

Pressure-amorphized cubic structure II clathrate hydrate: crystallization in slow motion

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Received 28th July 2010, Accepted 26th October 2010

DOI: 10.1039/c0cp01351j

A range of techniques has so far been employed for producing amorphous aqueous solutions. In case of aqueous tetrahydrofuran (THF) this comprises hyperquenching of liquid droplets, vapour co-deposition and pressure-induced amorphization of the crystalline cubic structure II clathrate. All of these samples are thermally labile and crystallize at temperatures above 110 K. We here outline a variant of the pressure-amorphization protocol developed by Suzuki [*Phys. Rev. B*, 2004, **70**, 172108], which results in a highly crystallization resistant amorphous THF hydrate. The hydrate produced according to our protocol (annealing to 180 K at 1.8 GPa rather than to 150 K at 1.5 GPa) does not transform to the cubic structure II THF clathrate even at 150 K. We track the reason for this higher stability to the presence of crystalline remnants when following the Suzuki protocol, which are removed when using our protocol involving higher pressures and an annealing step. These crystalline remnants later serve as crystallization seeds lowering the thermal stability of the amorphous sample. Our protocol thus makes a purely amorphous THF hydrate available to the research community. We use powder X-ray diffraction to study the process of nucleation and slow crystal growth in the temperature range 160–200 K and find that the local cage structure and periodicity of the fully crystalline hydrate develops even at the earliest stages of crystallization, when the “clathrate crystal” has a size of about two unit cells.

Introduction

Clathrate hydrates are inclusion compounds, in which small guest molecules are trapped in ice-like cages.¹ Huge reservoirs of methane clathrate hydrates are found on the ocean floor and in permafrost regions, and possibly in outer space, *e.g.*, on Mars² and on Titan.³ Research on this crystalline material has been motivated partly by the idea of harvesting it as an energy source and a rising number of applications⁴ such as hydrogen storage in tetrahydrofuran (THF) clathrates.^{5,6} Sloan emphasizes in his recent review that “the largest challenge is to describe the kinetics of hydrates”.⁴ A lot of work has been devoted to the study of the formation kinetics of gas hydrates in natural environments, which may be limited by low solubility or mass- and thermal transfer issues.^{7–9} One approach that has been neglected in the literature is the study of the crystallization of non-crystalline solid solutions, *e.g.*, vitrified or pressure-amorphized solutions. It is the aim of this work in the first place to produce a solid THF solution free of crystalline material and in the second place to investigate the crystallization process. Pioneering studies on vapour deposited,^{10,11} vitrified¹² and pressure-amorphized^{13,14} THF solutions have been reported. The amorphous samples produced in the course of these studies showed a substantial fraction of crystalline

contamination, though, and were prone to crystallization at quite low temperatures of typically 110 K. Here, we have developed an improved procedure of pressure-amorphization, which avoids crystalline contamination largely. The samples are crystallization resistant up to ~150 K at ambient pressure, which provides the possibility of studying crystallization on kinetically immobilized states, *e.g.*, by diffraction techniques.

Experimental

For our experiments we used a solution of THF in water of mole fraction 1 : 16.65. The solution freezes at about 4.4 °C to the cubic structure II (CS-II) THF clathrate hydrate. The ideal composition for this hydrate is 1 : 17 THF : H₂O.¹⁵ The slight excess of THF ensures complete conversion of ice to hydrate, whereas solid THF is below the detection limit. In analogy to our earlier studies of the compression and decompression behaviour of amorphous^{16–18} and crystalline ice,^{19,20} we employ a piston–cylinder setup, which is compressed in a controlled manner by the crossbeam of a computerized material testing machine (Zwick, model BZ100/TL3S). 500 µl of THF clathrate solution are pipetted into the 8 mm bore of a hardened steel cylinder, which is cooled to 77 K by immersion in liquid nitrogen and lined with a cup made of ~500–600 mg of thin indium foil, which is a ductile material even at 77 K largely eliminating friction between the ice sample and the cylinder. Temperature is measured using a Pt100 sensor counter-sunk in the steel cylinder, which is sitting at a distance of about 10 mm to the sample. The crystalline CS-II THF clathrate hydrate, which freezes within the cup by cooling with

