

PHYSICAL METHODS  
OF INVESTIGATION

## Hydrogenation and Dehydrogenation of the Clathrate $\text{Na}_x\text{Si}_{136}$

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**Abstract**—Samples of the clathrate  $\text{Na}_x\text{Si}_{136}$  were saturated with hydrogen to 100 atm at 25°C in a Sieverts-type apparatus and at pressures of 6 and 28 kbar in lentil-type high-pressure apparatuses at 100 and 250°C. X-ray powder diffraction analysis and Raman spectroscopy of the samples quenched after the saturation with hydrogen showed that the phase composition of the clathrates did not change. Heating of the quenched samples to room temperature in a thermal desorption setup produced not hydrogen, but hydrogen-containing gases, as we assumed, silanes. Heating to 650°C leads to decomposition of these compounds to form hydrogen.

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Owing to the wide use in various technologies and industries, silicon is one of the most studied chemical elements. Most of the studies were made of the silicon modification that is thermodynamically stable under normal conditions and has a diamond-type structure. The elemental composition and, correspondingly, the electronic and optical properties of this modification can be changed by controlled synthesis of substitutional and interstitial solid solutions. However, based on silicon, inclusion compounds (clathrates) can also be obtained, which form by the reversible insertion of “guest” atoms or molecules into “cages” created by “host” (silicon) atoms.

Inclusion compounds of silicon were discovered in 1965 in vacuum annealing of sodium silicide [1–3]. Those works showed that the frameworks of silicon atoms form cubic structures of two types: a type I structure contains 46 silicon atoms per unit cell (space group  $Pm\bar{3}n$ ); a type II structure, 136 silicon atoms per unit cell (space group  $Fd\bar{3}m$ ). The unit cell of a type I clathrate has eight cages occupied by guest atoms, and the unit cell of a type II clathrate has a total of 24 cages, of which 8 cages are large and 16 cages are small [4].

Guest atoms in cages of these structures can be atoms of Na, K, Rb, I, and Ba. A change in the type of guest atom radically changes the properties of the clathrate. For example, the clathrate  $\text{Na}_8\text{Si}_{46}$  has low thermal conductivity [5], the clathrate  $\text{K}_8\text{Si}_{46}$  has very low compressibility [6], and the clathrate  $\text{Ba}_8\text{Si}_{46}$  is a superconductor with a superconducting transition temperature of about 8 K [7].

The possibility of the insertion of molecular hydrogen formed by the reaction of  $\text{NH}_4\text{Br}$  with the silicon clathrates  $\text{Na}_{5.5}\text{Si}_{46}$  and  $\text{K}_7\text{Si}_{46}$  with the type I cubic structure was shown [8, 9]. It was also assumed [8, 9] that type I clathrates can be used for creating materials that efficiently store hydrogen even at relatively low hydrogen pressures.

However, in this context, we consider that the type II clathrates  $\text{Na}_x\text{Si}_{136}$  are more promising. It was determined for these compounds that their vacuum annealing with subsequent treatment in iodine vapor can decrease the number of sodium atoms in their structure down to zero [10]. This makes them superior to type I clathrates, from the structure of which guest atoms cannot be removed [10].

However, it should be noted that, for a material to be used as a hydrogen storage, not only should it sorb a significant amount of the gas at relatively low pressures, but also it should release hydrogen at sufficient rate at moderate temperatures.

The purpose of this work was to study the hydrogen sorption and desorption in the type II clathrates  $\text{Na}_x\text{Si}_{136}$  at  $x \leq 10$  with a large number of free cages in the lattice.

### EXPERIMENTAL

The initial samples of the clathrate  $\text{Na}_x\text{Si}_{136}$  were synthesized according to a modified published procedure [4, 11]. Because of the high chemical activity of the initial components, intermediates, and clathrate phases, all the operations with them were performed in

an argon atmosphere in an MBraun LabMaster SP glove box ( $O_2$  content  $\leq 0.1$  ppm,  $H_2O$  content  $\leq 0.1$  ppm).

