Article

Transitions in Pressure Collapsed Clathrate Hydrates

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ABSTRACT: Type II clathrate hydrates (CHs), or ice clathrates, are inclusion compounds in which a hydrogen-bonded cage-like structure of H_2O accommodates molecules of suitable size, known as "guest molecules". CHs have similar local geometrical arrangements of the hydrogen-bonded water network as ice and both are known to collapse to amorphous states on isothermal pressurization at temperatures below about 140 K. Moreover, the collapsed CH states undergo a glass, or glass-like, transition at 140 K on heating at 1 GPa, which is identical to that of collapsed ice, or high density amorphous ice. Here we use thermal conductivity and dielectric measurements to study the transition behavior of two type II CHs with tetrahydrofuran and 1,3 dioxolane, respectively, as guest molecules. After their collapsed states have been heated to well above the glass transition at 1 GPa, we find transitions corresponding to the high to low density amorphous ice transition of ice with only slightly shifted temperature−pressure ($T-p$) coordinates compared to those of pure water. Thus, collapsed CHs show the same transition behaviors as cold water, which provide the basis for the model that explains the unusual temperature and pressure behaviors of water's properties in terms of two distinct types of liquid water. Collapsed CHs are, however, more stable than collapsed ice and can therefore be studied in a wider $T-p$ interval. The results suggest sluggish homogenizing and phase separation processes, which affect the transition behaviors of collapsed CHs.
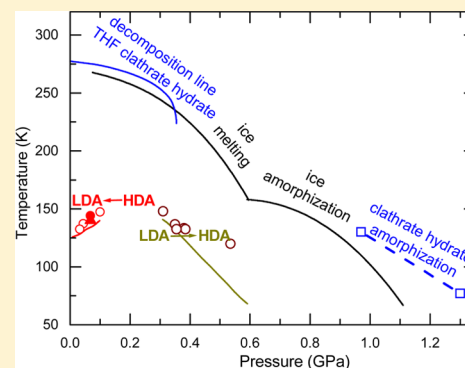
■ INTRODUCTION

Water is one of the few materials that show multiple, distinctly different, amorphous solid states. Two of water's amorphous solid states are produced under low temperature and high pressure conditions.[1] When hexagonal ice, ice Ih, is pressurized at temperatures below about 140 K, it collapses (or amorphizes) to a high density amorphous state (HDA), as depicted in the pressure−temperature ($p-T$) diagram (Figure 1). This state shows heterogeneities on a mesoscopic spatial scale after collapse,[2] but it slowly relaxes and densifies on heating up to slightly below the crystallization temperature at pressures near 1 GPa,[3] with a concurrent decrease of nanometer-scale heterogeneities.[2] The ultimately densified state formed, e.g., by heating to 166 K at 1.1 GPa, appears to be a homogeneous amorphous state and it is commonly referred to as vHDA.[3] Thus, the collapsed ice state changes with both the $p-T$ conditions and the time by which it is produced or annealed,[4] which suggest that the collapsed states differ in the degree of completeness in collapse toward vHDA. Although the states differ slightly, the transformation on heating is gradual and the distinction between various HDA states produced through collapse by pressurization in the temperature range below 140 K remains subtle; these are all referred to here generically as HDA. (Nelmes et al.[5] have shown that various treatments of HDA at low pressures lead to further changes, and they introduced "expanded HDA" for a state obtained by annealing ice amorphized by pressurization near 77 K, or "unrelaxed HDA".) The essential difference in properties of the different HDA states, which is of concern for
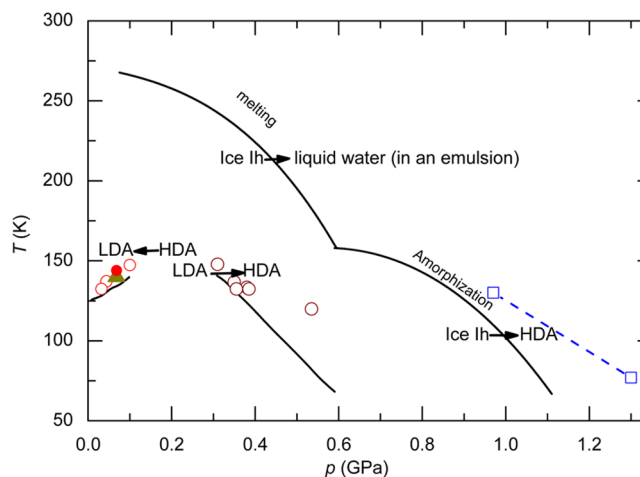