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liquid N₂, is then pressurized by moving a piston down the bore to pressures exceeding 1.3 GPa. In some experiments (Fig. 1) the sample is decompressed immediately, whereas in other experiments (Fig. 2) an annealing step is performed. In the annealing step the sample is heated at 1.5 GPa to 150 K (Suzuki-protocol, ref. 14) or at 1.8 GPa to 180 K (our protocol). The fully pressurized sample is then quenched to 77 K by immersing the pressure cell in liquid nitrogen. Finally, the sample is recovered at 77 K from the cell by releasing the pressure at a controlled rate and pushed out of the cylinder. The high pressure phase produced is identified by powder X-ray diffractograms (Cu K α 1) at \sim 80–90 K, which are recorded on a diffractometer in a Θ – Θ arrangement (Siemens, model D 5000), equipped with a low-temperature camera of Anton Paar. The instrumental resolution function was calibrated with a well-defined cordierite sample, and is

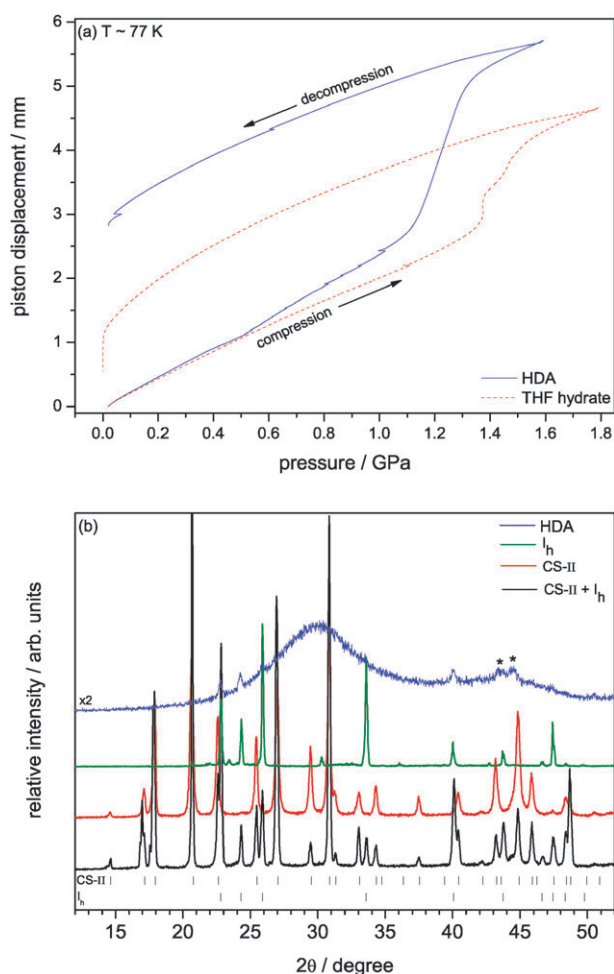


Fig. 1 (a) Compression and decompression experiments of hexagonal ice (solid) and CS-II THF clathrate (dashed) at 77 K up to 1.8 GPa. Piston displacement vs. pressure curves (an increase in piston displacement corresponds to an increase in density) are employed to locate structural transitions. (b) Powder X-ray diffractograms obtained before and after the compression–decompression experiments shown in (a). While hexagonal ice (2nd from top) can be recovered as an amorphous solid (topmost), the CS-II hydrate (bottom) does not transform to an amorphous solid (2nd from bottom). Reflexes caused by the sample holder are marked with asterisks.

