



# High-pressure solid solutions of molecular hydrogen in amorphous magnesium silicates



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## ABSTRACT

New amorphous solutions  $Mg_ySiO_{2+y}XH_2$  with the magnesium concentration varying from  $y = 0$  to  $y = 0.88$  were synthesized at a hydrogen pressure of 75 kbar and a temperature of 250 °C, followed by quenching to the temperature of liquid nitrogen. The quenched samples were studied by thermal desorption, X-ray diffraction and Raman spectroscopy. The X-ray diffraction study showed that all hydrogenated samples preserved the amorphous state and had no crystalline inclusions. At the same time, the positions of the first sharp diffraction peak (FSDP) of the samples with  $y = 0.32$  and 0.6 were shifted by  $\Delta Q = 0.14 \text{ \AA}^{-1}$  after the hydrogenation thus signaling on changes in the amorphous network and even its small depolymerization.

According to the thermal desorption analysis, the hydrogen content  $X$  of the quenched  $Mg_ySiO_{2+y}XH_2$  samples nonlinearly decreased with increasing concentration  $y$  of the magnesium ions  $Mg^{2+}$  from  $X = 0.600(3)$  at  $y = 0$  to  $X = 0.259(3)$  at  $y = 0.88$ . The samples with  $y \geq 0.49$  evolved a significant portion of the dissolved hydrogen on heating in vacuum above 0 °C therefore showing a higher thermal stability than the hydrogenated silica and silicates with low magnesium concentrations. Raman spectroscopy demonstrated that hydrogen was dissolved in all samples in the form of  $H_2$  molecules, and the width of the  $H_2$  stretching line narrowed approximately four-fold with increasing magnesium concentration. Both this effect and the changes in the  $H_2$  desorption kinetics presumably resulted from the decreasing dispersion in the size of silicate cavities in the amorphous matrix, which changes from the silica glass structure at  $y \leq 0.32$ –0.49 to the close-packed enstatite glass structure at higher magnesium concentrations.

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## 1. Introduction

Among different types of hydrogenated substances, there is one that does not have a name yet. In the solid solutions and compounds of this type, hydrogen is present in the form of  $H_2$  molecules, which are weakly bound to the host structures by Van der Waals forces. Earlier, the only representatives of hydrides of this type were hydrogen hydrates, such as the sII clathrate phase (5.6 wt %  $H_2$ ) [1] and  $C_2$  phase (10 wt %  $H_2$ ) [2]. These hydrates were thoroughly investigated and the sII phase was even proposed as material for hydrogen storage [3].

Our recent studies revealed a considerable solubility of hydrogen in amorphous silica reaching 1.8 wt %  $H_2$  (or a molar ratio

$H_2$ /f.u. of  $X = 0.53$ ) at a hydrogen pressure of 75 kbar and a temperature of 250 °C [4]. Thus, the hydrogenated silica became the second example of concentrated solid solutions of molecular hydrogen.

Adding 0.6 mole of MgO to the silica network decreased the hydrogen solubility at  $P = 75$  kbar in the amorphous silicate  $Mg_{0.6}SiO_{2.6}$  to  $X = 0.31$  [5]. On the other hand, the obtained amorphous compound  $Mg_{0.6}SiO_{2.6}-0.31H_2$  showed a higher thermal stability in vacuum than  $SiO_2-0.53H_2$  and evolved most of its hydrogen only after heating above 0 °C. Our studies by X-ray diffraction and Raman spectroscopy also showed [5] that the amorphous silicate network of the hydrogenated  $Mg_{0.6}SiO_{2.6}$  undergoes a phase transition at 55 kbar, whereas the hydrogen dissolved in the amorphous silica prevents any changes in its structure at pressures up to 75 kbar [4]. Additionally, the stretching mode of  $H_2$  molecules in the hydrogenated  $Mg_{0.6}SiO_{2.6}$  samples proved to be

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considerably narrowed both before and after the phase transition compared to that in the hydrogenated silica glass.