Figure 1. Transition lines showing the collapse pressure of ice and the HDA−LDA transitions.[7] Circles and triangles show the transition coordinates obtained in this work for DXL CH and THF CH, respectively. Open and filled symbols represent isothermal and isobaric results, respectively. The squares show the collapse pressure for THF CH obtained in this work at 130 K (onset of major collapse) and previous work at 77 K.[12]

this study, is a change in the transition behavior. When an HDA state is depressurized and heated from low temperatures at ambient pressure, it generally transforms to a distinctly different amorphous state, low-density amorphous ice (LDA), but the transition temperature depends on the thermal history of the HDA state. States produced by isothermal pressurization at high temperatures, or annealed at high temperatures and high pressures after being produced at low temperatures, are more stable than HDA produced at 77 K by pressurizing in liquid nitrogen. The most stable HDA (vHDA) transforms to LDA at ~130 K whereas HDA produced at 77 K, i.e., unrelaxed HDA, transforms at ~117 K on heating at 2−4 K/min rate at 1 bar.[6] Moreover, isothermal depressurization of HDA in a suitable temperature range (117−140 K) may also produce LDA at low pressures (less than about 0.05 GPa).[7,8] On a subsequent repressurization, the transition reverses. This occurs at a significantly higher pressure than on depressurization, and the transition pressure increases with decreasing temperature, as shown in Figure 1. The negative dT/dp of the transition line for the LDA to HDA transition suggests that HDA has higher entropy than LDA,[9] which corresponds with their properties. It is still an unresolved issue whether the HDA−LDA transition is first-order[10] or continuous.[11]

The more extensively studied HDA state shows structural and physical properties, which are similar to those of water at ambient conditions.[13,14] Its thermal conductivity properties are typical of an amorphous state, i.e., it has a low thermal conductivity which increases slightly with increasing temperature and pressure.[8] Inelastic X-ray data show phonon-like excitations,[15] but these are limited to low enough energies to be consistent with the amorphous-like thermal conductivity.[8]

LDA has been less frequently studied, but structural investigations show that its local order structure resembles that of ice Ih and Ic, i.e., a structure with tetrahedrally coordinated water molecules.[13] Its properties also resemble those of ices I rather than liquid water. LDA shows crystal-like excitations up to higher energies than HDA,[15] a transverse sound velocity which decreases with pressure,[16] and a thermal conductivity which decreases with both temperature and pressure, which is the same behavior as that of the ices I and atypical of an amorphous state.[8] Moreover, LDA shows dielectric properties[17] which suggest that the ice-rules[18,19] limit H_2O reorientational motions, i.e., a feature normally associated with crystalline ices. The crystal-like features of LDA, which indicates some kind of unusual amorphous structure that allows for high-frequency crystal-like phonon excitations, and in which the ice-rules appear to apply, still awaits a detailed explanation. Tse and Klug[20] have suggested that amorphous ices are metastable frustrated structures and they also argued that LDA ice is an ill-formed crystalline ice.

The unusual properties of LDA and the existence of at least two distinctly different amorphous solid states of water are fundamentally important. The latter has been used in support of two distinct liquid water states with a coexistence phase line that end in a (second) critical point, as discussed in more detail in reviews.[21,22] These states have also formed the foundation for a recently suggested heterogeneous structural model of ambient liquid water.[23] In this model, which is controversial,[24] nanometer-sized domains of LDA- and HDA-like water (LDL and HDL) coexist in a dynamical equilibrium, which changes with pressure and temperature. A gradual transformation from HDL to LDL on cooling is one of the suggested explanations for the abnormal behavior of water's properties, e.g., the

decrease in density on supercooling of liquid water. Recent results also suggest that a transition between HDL and LDL states can be observed in homogeneous glycerol/water solutions and that the transition line ends in a critical point.[25,26]

