

## Fast synthesis method and phase diagram of hydrogen clathrate hydrate

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We report a very fast method for hydrogen clathrate production. The formation of hydrogen clathrate from H<sub>2</sub> gas and ice-Ih at 77–273 K occurs at least 100 times faster compared to the reaction with water. This effect is probably the result of a partial penetration of hydrogen into the ice-Ih body, which favors clathrate formation. With the ice method, the ice-Ih/48H<sub>2</sub>\*136H<sub>2</sub>O system can quickly trap and release up to 3.77 mass % of hydrogen, which gives it an advantage over other chemical-bonding hydrogen storage technologies. New data on the hydrogen-water phase diagram are presented and discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2190273]

Clathrate hydrates are a large class of inclusion compounds, in which the host framework structure is made up of hydrogen-bonded water molecules, and the guest molecules are trapped inside the polyhedral cages. Increasing scientific interest in clathrate hydrates research reflects their importance in Earth and planetary sciences, energy resources and environmental concerns, as well as fundamental chemistry and physics. Immense deposits of methane clathrate hydrates (CH<sub>4</sub>-H<sub>2</sub>O) have been discovered on ocean floors and suggested as the future fuel source.<sup>1</sup> Hydrates of natural gases have also been found in continental shelves, permafrost, and even in the planet nebulae.<sup>1–4</sup> Clathrate of carbon dioxide plays a crucial role in the carbon sequestration on the planet.

Hydrogen clathrate hydrate, first recognized only in 1999,<sup>5,6</sup> presents a completely new technological means for hydrogen storage.<sup>7–9</sup> Polyhedral cage framework of (32+x)H<sub>2</sub>\*136H<sub>2</sub>O, x=0–16 hydrate can hold substantial amounts of guest molecular hydrogen, up to 3.77% of total mass at atmospheric pressure and moderately low temperatures (below 160 K).<sup>10</sup> Both pressure-temperature stability range and storage capacity could be improved by partial substitutions.<sup>11,12</sup> These properties along with the simplicity and low cost of hydrate composition make hydrogen clathrate a good candidate for a hydrogen storage material. However, a simple and easy method of clathrate production is necessary for their successful application in industry. Here, we present the first experimental data on fast synthesis of hydrogen clathrate from H<sub>2</sub> and ice-Ih (regular ice).

The *in situ* synthesis and kinetics studies of hydrogen clathrate were performed by high-pressure neutron diffraction at the Los Alamos Neutron Science Center (LANSCE). We used a setup specifically designed for the high-pressure preferred orientation (HIPPO) time-of-flight neutron diffractometer.<sup>13</sup> Large sample volume (~1.5 cm<sup>3</sup>) of our high-pressure Al alloy cell, very high neutron flux (~2.4 × 10<sup>7</sup> neutrons/cm<sup>2</sup> s) of the instrument and the setup design allow kinetics study with a time step (data collection time) as low as ~1 min. In order to minimize the background of the collected diffraction patterns, D<sub>2</sub>O water/ice and D<sub>2</sub> gas were used for the study instead of hydrogen analogs. Deuterium gas was supplied through the high-pressure tubing equipped with the pressure gauge, thus allowing the variation and

measurement of D<sub>2</sub> pressure up to 4 kbar in the temperature range of 10–300 K during the experiment.

For the study of formation kinetics of hydrogen clathrate from water, a sample was pressurized at room temperature and then cooled down to 100–260 K, while maintaining constant pressure. It was found that formation of the hydrogen clathrate from water and hydrogen occurs very slowly. The diffraction patterns of hydrogen clathrate prepared from water at 260 K and 1.5 kbar after 3 and 20 h are shown in Figs. 1(a) and 1(b). All diffraction peaks on the patterns belong to the hydrogen clathrate, while high background is mostly originated from the diffuse scattering of water. The conversion rate of water to the clathrate phase was approximately estimated as  $(B_w - B)/(B_w - B_c)$  by a comparison of background level ( $B$ ) on a diffraction pattern with those of the pure clathrate ( $B_c$ ) and water ( $B_w$ ) phases. About 30% and ~70% of water to clathrate conversions were achieved after 3 and 20 h, respectively. It should be noted that in some instances, the full conversion of water to clathrate was not achieved even after 5–10 days of synthesis.