It seems worth mentioning here, too, that results of high-pressure high-temperature studies of the interaction of amorphous magnesium silicates with hydrogen could appear important for planetology and geophysics. For example, the magnesium silicates with Mg/Si from 0.7 to 2.4 in the amorphous form were found in the circumstellar dust of the evolved stars [6]. Such an amorphous dust compressed and heated by the gravitational forces together with hydrogen (the most abundant element of the Universe) could undergo the reactions playing a key role in the birth and first stages of evolution of planetary systems.

The present paper reports on the hydrogen content (X), network transformations, hydrogen state (atomic or molecular) and thermal stability of amorphous compounds  $\text{Mg}_y\text{SiO}_{2+y}\text{-XH}_2$  with  $y = 0\text{--}0.88$  loaded with hydrogen at  $P = 75$  kbar and  $T = 250$  °C. Each hydrogenated sample was rapidly cooled (quenched) from 250 °C to the  $\text{N}_2$  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  $T = -188$  °C.

## 2. Materials and methods

The silica glass was purchased from Sigma–Aldrich. Powders of the amorphous magnesium silicates were produced by a sol-gel method followed by sintering at 700 °C as described in Ref. [7]. According to results of the energy dispersive X-ray spectroscopy (EDX), the magnesium concentrations in the initial silicate samples  $\text{Mg}_y\text{SiO}_{2+y}$  thus produced were  $y = 0, 0.136, 0.32, 0.49, 0.6$  and  $0.88$ . These initial samples were examined by X-ray diffraction at room temperature on the Oxford diffraction equipment using Mo  $K\alpha$  radiation.

The hydrogenation of the silicates and silica glass was carried out in a Toroid-type high-pressure apparatus [8] using  $\text{AlH}_3$  [9] or  $\text{NH}_3\text{BH}_3$  [10] as an internal hydrogen source. The high-pressure cell was made of Teflon and the silicate and hydrogen source were separated by a Pd foil. To evolve hydrogen,  $\text{AlH}_3$  or  $\text{NH}_3\text{BH}_3$  was decomposed at  $P = 15$  kbar by heating to  $T = 250$  °C. The pressure was then increased and the silicate sample was exposed to an  $\text{H}_2$  atmosphere at  $P = 75$  kbar and  $T = 250$  °C for 24 h and further rapidly cooled (quenched) to  $-196$  °C to prevent hydrogen losses in the course of the subsequent pressure release. The molar ratio  $X = \text{H}_2/\text{f.u.}$  of the samples was determined with an accuracy of  $\delta X = 0.03$  by hot extraction into a pre-evacuated volume [11].

The hydrogenated samples were stored in liquid nitrogen and further studied at ambient pressure by Raman spectroscopy at the liquid  $\text{N}_2$  temperature and by X-ray diffraction at  $T = -188$  °C. In view of the strong luminescence background from the powdered amorphous silica, we eventually switched to bulk samples of silica glass.

Raman spectra from the hydrogenated and initial samples were recorded in back-scattering geometry using a micro-Raman setup

comprised 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 in the spectral range from 140 to 4500  $\text{cm}^{-1}$ . The 532 nm line of a single-mode YAG CW diode pumped laser was focused on the sample by an Olympus 50  $\times$  objective in a  $\sim 2$   $\mu\text{m}$  diameter spot that was slightly defocused due to the light refraction in the nitrogen vapors. The spatial resolution was also  $\sim 2$   $\mu\text{m}$  and the spectral resolution varied between 2.3 and 4.1  $\text{cm}^{-1}$ . The laser line was suppressed by a super-notch filter with the optical density  $\text{OD} = 6$  and bandwidth  $\sim 160$   $\text{cm}^{-1}$ , while the beam intensity before the sample was  $\sim 5$  mW.