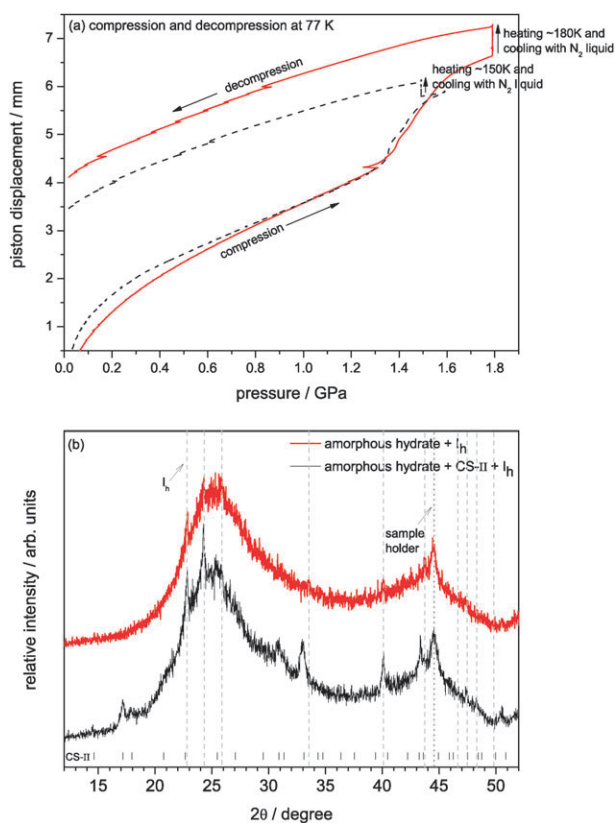


Fig. 2 (a) (De)compression experiments of CS-II THF hydrate at 77 K including a high-pressure annealing step. The protocol according to Suzuki¹⁴ (dashed line) is compared to annealing at 1.8 GPa to 180 K (solid line). (b) Both protocols produce mainly an amorphous solid characterized by the broad halo at $2\theta \approx 25^\circ$. While CS-II Bragg peaks are evident when following the Suzuki protocol (bottom), these are absent after annealing at 1.8 GPa to 180 K (top). Ticks indicate Bragg peaks of CS-II hydrate, vertical lines correspond to Bragg peaks of the sample holder and hexagonal ice, which may condense onto the sample during transfer to the precooled PXRD chamber.⁴⁴

expressed as a TCH pseudo-Voigt profile function.²¹ The instrumental FWHM is 0.11–0.23° in the experimental angular range. Phase identification was done by employing the known crystal structures with the aid of the program PowderCell.²² In figures, ticks indicate the position of Bragg peaks for the crystalline phases hexagonal ice (I_h)²³ and CS-II.²⁴

Results

Unannealed pressure-amorphized THF-hydrates: unstable at 77 K and 1 bar

One of the main challenges in our approach is producing a purely amorphous solid. The technique of hyperquenching liquid solutions at cooling rates of 10⁷ K s^{−1} results in crystalline contamination of up to a few percent.^{25,26} This was also observed by Tulk *et al.*, who obtained a hyperquenched glassy THF hydrate stable only up to \sim 110 K at ambient pressure.¹² Vapour co-deposited samples are highly porous and need to be treated at temperatures of 150 K or higher in vacuum for removal of the pores.²⁷ These conditions result not only in the removal of pores, but partly also in crystallization, and so we