When ice was used as a starting material, the D<sub>2</sub>O ice sample was instantly pressurized to the desired pressure at a preset temperature. The completion of ice to water conver-

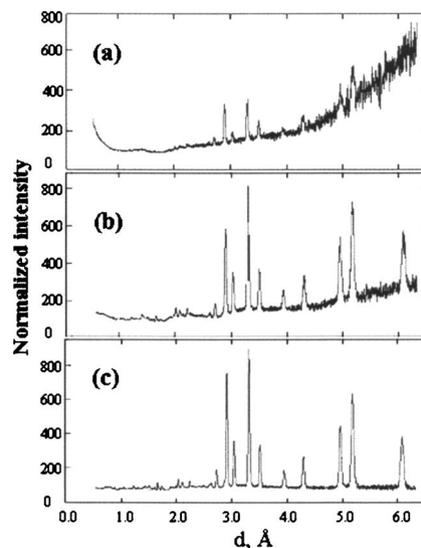


FIG. 1. The diffraction patterns of hydrogen clathrate prepared from water at 260 K under 1.5 kbar after (a) 3 h and (b) 20 h and from ground ice-Ih (c) at 250 K, 1.5 kbar after 10 min.

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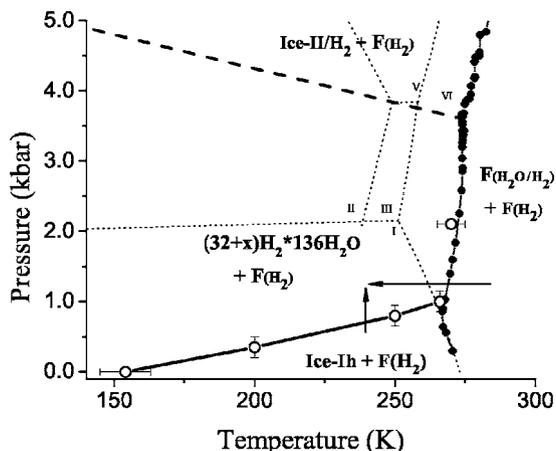


FIG. 2. Pressure-temperature phase diagram of the  $\text{H}_2\text{-H}_2\text{O}$  system in excess of hydrogen (heavy lines and symbols) plotted together with the  $\text{H}_2\text{O}$  phase diagram [thin dotted lines and Roman numerals for the stable ice phases, from (Ref. 15)]. Solid circles ( $\bullet$ ) represent the data taken from Dyadin *et al.* (Ref. 5), open diamonds ( $\diamond$ ) — our data. The heavy dashed line is plotted based on 80 K data from Mao *et al.* (Ref. 9).  $F(\text{H}_2)$  and  $F(\text{H}_2\text{O}/\text{H}_2)$  correspond to the fluid/liquid phases for  $\text{H}_2$  and hydrogen solution in water,  $(32+x)\text{H}_2\cdot 136\text{H}_2\text{O}$  — clathrate phase, ice-II/ $\text{H}_2$ —hydrogen solution in ice framework with the structure close to ice-II (Ref. 14).

sion was recognized when all ice diffraction peaks disappeared. Figure 1(c) represents the diffraction pattern of hydrogen clathrate prepared from powdered ice with an average grain size of  $\sim 0.5$  mm at about the same conditions (250 K and 1.5 kbar). Note that the formation of  $\sim 100\%$  clathrate phase was complete in less than 10 min.