The quenched samples were also studied by powder X-ray diffraction at ambient pressure and  $-188$  °C using a Siemens D500 diffractometer equipped with a home-designed nitrogen cryostat that permitted loading metastable powder samples without their intermediate warming.

## 3. Results

The initial samples were shown to be amorphous and contain no crystalline inclusions. The positions, half-widths and integral intensities of the observed diffraction peaks are shown in Table 1. The obtained parameters vary from sample to sample, which indicates significant changes in the amorphous structure of the silicates caused by the varying Mg concentration. The first sharp diffraction peak (FSDP) gradually shifts from  $Q = 1.58$   $\text{\AA}^{-1}$  for pure  $\text{SiO}_2$  to  $1.89$   $\text{\AA}^{-1}$  for  $\text{Mg}_{0.88}\text{SiO}_{2.88}$  due to the structural changes in the amorphous matrix of the samples with increasing magnesium concentration.

Fig. 1 depicts thermal desorption curves of the  $\text{Mg}_y\text{SiO}_{2+y}\text{-XH}_2$  samples hydrogenated at  $P = 75$  kbar. All samples start evolving hydrogen at a temperature near  $-187$  °C. The pressure of the

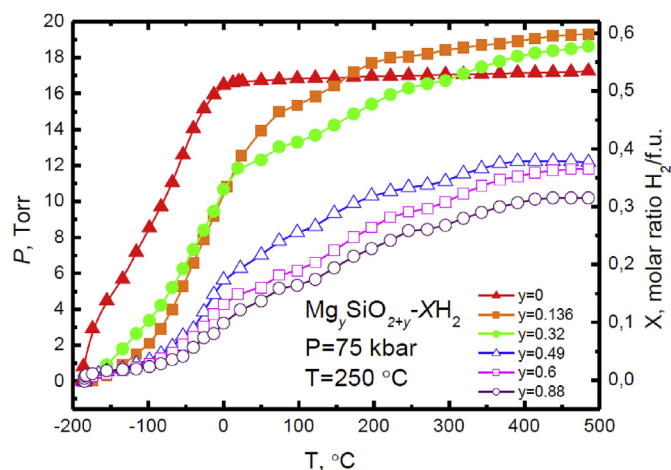


Fig. 1. Thermal desorption curves of the  $\text{Mg}_y\text{SiO}_{2+y}\text{-XH}_2$  samples synthesized at  $P = 75$  kbar and  $T = 250$  °C and heated in vacuum at a rate of 20 °C/min. The curve for the hydrogenated amorphous silica ( $y = 0$ ) is from Ref. [4].

Table 1  
Positions ( $Q$ ), half-widths ( $\Delta_{1/2}$ ) and integral intensities ( $I$ ) of peaks in the X-ray diffraction patterns of the initial  $\text{Mg}_y\text{SiO}_{2+y}$  samples. Room temperature, Mo  $K\alpha$  radiation.

$\text{Mg}_y\text{SiO}_{2+y}$	$Q_1$ $\text{\AA}^{-1}$	$\Delta_{1/2}$ $\text{\AA}^{-1}$	$I_1$ a.u.	$Q_2$ $\text{\AA}^{-1}$	$\Delta_{1/2}$ $\text{\AA}^{-1}$	$I_2$ a.u.	$Q_3$ $\text{\AA}^{-1}$	$\Delta_{1/2}$ $\text{\AA}^{-1}$
$y = 0$	1.579	0.510	1.40	4.920	1.416	0.124	6.55	–
$y = 0.136$	1.735	0.666	1.08	4.743	1.357	0.173	6.5	–
$y = 0.32$	1.832	0.811	0.84	4.620	1.417	0.181	6.4	–
$y = 0.49$	1.815	0.832	0.80	4.524	1.297	0.191	6.35	–
$y = 0.6$	1.869	0.905	0.75	4.360	1.296	0.170	6.2	0.76
$y = 0.88$	1.889	0.978	0.61	4.530	1.176	0.240	6.35	–

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