To synthesize sodium silicide NaSi, sodium and silicon (fine powder) in amounts corresponding to the composition  $Na_{56}Si_{44}$  (at %) were placed in Alundum crucible. The total weight of the sample was about 3 g. The crucible with the sample was covered with a lid and was put into a stainless steel bomb. The interior of the bomb was insulated with a ring gasket washer made of annealed copper. Sodium silicide was synthesized by keeping the bomb with the crucible in a furnace at a temperature of about  $600^\circ C$  for 30 h with subsequent cooling with the furnace.

The clathrate  $Na_xSi_{136}$  was produced by annealing a NaSi sample (about 250 mg) for 14 days at  $380\text{--}400^\circ C$  in a vacuum of  $10^{-8}\text{--}10^{-9}$  mbar. The obtained sample was a fine powder.

The clathrates were saturated with hydrogen according to two techniques.

(1) Saturation at pressures of 6 and 28 kbar with hydrogen formed by  $AlH_3$  thermolysis at  $250^\circ C$  was carried out in lentil-type high-pressure apparatuses according to a published procedure [12]. The sample was kept for 1 day at required pressures and temperatures, after which it was cooled under pressure to approximately  $-180^\circ C$ , and the pressure was decreased to atmospheric pressure. All the samples of the clathrates synthesized to be used in further investigations were stored in liquid nitrogen.

(2) Saturation with hydrogen at pressures to 100 atm was performed in a Sieverts-type apparatus, which allowed one to determine the hydrogen content of the sample directly under pressure and to quench the sample for further investigation under normal pressure. The design of this apparatus and the method for calculating the fraction of hydrogen dissolved under pressure were described in detail in the literature [13, 14]. The total time of keeping at a given pressure was 1 day. The pressure determination error was 0.07 atm, and the total error of determining the fraction of hydrogen (at 100 atm) was 0.1 wt %  $H_2$ .

The release of gases from clathrate samples saturated with hydrogen was studied by thermal desorption analysis in a setup, which enabled one to find the gas content of the sample and explore the gas release kinetics while heating the sample from the liquid nitrogen temperature to  $650^\circ C$  at an average rate of about  $20^\circ C/min$ . The amount of the released gas was determined from the pressure it created in a calibrated volume. The setup design and calculation methods in detail were described elsewhere [15]. The error of determining the fraction of the released gas was 5% of the measured value.

The quenched hydrogen-containing samples were studied (without removing from liquid nitrogen) by Raman spectroscopy. The spectra were recorded in backscattering geometry on a previously described

setup [16] with an Acton SpectraPro-2500i spectrograph with a Pixis 2K CCD detector cooled to  $-65^\circ C$ . The excitation was performed with a solid-state laser at a wavelength of 532 nm and a notch filter for this wavelength. To record the spectra of the quenched samples, they were placed in a special container cooled with liquid nitrogen. To minimize the heating of the samples by the laser beam, its power on the sample was limited to 0.5 mW.

X-ray powder diffraction analysis was made with a Siemens D-500 diffractometer ( $CuK_\alpha$  radiation) equipped with a nitrogen cryostat, constructed for loading samples and recording their diffraction spectra at a temperature of  $-188^\circ C$ . The recorded spectra were processed using the PowderCell software, which determines the phase composition of samples as volume percentages.

The elemental composition of the samples was found at room temperature by energy-dispersive X-ray spectroscopy with a Supra 50VP scanning electron microscope with a field emission gun and an Oxford Inca Energy 450 energy-dispersive X-ray analysis system.