The inevitable crystallization on cooling of aqueous solutions with low solute concentrations is normally associated with a phase separation into pure, or almost pure, ice and solute phases, but there are a few interesting exceptions. Some aqueous solutions form clathrate structures upon crystallization. Clathrate hydrates (CHs), or ice clathrates,[27,28] are inclusion compounds in which a hydrogen-bonded cage-like structure of H_2O accommodates molecules of suitable size, known as "guest molecules". In ice clathrates of type II structure,[26] the hydrogen-bonded H_2O network combines to form two types of cages: pentagonal dodecahedron and hexakaidecahedral with cage radii of ~3.9 Å and ~4.7 Å, respectively. Type II CHs can enclathrate relatively large molecules, e.g., 1,3-dioxolane (DXL) and tetrahydrofuran (THF) molecules, but then these accommodate the larger cages only, which corresponds to a composition of 17 H_2O per guest molecule. CHs and ice show similar geometrical arrangements of the hydrogen-bonded water network with orientational disorder of water molecules. Without the guests, the H_2O cage-like structure of CHs is normally unstable, but it was recently shown that the host framework of Ne type II clathrate hydrate remains stable when the Ne guests slowly escape under reduced pressure below 145 K.[29]

If subjected to high pressure, then the CH structure also becomes unstable despite structure stabilizing guest molecules. Suzuki[12] has shown that THF clathrate hydrate (THF CH), like ice I, collapses to an amorphous state at 1.3 GPa on pressurization at 77 K, and that the stability of the collapsed structure was improved by heating to 150 K at 1.5 GPa. Unless the collapsed state is subjected to this treatment, it reverts (partially) to the crystalline CHs phase on depressurization to 1 atm. More recently, it was noted that annealing at even higher temperatures and pressures (180 K at 1.8 GPa) improves the stability of the collapsed CH to the extent that it becomes more stable than collapsed ice at pressures near 1 atm.[30]

Since the guest molecules are equidistantly dispersed in the crystalline clathrate structure, CHs may produce a perfectly homogeneous solid amorphous water mixture on pressure amorphization. Thus, this feature provides an interesting new possibility for studies of cold water with low concentrations of solute molecules. Instead of trying to circumvent crystallization to avoid phase separation into ice, it becomes a useful process to distribute the solute. We have previously reported that type II CHs collapse in a similar, time-dependent manner as ice I on pressurization at 130 K[31] and that the collapsed states show almost identical glass transition behavior as HDA.[32−34] We show here that pressure-collapsed DXL CH and THF CHs heated to well above their glass transition temperatures (T_g) subsequently also display transitions corresponding to that between HDA and LDA ice and, thus, that collapsed type II CHs show all the unusual transition features of collapsed ice.

■ MATERIALS AND METHODS

1,3-Dioxolane (99.8%, ~75 ppm BHT as inhibitor) and tetrahydrofuran (puriss. p.a., 99.9%, less than 0.005% water) were purchased from Sigma-Aldrich Chemicals. Their solutions in pure water were prepared by weighing in concentrations of about M·16.5 H_2O, where M is the guest molecule, which is

slightly less than the ideal stoichiometry of M·17 H_2O for type II CHs.

The transient hot-wire method, which has been described in detail previously, was used for measuring the thermal conductivity.[34] The hot-wire probe used was a Ni-wire (0.1 mm diameter) placed horizontally in a ring of constant radius. The probe, surrounded by the sample, was heated by a 1.4 s pulse of almost constant power and the wire resistance was measured versus time. This enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding thermal conductivity with an estimated inaccuracy of ±2%.

In another experiment, the capacitance and conductance of a concentrical dielectric capacitor immersed in the sample were measured from 10 mHz to 1 MHz, and stored in the form of the real C' and imaginary C'' parts of the complex capacitance. In the range 10^2 Hz to 1 MHz, we used a Solartron 1260 impedance analyzer. Below 100 Hz, a HP33120A function generator was instead used to provide a sinusoidally varying signal to the sample capacitor and a reference capacitor placed in series. The voltages over the capacitors were measured simultaneously by two HP3457A voltmeters and the capacitance and conductance of the sample were determined.