regard hyperquenching and vapour co-deposition routes as unsuitable. We have, therefore, chosen to make use of the technique of pressure-amorphization of the crystalline solid. This works well at 77 K and > 1.0 GPa in case of pure water, but not in case of aqueous THF solutions (see Fig. 1). Hexagonal ice amorphizes at ~ 1.1 GPa and can be quench-recovered to ambient pressures as a metastable amorphous solid without back-transformation to hexagonal ice at 77 K (Fig. 1a, solid curve). By contrast, CS-II hydrates such as THF clathrates amorphize at ~ 1.3 GPa and show a back-transformation at pressures below 0.0004 GPa (4 bar) even at 77 K (Fig. 1a, dashed curve). The higher stability against amorphization of the CS-II hydrate was also inferred from other measurements, *e.g.*, thermal conductivity.^{15,28} The beginning of back-transformation is indicated by the step in piston-displacement, *i.e.*, density, at 0.0004 GPa in Fig. 1a. This instability of the amorphous THF hydrate at 77 K and ambient pressure has also been noted earlier.^{28,29} At higher temperatures (*e.g.*, 130 K) the back-transformation occurs at higher pressures (*e.g.*, 0.35 GPa) when decompressing.³⁰ Fig. 1b shows the diffractograms for the starting and the resulting material. The two diffractograms on top correspond to the pure water experiment. The 2nd from top shows the sharp Bragg-peaks in the starting material I_h , the topmost shows the broad halo peak representative of the amorphous solid called high-density amorphous ice (HDA). The two diffractograms below show the starting material (bottom) and the recovered sample (2nd from bottom) of the THF hydrate experiment. Both show the crystalline CS-II structure as the main component. In the starting material also some I_h Bragg peaks are detected, which indicates that a small fraction of the starting material is hexagonal ice. After decompression the small fraction of I_h does not transform back, whereas the CS-II hydrate reverts entirely. That is, the technique, which produces an amorphous solid (HDA) in case of water produces a crystalline solid (CS-II) in case of THF-solutions.

Annealed pressure-amorphized THF-hydrates

An annealing step at high-pressures, *e.g.*, heating to 165 K at 1.1 GPa, is known to produce an amorphous solid of 10% higher density (very high-density amorphous ice, VHDA) in case of pure water.³¹ VHDA shows a higher thermal stability at ambient pressure compared to HDA.³² Using an additional annealing step on pressurized THF CS-II clathrates, Suzuki¹⁴ achieved the recovery of an amorphous form of THF hydrate at ambient pressure, which is stable up to ~ 110 K. Fig. 2a again shows compression and decompression experiments of CS-II clathrates. In contrast to Fig. 1a, a high-pressure annealing step is performed in addition in these experiments. The dashed curve closely follows the protocol employed by Suzuki,¹⁴ which involves pressurizing the sample up to 1.6 GPa, decompression to 1.5 GPa and heating under pressure to 150 K. The quench-recovered amorphous hydrate is stable up to ~ 110 K at ambient pressure and does not show back-transformation at 77 K in the dilatometry curves. The diffractogram (see Fig. 2b, bottom) shows mainly an amorphous halo, but also some sharp CS-II THF hydrate Bragg peaks. This indicates that the amorphization is not complete at

1.5 GPa and 150 K. Upon heating at ambient pressure the CS-II remnants likely serve as crystallization seeds, which lower the thermal stability compared to a pure amorphous hydrate. For optimising the amorphization process and bringing it to completion, we annealed another sample at a higher pressure (1.8 GPa) to a higher temperature (180 K, see Fig. 2a solid line). Again, no back transformation is seen in dilatometry curves. The diffractogram of the quench-recovered sample is entirely amorphous and free of CS-II reflexes (Fig. 2b, top). *E.g.*, the Bragg peaks at $2\theta \approx 17.2^\circ$, 30.8° , 33.0° and 43.3° are missing entirely. The only sharp Bragg peaks can be attributed to traces of the sample holder and I_h (vertical lines), which sometimes condenses in tiny amounts onto the surface of the sample when transferring the sample from liquid nitrogen into the chamber. We emphasize that there is a good match for the Bragg-peaks observed as a contaminating component in Fig. 2b (top) with hexagonal ice (Fig. 1b, 2nd from top), but no good match with CS-II (Fig. 1b, bottom). Both the amorphous phases seem to be identical, with a halo maximum at $2\theta \approx 25^\circ$. That is, an annealing step at sufficiently high pressures to sufficiently high temperatures is required to recover an amorphous THF solution devoid of detectable crystalline impurities. This amorphous material is ideal for the study of crystallization at low temperatures.