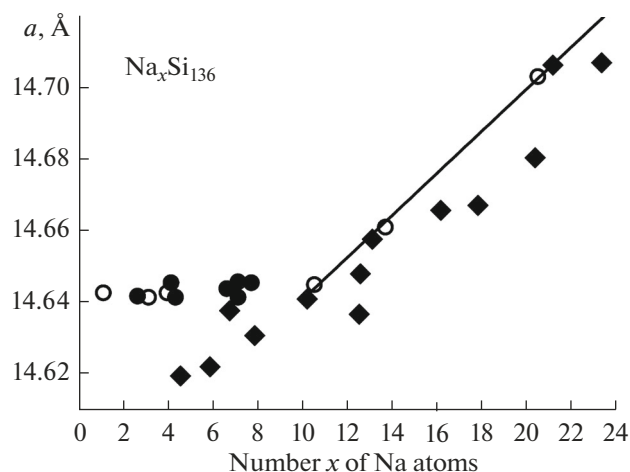
## RESULTS AND DISCUSSION

According to the X-ray powder diffraction analysis data, the initial samples obtained by vacuum annealing of sodium silicide contained 82 to 98 vol % clathrate  $Na_xSi_{136}$  and several percent of the clathrate  $Na_8Si_{46}$  and elemental silicon with the diamond-type structure. Based on these values, on the total amount of sodium in the samples as determined by electron microprobe analysis, and also on the fact that the clathrate  $Na_8Si_{46}$  has strictly constant composition [10], we calculated the number  $x$  of sodium atoms in the clathrate  $Na_xSi_{136}$  that remained after the vacuum annealing. Figure 1 illustrates the dependences of the unit cell parameter of the clathrate phase on the sodium content of it. They are seen to generally agree with the published data [17].

The thermal desorption analysis of the initial samples of the clathrate  $Na_xSi_{136}$  showed that they always contained a small amount of hydrogen. For example, the  $Na_xSi_{136}$  sample that was further used for studying hydrogen sorption initially contained 0.15 wt % hydrogen. How it entered the clathrate lattice remains unclear.

### *Hydrogen Sorption by the Clathrate $Na_xSi_{136}$*

A clathrate sample for studying hydrogen sorption in the Sieverts-type apparatus was prepared by mixing several batches, in which the concentration of the clathrate  $Na_xSi_{136}$  phase was 86–97 vol % and the unit cell parameter of the cubic lattice was 14.640–14.645 Å. This corresponded to the sodium content of  $\leq 10$  atoms per unit cell (Fig. 1).



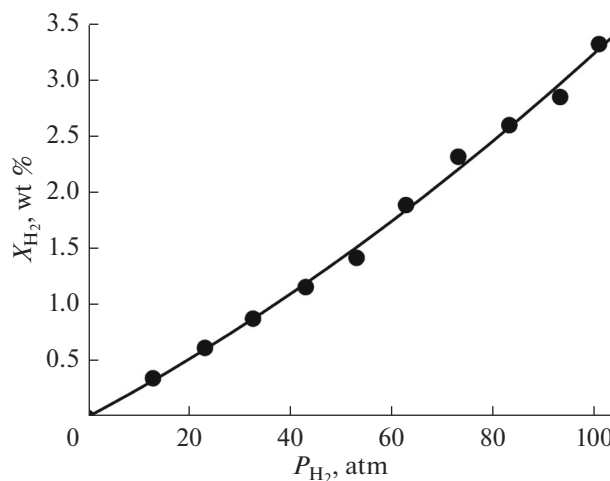
**Fig. 1.** Dependence of the unit cell parameter of the initial clathrate  $\text{Na}_x\text{Si}_{136}$  on the number  $x$  of sodium atoms in the unit cell. The filled circles represent the data of this work; the empty circles, the data of the work [17]; the line, the approximation of these data; and the diamonds, the data the work [4].

Figure 2 presents the hydrogen sorption isotherm of this sample within the pressure range 1–100 atm at room temperature.

As Fig. 2 shows, the hydrogen content of the clathrate with increasing pressure increases nonlinearly and reaches 3.3 wt %, which corresponds to an H:Si atomic ratio of  $\sim 1$ . This value significantly exceeds the hydrogen solubility in the isostructural clathrate phase of ice sII (2.52 wt % at 1.8 kbar) [18]. At the same time, the unit cell volume of the clathrate  $\text{Na}_x\text{Si}_{136}$  ( $V = 3138 \text{ \AA}^3$ ) is much smaller than that of the ice clathrate ( $V = 4954 \text{ \AA}^3$ ) [19]. If we assume that, in the clathrate  $\text{Na}_x\text{Si}_{136}$ , as in the ice clathrate, hydrogen dissolves as molecules, then the value obtained at 100 atm looks implausibly high.

