<sup>13</sup> A peak at a slightly lower frequency of  $4142\text{ cm}^{-1}$  was earlier observed in the Raman spectrum of hydrogenated amorphous silica with  $\text{H}_2/\text{SiO}_2 = 0.03$ , and it was ascribed to the vibrational modes of  $\text{H}_2$  molecules<sup>3</sup> occupying voids in the silica glass network and bind only weakly to the silica. At the same time, as was noticed in ref 3, the weak interactions of the  $\text{H}_2$  molecules with the walls of the voids restricted the rotational freedom of the molecules, so that no hydrogen rotational modes were seen in the Raman spectra. No peaks that could be attributed to  $\text{H}_2$  rotational modes are seen in the spectrum of our  $\text{SiO}_2\text{-H}_2$  sample with a much higher hydrogen content as well (Figure 3).

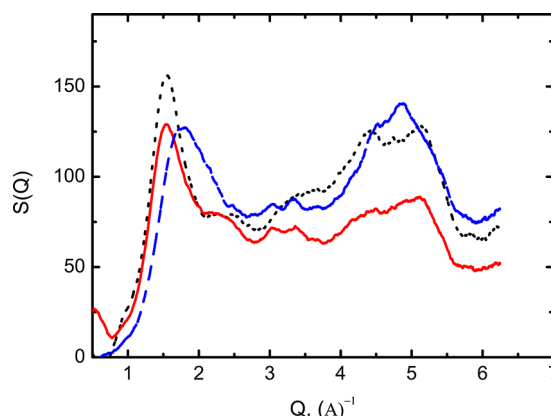
The strongest peak in Figure 3 is the peak at  $4374\text{ cm}^{-1}$ . Such a peak was not present in the Raman spectra of the samples of hydrogenated silica glass with  $\text{H}_2/\text{SiO}_2 \leq 0.03$  studied earlier,<sup>3</sup> and its frequency much exceeds the highest observed stretching frequency  $\sim 4280\text{ cm}^{-1}$  of the hydrogen molecule in solid hydrogen compressed to a pressure of 350 kbar at  $T = 5\text{ K}$ .<sup>14</sup> On the other hand, substances with resonance vibrations at  $4374\text{ cm}^{-1}$  are not known; therefore, we can only conjecture that the  $4374\text{ cm}^{-1}$  peak is due to the stretching vibrations of the  $\text{H}_2$  molecules occupying the voids other than those occupied by the molecules vibrating at  $4168\text{ cm}^{-1}$ . Presumably, these are the “connected voids” proposed in ref 6 in order to explain the large solubility of He in amorphous silica. The locations and shapes of the “connected voids” are

not yet identified, but they should obviously be smaller, at least, in some directions, than the largest individual voids that can only give room to the  $\text{H}_2$  molecules according to the standard model.<sup>4</sup> Consequently, the  $\text{H}_2$  molecules stacked in the “connected voids” should interact stronger with their walls that manifests itself in the increase in the  $\text{H}_2$  vibrational frequency.

On the basis of the said above, it is reasonable to assume that the peak at  $4168\text{ cm}^{-1}$  in Figure 3 corresponds to  $X_v \approx 0.05$  of the  $\text{H}_2$  molecules occupying the largest individual voids (mostly those inside the six-membered rings of silica),<sup>4</sup> while the peak at  $4374\text{ cm}^{-1}$  stems from the remaining  $X_{cv}$  molecules located in the “connected voids”. From the intensity ratio  $I_{4374}/I_{4168} \approx 8$  of these peaks, one can roughly estimate that  $X_{cv} \approx 8X_v \approx 0.4$ . The value of  $X_v + X_{cv} \approx 0.45$  thus estimated agrees with the experimental value of the total hydrogen content  $X = 0.47(3)$  of the  $\text{SiO}_2\text{-H}_2$  sample studied by Raman spectroscopy.

As seen from Figure 3, the width of the  $4168$  and  $4374\text{ cm}^{-1}$  peaks is much less than the distance between them. This suggests that most voids in amorphous silica incorporating  $\text{H}_2$  molecules under high pressure can roughly be divided into two different groups, and the scatter in the shapes, sizes, and other determinative properties of the voids within each group is much smaller than the difference in these properties of the voids from different groups.