The capacitor or the hot-wire probe was placed inside a Teflon container, filled with ca. 20 mL of sample, which itself closely fit inside a high pressure cylinder with 45 mm internal diameter. The whole assembly was placed in a vacuum chamber and load was applied via a steel piston by using a 5 MN hydraulic press. The pressure in the cell was determined from the ratio of load to area to which a correction for friction was applied. This correction had been previously established in a separate experiment by using the pressure dependence of the resistance of a manganin wire. The pressure of the hydraulic oil used to push the piston into the cylinder was computer-controlled at the desired rate of increase or decrease. The temperature of the pressure vessel was varied by using a built-in helium cryostat equipped with a heater. The data are accurate to within 0.05 GPa for pressure (at 1 GPa) and 0.5 K for temperature.

To form the crystalline CH, the high pressure vessel was cooled at ambient pressure until the exothermic freezing of the sample was observed; it was annealed at least 1 h near the CH freezing point to allow the solution to freeze completely to clathrate. (One sample cycled in the range 252−275 K at 1 bar during 8 h, cooled to 100 K with simultaneous pressure increase to 0.09 GPa, reheated to 260 K at 0.09 GPa, and subsequently cooled down to 132 K and collapsed by isothermal pressurization, showed identical transition behavior as a sample with only 1 h annealing.)

■ RESULTS AND DISCUSSION

Transition Behavior on Pressure Cycling at 130 K. The THF and DXL water solutions were initially cooled to ∼260 K at 1 bar to crystallize the samples and then kept a few degrees below the clathrates' freezing points of 277.4 K for THF CH and 270.5 for DXL CH for more than 1 h to ensure complete clathrate formation. Thereafter, the temperature was decreased to 100 K simultaneously as the pressure was slowly raised to a pressure in the 0.05−0.1 GPa range. After the temperature had been raised and stabilized at 130 K, κ was measured on isothermal pressurization up to 1.3 GPa as shown in Figure 2. The thermal conductivity initially increases on pressurization up to about 0.8 and 0.9 GPa for DXL CH and THF CH,
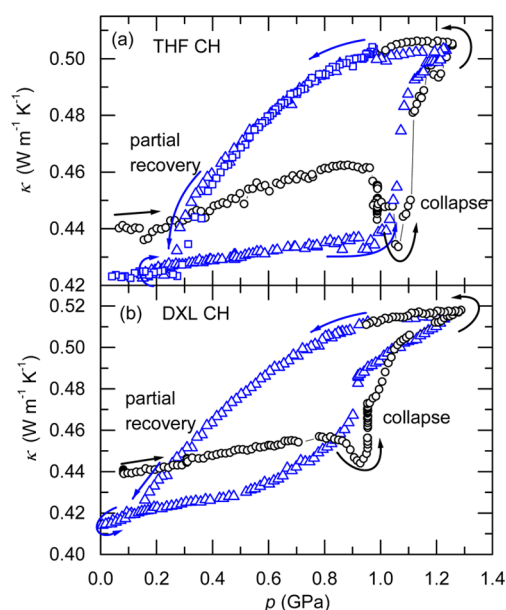

Figure 2. Thermal conductivity of CHs during pressure cycling at ∼130 K. (a) THF CH and (b) DXL CH during initial pressurization up to 1.3 GPa and depressurization to 1 GPa (○), which was followed by an isobaric temperature cycle 130−100−130 K overnight (not shown), depressurization to near 1 atm and repressurization (△), and second depressurization (□, only THF CH).

respectively. This is the normal behavior of κ upon densification of a phase. But above these pressures, κ decreases in a narrow pressure interval, which is an indication of the initial distortion of the cages before the major collapse.[30] On further increase the two CHs collapse and the density increases significantly, which is reflected in κ as an abrupt increase. This is different from the large decrease observed in κ when ice I collapses and which is typical for a change from a crystalline phase to an amorphous state (Figure 3a). The uncommon behavior for the CHs is due to the remarkably low and amorphous-like κ of crystalline CHs. Their low and glass-like κ was observed already in 1981 but is still not fully understood.[35−37] Thus, the increase in κ observed at the collapse of the CHs reflects the change from a low-density to high-density state in which phonons are strongly scattered in both states. In other words, the sample transforms from a (crystalline) phonon glass to a real glass. Therefore, κ is mainly determined by the density and, hence, increases due to the strong densification at the collapse.