All these facts suggest that the silicon clathrate not simply sorbs molecular hydrogen, but is likely to enter into a chemical reaction with it to form hydrides. Reactions between silicon and hydrogen, as well as between silicon and water, are impossible under ordinary conditions. Nonetheless, sodium silicide reacts with water to yield silane [20]. One can assume that, in our case, too, the presence of a certain amount of sodium in the clathrate  $\text{Na}_x\text{Si}_{136}$  favors the formation of silane.

To determine the phase and elemental composition, the  $\text{Na}_x\text{Si}_{136}\text{-H}$  sample quenched at  $P = 100$  atm in liquid nitrogen was investigated at atmospheric pressure by X-ray powder diffraction (at  $-188^\circ\text{C}$ ) and electron microprobe analysis (at  $25^\circ\text{C}$ ). The sample contained 97 vol % cubic clathrate phase II with the unit cell parameter  $a = 14.63 \text{ \AA}$  and about 3 vol % cubic clathrate phase I with the unit cell parameter  $a = 10.18 \text{ \AA}$ . The electron microprobe analysis of the sam-



**Fig. 2.** Hydrogen sorption isotherm of the clathrate  $\text{Na}_x\text{Si}_{136}$  at room temperature as measured in a Sieverts-type apparatus.

ple showed that it contained  $7 \pm 2$  sodium atoms per 136 silicon atoms, which is close to that in the initial samples. Thus, the saturation of a sample with hydrogen at a pressure of 100 atm and room temperature does not change its elemental and phase composition, and also the unit cell parameters of the clathrate phase.

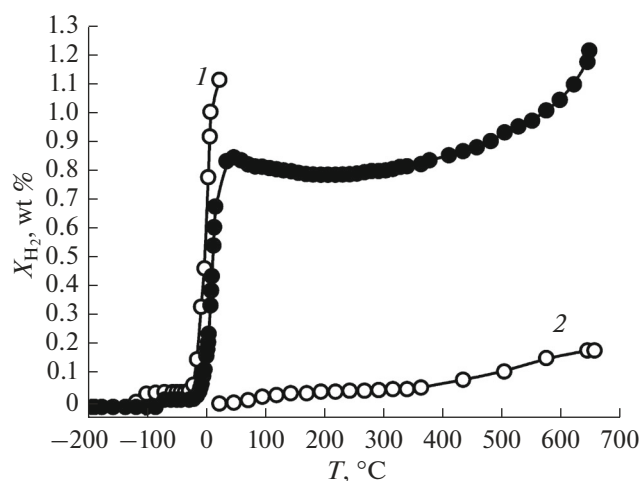
A similar result was obtained by studying the samples saturated with hydrogen at pressures of 6 and 28 kbar and temperatures of 100 and  $250^\circ\text{C}$  in lentil-type apparatuses by X-ray powder diffraction analysis and Raman spectroscopy.

#### *Hydrogen Desorption from the Clathrate $\text{Na}_x\text{Si}_{136}\text{-H}$*

The desorption of gases from the quenched samples synthesized at 100 atm and 6 and 28 kbar was qualitatively studied by the thermal desorption method. Figure 3 presents typical curves recorded while heating the samples.

The gas release began at temperatures from  $-100$  to  $-70^\circ\text{C}$ , proceeded in three steps, and, while continuously heating to  $650^\circ\text{C}$  (Fig. 3, filled circles), reached 1.2–1.3 wt %  $\text{H}_2$ . The final weight percentage of hydrogen was calculated from the pressure of the gas remaining after cooling of the ampule with the sample to the liquid nitrogen temperature. The thus determined content of hydrogen released from the hydrogenated samples after continuously heating to  $650^\circ\text{C}$  ranged from 0.46 to 1.05 wt %  $\text{H}_2$ .