Growth of cubic-structure II THF-hydrate at ambient pressure

The inability to detect events over nanoscopic time and length scales has hindered the experimental study of hydrate nucleation mechanisms^{33,34} and the issue of hydrate nucleation has, therefore, been addressed in computer simulations.^{34–36} Here we study the initial crystal growth modes at much lower temperatures, and therefore the events take place on the minute time scale rather than in nano- or microseconds. By carefully analyzing the evolution of X-ray powder diffractograms with temperature we are able to detect “crystals” of very small dimensions. The thermal stability and crystallization behaviour of this entirely amorphous hydrate is demonstrated in Fig. 3a, which shows a set of powder X-ray diffractograms recorded at ~ 80 K. The sample is heated in steps, first 5 minutes to 140 K, and then 5 minutes to 150 K, *etc.* until a final temperature of 200 K is reached. By quenching back to ~ 80 K after each heating step we effectively stop any conversion and are able to record a series of diffractograms showing step-by-step how the amorphous hydrate finally crystallizes to CS-II. In general Fig. 3a shows that CS-II clathrate and cubic ice (I_c) Bragg peaks are growing by heating the sample. We observe how the amorphous halo develops additional broad features, which slowly sharpen and even split and finally produce CS-II Bragg peaks. Initially, after heating for 5 minutes to 110 K and quenching-back to 80 K we obtain a powder X-ray diffractogram indistinguishable from the one at the bottom in Fig. 3a, *i.e.*, at 110 K no crystal growth is observable. Slight changes are first noticed after heating to 140 K for 5 minutes, and additional broad features are not observable prior to reaching ~ 160 K. This demonstrates that the crystallization resistance is indeed much higher compared to the recovered amorphous samples first prepared by Suzuki.¹⁴ Cubic ice crystallizing from the sample is first evident at 140–150 K (vertical dashed lines).

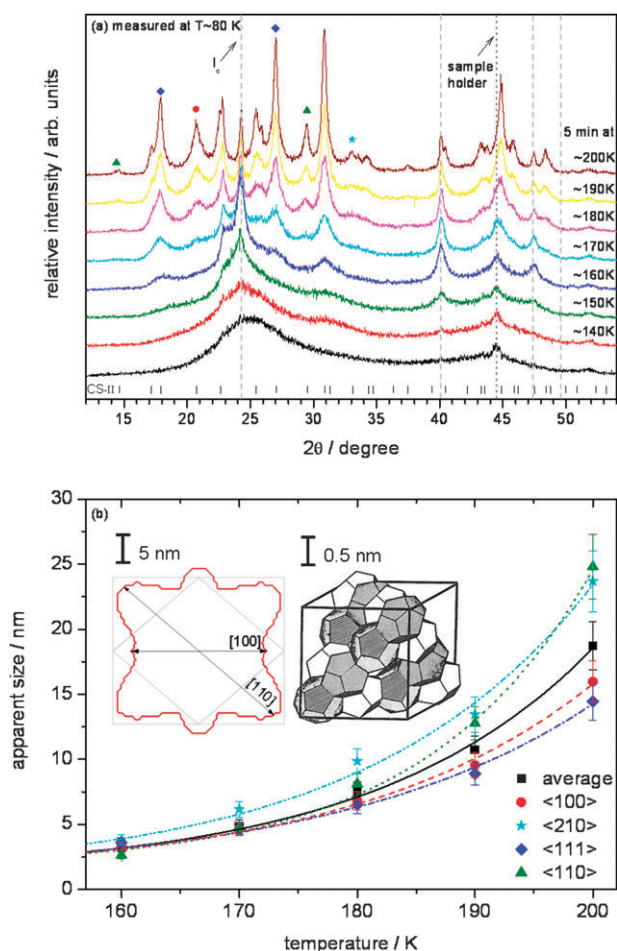


Fig. 3 (a) Crystallization of the amorphous THF hydrate as obtained after annealing at 1.8 GPa to 180 K (bottom) to CS-II hydrate. All powder X-ray diffractograms have been recorded at ~ 80 K after keeping the sample for 5 minutes at the indicated temperature. Ticks indicate CS-II Bragg peaks, vertical lines indicate cubic ice, which also grows from the amorphous hydrate, and the sample holder. (b) Apparent crystal size in the $\langle hkl \rangle$ -directions indicated as a function of temperature. Respective Bragg peaks are marked in (a) by the same symbols. Inset: crystalline domain shape at 200 K (thick line). The domain shape of a cube and an octahedron spanned by the fast growing directions is shown for comparison (thin lines). A unit cell of the CS-II clathrate is shown for size comparison (as published by Mak *et al.*⁴⁵). Please note that the scale bars in the inset differ.