The common unusual feature of pressure induced amorphization in ice and CHs, which occurs at almost identical pressures (Figure 3), has likely the same origin. In the case of ice I, it has been attributed to a mechanical instability of the lattice.[38] We note that the low-density crystal structures of CHs and ice have similar local geometrical arrangements of the hydrogen-bonded water network, with orientational disorder of water molecules, which may explain the destabilization of the lattice at similar conditions. As shown in Figure 1, there is, however, a slight guest induced stabilization effect which pushes the collapse of CHs to marginally higher pressures than that of ice.

The samples were thereafter pressure cycled, both before and after heating to a temperature well above T_g at 1 GPa, which is 139 K on a time-scale of ∼1 s,[31] to study changes in transition behaviors. Results measured by isothermal pressure cycling at 130 K, and obtained without prior treatment at higher
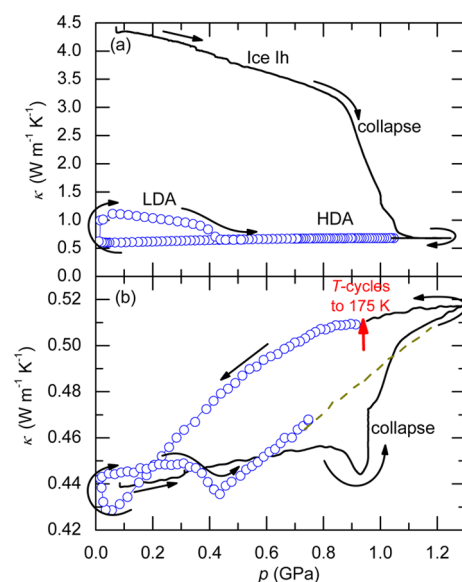
Figure 3. (a) The solid line represents κ during pressurization of ice Ih at 130 K, and circles the subsequently measured results for HDA and LDA. Arrows show the direction of pressure and κ changes. (b) The solid line represents κ during pressurization of DXL CH at 130 K. The circles show results for collapsed DXL CH on depressurization and repressurization at ~137 K after the sampled had been temperature cycled twice up to ~175 K at 1 GPa (~0.3 K/min average rate), which is a temperature well above T_g. (Results recorded during a pressurization from 0.07 to 1.2 GPa at 134 K are shown by the dashed line where the initial part of the pressurization has been removed.)

temperatures, are shown in Figure 2. The results for THF CH display a transition near 0.3 GPa on depressurization, which is due to a partial transition back to the as-made CH, as reported previously.[30] On repressurization, the partially recovered THF CH collapses again near 1 GPa, as shown by the abrupt increase of κ, which occurs at almost the same pressure as the initial collapse. The lower κ, and its weaker pressure dependence, distinguish the state from the as-made sample and suggest that the state is a partially recovered CH with significant disorder. The corresponding results for DXL CH show more gradual changes with a large hysteresis. These results can be accounted for by a hysteresis in the density, which is partly due to the reversal of frictional on repressurization, but a small abrupt increase near the collapse pressure indicates that the sample also transformed (partly) back to the as-made CH. These transformations do not have the same signatures as the HDA to LDA ice on depressurization after pressure-collapse of ice Ih, and the subsequent LDA to HDA ice transition on repressurization. In particular, κ of the collapsed CHs decreases at the transition on depressurization, whereas it increases at the HDA to LDA transition (Figure 3a), and the transition pressure is significantly higher than that shown by collapsed ice in Figure 3a. On repressurization, the LDA to HDA transition is characterized by an abrupt decrease in κ (Figure 3a), whereas the results shown in Figure 2 increase gradually up to the collapse pressure and then more abruptly as a result of the renewed (partial) collapse.

Transition Behavior after Heat Treatment above T_g at 1 GPa. A series of measurements were thereafter done on samples that had been heated to above 130 K at 1 GPa. The samples were typically heated twice to a temperature in the

165−175 K range at 1 GPa, which is well above T_g of HDA and collapsed CHs, but below the crystallization temperature of the latter.[31,39] Figure 3 shows the transition behavior on depressurization and subsequent repressurization of DXL CH at 137 K. The results mimic the behavior of the HDA−LDA transformations of ice with a slight shift in the transition coordinates, especially at the lowest temperature (Figure 1).[40] This can be an effect of the guest molecules similar to that observed for the collapse, which is also shifted to increasingly higher pressure as the temperature of the amorphization process decreases, as shown in Figure 1.