**X-ray Diffraction.** Figure 4 compares the structure factors  $S(Q)$  of the initial silica glass, the silica glass loaded with



**Figure 4.** Structure factor,  $S(Q)$ , of the  $\text{SiO}_2\text{-H}_2$  sample synthesized at  $P = 75$  kbar and  $T = 250$  °C (red solid line) in comparison with  $S(Q)$  of the sample of silica glass exposed to the same pressure and temperature without hydrogen (blue dashed line) and the initial silica glass (black dotted line). Cu  $K\alpha$  radiation, ambient pressure,  $T = 85\text{ K}$ .

hydrogen to  $X = 0.53$  at a hydrogen pressure of 75 kbar and  $T = 250$  °C, and also the silica glass exposed to the same pressure and temperature without hydrogen (in Teflon as the pressure transmitting medium) and quenched to the  $\text{N}_2$  temperature. As seen from Figure 4, the positions of the first sharp diffraction peak (FSDP) for the initial and hydrogenated samples coincide at  $Q = 1.55\text{ }\text{\AA}^{-1}$ . The FSDP position of the sample exposed to  $P = 75$  kbar and  $T = 250$  °C without hydrogen is  $Q = 1.78\text{ }\text{\AA}^{-1}$ . The observed shift of the FSDP by  $\Delta Q = 0.23\text{ }\text{\AA}^{-1}$  in the silica glass subjected to high pressure stems from the pressure-induced reduction of the ring sizes and a collapse of void spaces in the silica network.<sup>15</sup> The absence of such a shift in the sample exposed to the same pressure and temperature in a hydrogen atmosphere suggests that the hydrogen penetrated in



the voids should have protected them from contracting. A similar effect of preventing the voids in amorphous silica from contracting at high helium pressures due to their filling with He atoms was earlier observed and thoroughly discussed in refs 6 and 7.

The behavior of silica glass compressed in diamond anvil cells up to ~190 kbar at room temperature was studied in ref 7 by in-situ X-ray diffraction and Raman spectroscopy using helium and hydrogen as the pressure-transmitting medium and also without such a medium. In agreement with earlier results,<sup>6</sup> the FSDP position in the X-ray patterns of the silica glass in helium was nearly pressure-independent, thus demonstrating that the helium atoms were likely to enter the voids in the glass. Compressing silica glass in hydrogen resulted in approximately the same strong shift of FSDP to higher frequencies as in the case of using no pressure-transmitting medium. On the basis of this result, the authors of ref 7 concluded that, in contrast to helium, hydrogen cannot dissolve in silica glass in a large amount because of the larger kinetic diameter of H<sub>2</sub> molecules (2.9 Å<sup>8</sup>) compared to that of He atoms (2.6 Å<sup>12</sup>).

This conclusion actually predicts that concentrated hydrogen solutions in silica glass cannot be formed at any pressure and temperature and therefore contradicts our experimental results demonstrating that at a pressure of 75 kbar the H<sub>2</sub> solubility in silica glass reaches a value of H<sub>2</sub>/SiO<sub>2</sub> ≈ 0.5, which is similar to the estimated He solubility He/SiO<sub>2</sub> ≈ 0.8–2<sup>6</sup> (see Figure 2). It can also be added that the He solubility in silica glass at high pressures has never been measured experimentally, so the difference between the He and H<sub>2</sub> solubilities can even appear smaller. We think that the absence of any detectable H<sub>2</sub> solubility in silica glass in the high-pressure experiments of ref 7 was a result of the low diffusion rate of hydrogen at room temperature. In fact, the diffusion coefficient for H<sub>2</sub> molecules in silica glass at room temperature is  $D = 1 \times 10^{-11}$  cm<sup>2</sup>/s,<sup>16</sup> which is by 3 orders of magnitude lower than  $D = 2.4 \times 10^{-8}$  cm<sup>2</sup>/s for He atoms.<sup>17</sup> At the temperature of 250 °C used in the present work, the H<sub>2</sub> diffusion coefficient in silica glass rises to a value of  $D = 1.9 \times 10^{-8}$  cm<sup>2</sup>/s,<sup>16</sup> close to that for the He coefficient at room temperature, and the concentrated SiO<sub>2</sub>–H<sub>2</sub> solid solutions are easily formed.