At 150 K very broad features appear, which we interpret in the sense that nucleation has taken place and “crystal-domains” of roughly unit cell size have formed. At higher temperatures these domains grow to larger sizes. Other crystalline phases such as crystalline THF (which would show the most intense Bragg peaks at 19.1° , 24.2° and 30.5°) are not evident. The latter was observed by Tulk *et al.* when crystallizing hyperquenched solutions.¹²

For a quantitative analysis of domain growth a LeBail refinement was done with the program FullProf.³⁷ Anisotropic Lorentzian broadening of the sample peaks is treated phenomenologically using the Scherrer formula, calculating the apparent size of the coherent domains from a linear combination of cubic harmonics.^{38,39} A careful analysis

showed that only K00, K61, and K62 have significant contributions. The strong sample-dependent broadening caused by the very small apparent domain sizes observed exceeds the instrumental resolution by far. The calculated values are thus highly significant as long as peaks of the respective phase can be distinguished at all. The refinement fits the data well and thus the hypothesis of domain growth being at the origin of the appearance of the broad features is justified. In Fig. 3b the apparent domain size as a function of temperature is shown for some selected crystal growth directions (marked in Fig. 3a). At the beginning the domain sizes are very small, with an apparent size of about 3 nm (this is only two unit cells!) at 160 K. Even at these small “crystal” sizes the periodicity of the fully crystallized CS-II hydrate is present. This is consistent with growth following the “local structuring hypothesis” as favoured by Conrad *et al.* for THF hydrates crystallized from the liquid solution.⁴⁰ However, the appearance of “hydrate precursors” cannot be excluded on the basis of the data in Fig. 3 since their appearance would remain unnoticed in X-ray experiments because of their small sizes and lack of periodicity. All data points can be reasonably fitted with an exponential growth function, and crystallographic directions which grow slower than others can be identified. A graphic representation of the directionality of crystal growth is shown as an inset in Fig. 3b. According to the literature clathrates crystallized from liquid 1 : 17 THF : water solutions show the slowest growth in the $\langle 111 \rangle$ direction, resulting in isotropic octahedral crystals.^{33,41–43} This is observed in this work, too, for growth from the pressure-amorphized solid. The difference in growth rates between $\langle 110 \rangle$ and $\langle 100 \rangle$ results in the curvilinear domain shape at 200 K (inset Fig. 3b). That is, crystal growth from the amorphous solid seems to be quite similar to crystal growth from the aqueous solutions, albeit the former takes place in slow motion.

Conclusions

In summary, we report how to prepare an amorphous THF hydrate free of CS-II clathrate and follow the initial stages of crystallization at low temperatures in slow motion at ambient pressure. We show that pressure-amorphization of CS-II clathrates requires an annealing step at ≥ 1.8 GPa and ≥ 180 K in order to bring the amorphization to completion, *i.e.*, in order to remove any crystallinity detectable by powder X-ray diffraction. The removal of crystalline remnants greatly increases the thermal stability of the amorphous samples at ambient pressure. While previously such samples showed crystallization at temperatures ≤ 110 K, our samples can sustain temperatures of at least 150 K without crystallization. The availability of an amorphous solution free of crystalline impurities now allows for further characterization of the “pure” material such as structural studies by neutron diffraction methods or dynamic studies such as dielectric spectroscopy. When crystallizing the sample at 160 K, interestingly, the periodicity of the CS-II crystal appears even at the very beginning of the crystallization process, when the crystal has a size of only two unit cells. That is, the local cage structure (both large ($5^{12}6^4$) and small (5^{12}) cages) of the crystalline hydrate develops very early in the crystallization process.

Acknowledgements

The work was supported by a grant of the European Research Council ERC (SULIWA) and the Austrian Science Fund FWF (Y391).

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