Isobaric results showed the same transition behavior as the isothermal results. That is, samples that had not been subjected to temperatures above 130 K at 1 GPa did not display a HDA to LDA type of transition on heating, whereas samples that had been heated to well above T_g did show the transition. Figure 4a
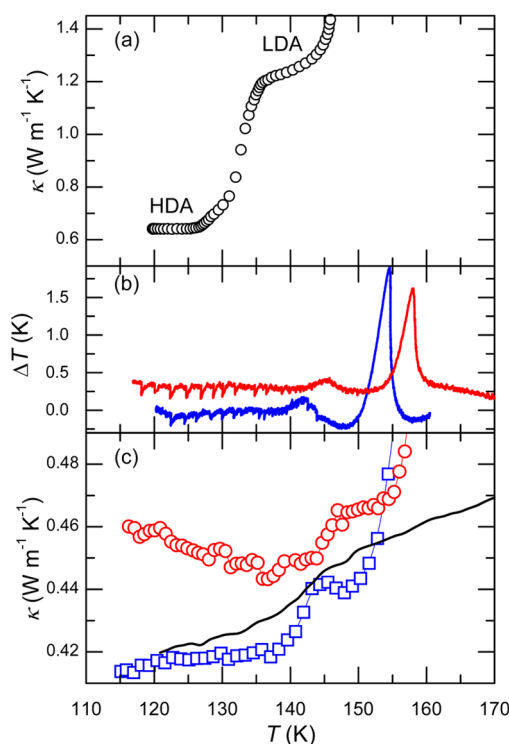

Figure 4. (a) Thermal conductivity plotted against temperature during heating of HDA at 0.04 GPa. (b) Excess temperature plotted against temperature for THF CH and DXL CH during heating at 0.07 GPa. (The latter has been shifted vertically by 0.3 K for clarity. The excess temperature was calculated by extracting a baseline from the data for temperature versus time.) (c) Thermal conductivity plotted against temperature for: (□) THF CH and (○) DXL CH during heating at 0.07 GPa after heat treatment well above T_g at 1 GPa. The line shows corresponding results for THF CH at 0.05 GPa without heat treatment. (The results for DIOX CH have been shifted vertically by 0.01 W m^{-1} K^{-1} for clarity.)

shows the transition behavior on heating of HDA at 0.04 GPa, where the sample transforms in the sequence HDA → LDA → ice Ic. The two collapsed CHs, which had been heated to well above T_g at 1 GPa, show similar behavior but with the transitions shifted to somewhat higher temperatures (Figure 4b and c). However, a CH that had been collapsed at 130 K, but subsequently not heated above 130 K before cooling to 120 K and then reheated at 0.07 GPa, did not display a similar sequence on heating (Figure 4c).

We can conclude that pressure-collapsed CHs, which have been heated to temperatures well above T_g at 1 GPa, display a transition that shows all the features as the HDA−LDA transition of ice. On isothermal depressurization, the collapsed CH transforms to a low pressure state near ambient pressure, and on a subsequent repressurization, the reverse transition occurs at a higher pressure, i.e., there is a significant pressure hysteresis and it increases on temperature decrease. Thus, the reversal transition has a negative dT/dp like that of the LDA to HDA transition, and the transition coordinates are almost identical, as shown in Figure 1. The thermal conductivity also changes in a similar manner; it increases at the transition from the high to low pressure state, and decreases at the reverse transition. Moreover, the thermal conductivity of the low pressure state is independent of pressure, which is unusual, and the slight difference from the likewise unusual decreasing thermal conductivity of LDA is likely an effect caused by the guest molecules.