The difference between the synthesis ways from water and ice can be explained by the water-hydrogen  $p$ - $T$  phase diagram as shown in Fig. 2. Three boundary lines limit the stability field of hydrogen clathrate. The melting curve (diamond symbols) corresponds to the equilibrium of  $(32+x)\text{H}_2\cdot 136\text{H}_2\text{O}$  clathrate with water solution of hydrogen,  $F(\text{H}_2\text{O}/\text{H}_2)$ . The low-pressure boundary line (solid line) corresponds to the equilibrium of clathrate with the regular ice-Ih phase. We identified a number of points on this curve: 163(2) K at 1 bar, 200 K at 0.35(15) kbar, and 265 K at 1.0(1) kbar. The last point coincides with the melting curve obtained by Dyadin *et al.*,<sup>5</sup> thus revealing a quadruple point where the stable phases are hydrogen clathrate, ice-Ih,  $F(\text{H}_2\text{O}/\text{H}_2)$  and fluid hydrogen [ $F(\text{H}_2)$ ]. The high-pressure boundary line (dashed line) separates clathrate and the solution of hydrogen in ice-II (ice-II/ $\text{H}_2$ ). The latter phase was found stable at 7–20 kbar.<sup>14</sup> Taking into account the clathrate melting curve obtained by Dyadin *et al.*,<sup>5</sup> it can be hypothesized that another quadruple point coincides with the change of the slope at  $\sim 274$  K and  $\sim 3.7$  kbar, where the stable phases are hydrogen clathrate, ice-II/ $\text{H}_2$ ,  $F(\text{H}_2\text{O}/\text{H}_2)$  and  $F(\text{H}_2)$ .

Referring to the water-hydrogen phase diagram, the synthesis of hydrogen clathrate from water could be described as traversing from the [ $F(\text{H}_2\text{O}/\text{H}_2)$ + $F(\text{H}_2)$ ] field to the [ $(32+x)\text{H}_2\cdot 136\text{H}_2\text{O}$ + $F(\text{H}_2)$ ] field on the diagram. This process is indicated by the horizontal arrow in Fig. 2. Formation of hydrogen clathrate hydrate from ice occurs when traversing from the [Ice-Ih+ $F(\text{H}_2)$ ] field to the [ $(32+x)\text{H}_2\cdot 136\text{H}_2\text{O}$ + $F(\text{H}_2)$ ] field, as indicated by the vertical arrow in Fig. 2.

TABLE I. Synthesis time (in minutes) for clathrate prepared from ground ice-Ih and  $\text{H}_2$  gas.

Pressure (bar)	270 K	250 K	200 K	150 K
2000	<2	<2	<2	$\sim 5$
1500	...	5–10	5–10	5–10
1000	...	5–10	10–15	$\sim 20$
500	...	...	...	$\sim 30$

In order to study the formation kinetics of hydrogen clathrate from ice in more detail, we measured the synthesis time at various pressures and temperatures, as shown in Table I. At high pressures (above 1 kbar), the completion of the clathrate formation occurs within 2–10 min. A slight trend toward a higher conversion rate was observed at about the melting point of ice. At low pressures, synthesis time decreases with decreasing temperature. However, even at 150 K and 500 bar, hydrogen clathrate forms in about 30 min, which is still much faster than when it is prepared from water.

To clarify the role of surface area-to-volume ratio factor, we studied the formation of hydrogen clathrate from a bulk chunk of ice-Ih with volume, and consequently, the surface area, comparable to the water sample used in the previous experiments. The diffraction patterns taken during the synthesis of hydrogen clathrate from about 1 g chunk of ice at 250 K and 1.5 kbar are shown in Fig. 3. Formation of clathrate from the chunk of ice was complete in about 1.5–2 h, which is slower than synthesis from powdered ice, but is at least 100 times faster than synthesis from water.

We tried to prepare hydrogen clathrate from amorphous ice as well. About a 1 g sample of amorphous ice was synthesized by fast cooling of water from 300 to 200 K at 2.2 kbar. When formation was complete, the system was depressurized leaving  $\text{H}_2\text{O}$  in the form of metastable amorphous ice, which was checked with *in situ* neutron diffraction. We applied 1–2 kbar hydrogen pressure at 160–240 K to a sample of amorphous ice but no conversion to clathrate was observed within 1–10 h.