## CONCLUSIONS

The hydrogen solubility in amorphous silica at pressures up to 75 kbar and temperature 250 °C has been investigated for the first time. The composition study of the samples, hydrogenated under pressure and quenched to the liquid nitrogen temperature, revealed a linear dependence of the molar ratio H<sub>2</sub>/SiO<sub>2</sub> versus synthesis pressure, from  $X = 0.16$  at  $P = 6$  kbar to  $X = 0.53$  at  $P = 75$  kbar. A Raman study of the sample with  $X = 0.47$  showed that the hydrogen is dissolved in the form of H<sub>2</sub> molecules, which occupy at least two different types of voids in the amorphous silica network. The H<sub>2</sub> molecules occupying the voids of the first type (most likely, inside the six-membered rings of silica) and of the second type (not identified yet) have the vibration stretching bands at 4168 and 4374 cm<sup>−1</sup>, respectively. Judging by the ratio of integral intensities of these bands, the great majority (~90%) of the dissolved hydrogen molecules are located in the voids of the second, yet unidentified type. Also, our X-ray diffraction studies showed that the hydrogen molecules penetrated in the silica glass network at a hydrogen pressure of 75 kbar prevented the sample from the significant irreversible densification occurring in the case of compressing the silica glass to the same pressure

without hydrogen. A similar effect was earlier observed *in situ* at helium penetrations in the silica glass.<sup>6,7</sup>

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Montmerle, T.; Augereau, J. C.; Chaussidon, M.; et al. *Earth, Moon, Planets* **2006**, 98, 39–95.
- (2) Safronov, V. S. *Evolution of the Protoplanetary Cloud and Formation of the Earth and the Planets*; Nauka Press: Moscow, USSR, 1969; Trans. NASA TTF 677, 1972.
- (3) Hartwig, C. M. *J. Appl. Phys.* **1976**, 47, 956–959.
- (4) Shelby, J. E. *J. Appl. Phys.* **1977**, 48, 3387–3394.
- (5) Li, C. Y.; Price, J.; Tomozawa, M.; Watson, E. B. *J. Non-Cryst. Solids* **2011**, 357, 2081–2085.
- (6) Sato, T.; Funamori, N.; Yagi, T. *Nat. Commun.* **2011**, 2, 345–350.
- (7) Shen, G.; Meia, Q.; Prakapenka, V. B.; et al. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, 108, 6004–6007.
- (8) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; Wiley: New York, 1974.
- (9) Kirchheim, R. *Acta Metall.* **1982**, 30, 1069–1078.
- (10) Efimchenko, V. S.; Kuzovnikov, M. A.; Fedotov, V. K.; et al. *J. Alloys Compd.* **2011**, 509S, S860–S863.
- (11) Shackelford, J. F.; Masaryk, J. S. *J. Non-Cryst. Solids* **1978**, 30, 127–139.
- (12) Shelby, J. E. *J. Appl. Phys.* **1976**, 47, 135–139.
- (13) Herzberg, G. *Infrared and Raman Spectra*; Van Nostrand: Princeton, NJ, 1945.
- (14) Wijngaarden, R. J.; Lagendijk, A.; Silvera, I. F. *Phys. Rev. B* **1982**, 26, 4957–4962.
- (15) Inamura, Y.; Katayama, Y.; Utsumi, W.; Funakoshi, K. *Phys. Rev. Lett.* **2004**, 93, 015501–015504.
- (16) Shang, L.; Chou, L.; Lu, W.; Burruss, R. C.; Zhang, Y. *Geochim. Cosmochim. Acta* **2009**, 73, S435–S443.
- (17) Barrer, R. M.; Vaughan, D. E. W. *Trans. Faraday Soc.* **1967**, 63, 2275–2290.