Features in Thermal Conductivity and Complex Capacitance on Heating of the Collapsed States at 1 GPa. In order to investigate, in detail, the changes that occur on heating at 1 GPa, we have studied the behavior in both κ and complex capacitance. From these results, it is obvious that the collapsed CHs change irreversibly on heating. Figure 5a
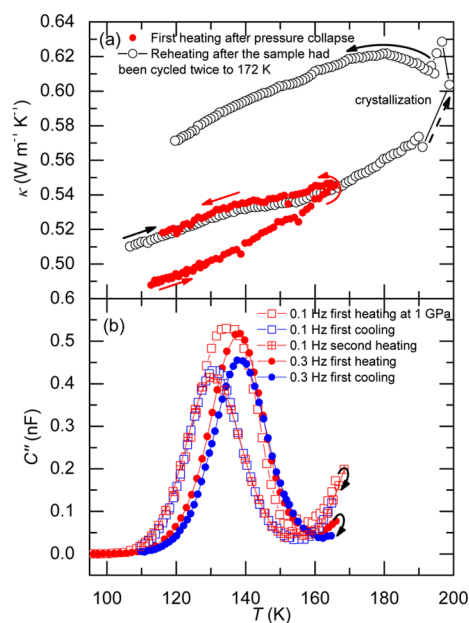

Figure 5. Results for collapsed THF CH on temperature cycling at 1 GPa after pressurization of as-made (crystalline) THF CH up to 1.3 GPa at ~130 K: (a) thermal conductivity and (b) imaginary part of the capacitance measured at constant frequency.

shows the changes in κ for collapsed THF CH on temperature cycling at 1 GPa after the collapsed state had been obtained by pressurizing the as-made CH to 1.3 GPa at 130 K. Although results on heating and cooling always differ slightly due to reversal of frictional forces and changes in thermal gradients, the difference shown in Figure 5a is larger than the normal difference. Results for a heating run after the sample had been heated twice to a temperature near 170 K range show, however, good agreement with results on cooling (Figure 5a). (This run also shows that the sample can remain in the metastable collapsed state up to about 190 K at 1 GPa, where it crystallizes

abruptly.) Data for C'' at constant frequency, shown in Figure 5b, also suggests that the sample changes irreversibly on heating. The major change in the dielectric response seems to occur below 140 K. This can be deduced by the difference in two data sets for probe frequencies 0.1 and 0.3 Hz, respectively. These data sets were recorded simultaneously during temperature cycling of a collapsed THF CH. (In this case, the sample had been pressure collapsed by pressurization to 1.3 GPa at ~135 K.) The temperatures of the maxima in C'' at 0.1 and 0.3 Hz probe frequency are 134 and 138 K, respectively. As shown, there is a significant difference between data on first heating and subsequent cooling for C'' measured at 0.1 Hz, whereas those measured at 0.3 Hz change less. This suggests that the most important changes in the dielectric response occur just below 140 K. We note that this is near the glass transition of collapsed CHs.[31]

The irreversible change that occurs on first heating of CHs up to ~165 K is reminiscent of the changes that occur on heating HDA ice at 1 GPa. For HDA it has been shown that the state homogenizes and densifies on heating.[2,3] That is, crystal remnants that may survive the collapse process are removed which improves the stability of the state. As a result, the HDA to LDA transition that occurs on heating at low pressures shifts to a 10 to 15 K higher temperature.[7] A similar homogenization and densification of collapsed CHs can explain the narrowing of the relaxation peak measured at 0.1 Hz frequency, which is observed on temperature cycling at 1 GPa. It also explains the increased stability of the collapsed state and the consequential vanishing of the partial transformation back to the as-made CH on depressurization.[29] The recrystallization transition observed in a collapsed CH without additional heat treatment is therefore probably restrained by a high energy barrier against the formation of crystalline nucleus. However, the homogenizing process does not explain the occurrence of a new transition, which corresponds to the HDA to LDA transition of pure pressure amorphized ice.