To determine the fraction of hydrogen in the total gas pressure while heating to  $650^\circ\text{C}$ , the dehydrogenation process was divided into two stages. At the first stage, a  $\text{Na}_x\text{Si}_{136}\text{-H}$  sample was heated from  $-196^\circ\text{C}$  to room temperature, after which the ampule with gas was cooled in liquid nitrogen. In this process, the pres-



**Fig. 3.** Typical curves of gas desorption from the  $\text{Na}_x\text{Si}_{136}$  samples saturated with hydrogen. The heating rate is  $20^\circ\text{C}/\text{min}$ . The filled circles represent the curve recorded while continuously heating from  $-196$  to  $+650^\circ\text{C}$ ; the empty circles, the curve for the sample synthesized at  $P = 100$  atm and  $T = 25^\circ\text{C}$  while heating in two steps: (1) from  $-196$  to  $+25^\circ\text{C}$  and (2) from  $+25$  to  $650^\circ\text{C}$ .

sure in the system decreased almost to zero; i.e., at this stage, the sample released not hydrogen, but other, easily condensable gases. At the second stage, the ampule was heated again to room temperature, the released gas was pumped out, and then the sample was heated from room temperature to  $650^\circ\text{C}$ . The gas release began at  $50^\circ\text{C}$  and reached  $0.2$  wt %  $\text{H}_2$  at  $650^\circ\text{C}$ . The ampule with the released gas was cooled again to  $-196^\circ\text{C}$ , but in this case the pressure in the system remained virtually unchanged, which indicated that then ampule was filled with hydrogen.

We noted above that the initial  $\text{Na}_x\text{Si}_{136}$  clathrate sample already contained  $0.15$  wt % hydrogen. If this fact is taken into account, then the concentration of hydrogen sorbed by the clathrate at  $P = 100$  atm and room temperature is only  $0.05$  wt %.

The significant difference between the mass fractions of hydrogen sorbed by the clathrate as determined by the volumetric and thermal desorption methods can be explained only by assuming that the gas released in thermal desorption within the temperature range from  $-100$  to  $+25^\circ\text{C}$  is not hydrogen but an unidentified hydrogen-containing compound, the condensation point of which should obviously exceed the liquid nitrogen temperature. The thermolysis of this compound and the formation of hydrogen while heating the reactor occur at temperatures above  $\sim 200^\circ\text{C}$ .

With the consideration of the elemental composition of the clathrate, some of these requirements can be met by such compounds as sodium hydride  $\text{NaH}$ , hydride  $\text{NaSiH}_3$ , or silanes  $\text{Si}_n\text{H}_{2n+2}$ . It is known from the literature that  $\text{NaH}$  and  $\text{NaSiH}_3$  are nonvolatile

[21, 22] and, while heating, decompose into sodium, sodium silicide, and hydrogen. Note also that both the formation and the thermolysis of these hydrides occur at temperatures above  $200^\circ\text{C}$ . These data allow one to reject from consideration these substances as possible hydrogen-containing compounds that released while heating the  $\text{Na}_x\text{Si}_{136}\text{-H}$  clathrate sample to room temperature.

As for silanes, the vapor pressure of the most volatile of them, monosilane, at  $-179^\circ\text{C}$  is 1 torr, its melting point is  $-185^\circ\text{C}$  [23], and the decomposition temperature is  $180$  to  $500^\circ\text{C}$ , depending on conditions [24]. Thus, the most probable gases released from the sample while heating to room temperature are in our opinion, silanes.

Based on our volumetric and thermal desorption data, we assume that the saturation of the clathrate  $\text{Na}_x\text{Si}_{136}$  with molecular hydrogen at 100 atm is not completed at the stage of gas sorption, but continues further, until silicon hydrogenation and formation of compounds of silicon with hydrogen with an  $\text{H} : \text{Si}$  atomic ratio of  $\sim 1$ .

However, to make the final conclusion on the nature of these compounds their composition and formation mechanism, the interaction of the clathrate  $\text{Na}_x\text{Si}_{136}$  with hydrogen should be studied by direct in situ methods under high pressure.

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