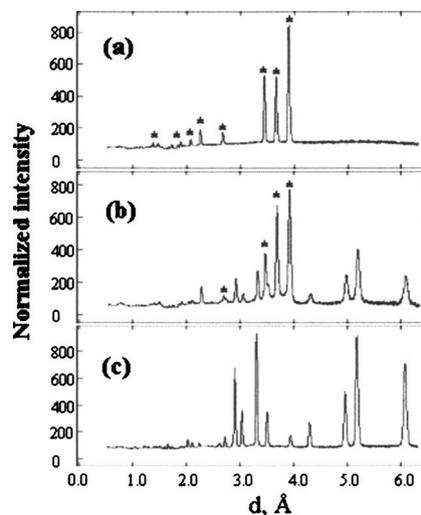


FIG. 3. The diffraction patterns of hydrogen clathrate prepared from a 1 g chunk of ice-Ih at 1.5 kbar after (a) 0.0 h (b) 1 h, and (c) 1.5 h. Ice peaks are marked with \*, while all the other reflections correspond to the clathrate phase.

A comparison of our kinetic results of clathrate formation from (i) water, (ii) a chunk of ice-Ih, and (iii) amorphous ice, shows that the formation mechanism for (ii) is different than for both (i) and (iii). Ice has a much lower density than water or amorphous ice and it has small cavities in its structure. It is also known that He and H<sub>2</sub> can penetrate into ice-II filling its cages.<sup>14,16</sup> We suggested that hydrogen under pressure may partially penetrate into ice-Ih cavities, too, thus creating a favorable mechanism for clathrate formation.

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<sup>1</sup>E. D. Sloan, *Clathrate Hydrates of Natural Gases*, 2nd ed (Dekker, New York, 1998).

<sup>2</sup>J. S. Loveday, R. J. Nelmes, M. Guthrie, S. A. Belmonte, D. R. Allan, D. D. Klug, J. S. Tse, and Y. P. Handa, *Nature (London)* **410**, 661 (2001).

<sup>3</sup>J. I. Lunine and D. J. Stevenson, *Icarus* **70**, 61 (1987).

<sup>4</sup>T. Gulluk, F. Slemr, and B. Stauffer, *J. Geophys. Res.* **103**, 15971 (1998).

<sup>5</sup>Y. A. Dyadin, E. G. Larionov, A. Yu. Manakov, F. V. Zhurko, E. Ya. Aladko, T. V. Mikina, and V. Yu. Komarov, *Mendeleev Commun.* **5**, 209 (1999).

<sup>6</sup>Y. A. Dyadin, E. G. Larionov, E. Ya. Aladko, A. Yu. Manakov, F. V. Zhurko, T. V. Mikina, V. Yu. Komarov, and E. V. Grachev, *J. Struct. Chem.* **40**, 790 (1999).

<sup>7</sup>W. L. Mao and H-K. Mao, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 708 (2004).

<sup>8</sup>W. L. Mao and H-K. Mao, U.S. Patent # 6,735,960 (May 2003).

<sup>9</sup>W. L. Mao, H-K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, and Y. Zhao, *Science* **297**, 2247 (2002).

<sup>10</sup>K. A. Lokshin, Y. Zhao, D. He, W. L. Mao, H-K. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, *Phys. Rev. Lett.* **93**, 125503 (2004).

<sup>11</sup>L. J. Florusse, C. J. Peters, J. Schoonman, K. C. Hester, C. A. Koh, S. F. Dec, K. N. Marsh, and E. D. Sloan, *Science* **306**, 469 (2004).

<sup>12</sup>H. Lee, J.-W. Lee, D. Y. Kim, J. Park, Y.-T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe, and J. A. Ripmeester, *Nature (London)* **434**, 743 (2005).

<sup>13</sup>K. A. Lokshin and Y. Zhao, *Rev. Sci. Instrum.* **76**, 063909 (2005).

<sup>14</sup>W. L. Vos, L. W. Finger, R. J. Hemley, and H-K. Mao, *Phys. Rev. Lett.* **71**, 3150 (1993).

<sup>15</sup>H. T. Haselton, I.-M. Chou, A. H. Shen, and W. A. Bassett, *Am. Mineral.* **80**, 1302 (1995).

<sup>16</sup>D. Londono, W. F. Kuhs, and J. L. Finney, *Nature (London)* **332**, 141 (1988).