Microstructural Changes on Heating at 1 GPa. Although it is difficult to exactly determine the recipe to obtain the HDA to LDA type of transition in collapsed CHs, it does require heating of the collapsed state at high pressure. Our results indicate that the transition arises when the collapsed state has been subjected to temperatures above 170 K at 1 GPa, or prolonged heat treatment near 170 K, and it may also be enhanced by the temperature gradient caused by the hot-wire probe. That is, it is not sufficient to homogenize the samples. In fact, it seems that it requires (new) inhomogeneities to arise in the collapsed CHs and that these arise due to additional heat treatment. Support for such inhomogeneities is obtained by a detailed comparison of the dielectric spectra shown in Figure 6. One of these was obtained for a collapsed THF CH, which had been heated once to 150 K at 1 GPa, and thereafter kept at 140 K during 8 h. According to the dielectric results obtained on temperature cycling, this treatment should be sufficient to complete the major irreversible changes that occur initially on heating the collapsed state at 1 GPa. The second spectrum was obtained after the sample had thereafter been cycled to 180 K at 1 GPa. Apparently, the treatment at higher temperatures than 170 K, which is well above T_g, causes a slight increase in the C'' peak width. This broadening of the spectrum suggests an inhomogeneous sample. A feature that can explain this is a very sluggishly occurring partial phase separation into water enriched and guest enriched water domains, i.e., the latter would have less H_2O content than the nominal one of the type
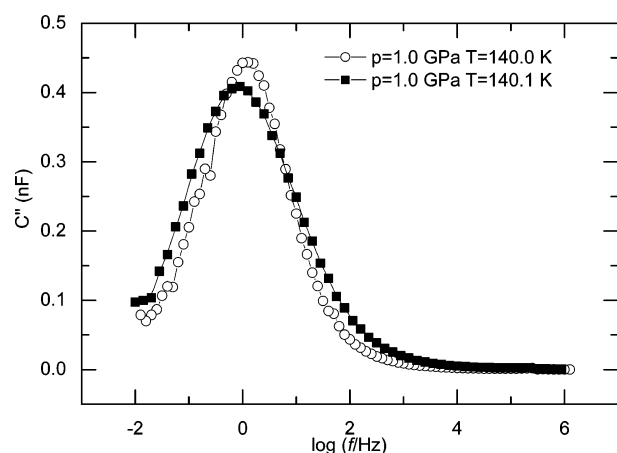
Figure 6. Dielectric loss plotted against logarithm of frequency for THF CH at about 1 GPa and 140 K. Open symbols show results after the pressure collapsed sample had been cycled once to 150 K at 1 GPa, and thereafter annealed at 140 K during 8 h (without noticeable change in the spectra). The filled symbols show the results after the sample had thereafter been cycled one time to 180 K at 1 GPa.

II CH (THF·17 H_2O). Subsequently, the former state would display a HDA to LDA transition concurrently as the removal of crystal residues remaining after the collapse and/or the increased THF (or DXL) concentration in the guest enriched water state inhibit recrystallization into the type II CH. If this is indeed the case, then the phase separation does not proceed to such an extent that it gives large domains of pure water as these would crystallize above 153 K,[33] whereas the collapsed CHs can remain stable up to 190 K (Figure 5a). It means that small domains of pure water in CHs can transform between the LDA and HDA states and still remain stable when heated well above T_g at high pressure. This scenario of a sluggish phase separation due to increased diffusivity above T_g appears as the most likely explanation but an HDA−LDA type of transition in a collapsed CH of ideal type II composition cannot be excluded. We note that the former would also explain the behavior on heating at low pressure, where the collapsed CHs display a transition sequence that suggests a final transition into a phase with high thermal conductivity, i.e., a crystalline ice.

The high stability of collapsed CHs compared to collapsed ice has also been discussed by Tulk et al.[41] for a type I CH of deuterated methane hydrate, $CF_4·6.26 D_2O$, which collapsed to an amorphous state at 3.2 GPa during pressurization at 100 K. Tulk et al.[40] showed that the collapsed CH state was stable up to high temperatures before it crystallized and phase separated, e.g., near 220 K in the 1.5 to 4 GPa range, which is significantly higher than for collapsed ice. They attributed the high stability to low mobility of the water network and calculated a very low self-diffusion coefficient of methane through the water network near the crystallization temperature at high pressure. Prior to crystallization, the collapsed state densified gradually on heating, and they referred to the densified state as a VHDA form of methane clathrate, in analogy with the ultimately densified state of pressure amorphized ice. These results of Tulk et al. are supported by English and Tse's simulation study of methane hydrate.[42] English and Tse also concluded that "amorphized hydrates cannot be assumed to be arrested disordered liquid mixtures". Besides the fact that our results for the type II CHs show a glass transition (see below), which could be due to a transformation from a glass to a liquid state,

these results are in good correspondence with our interpretations of the changes that occur on heating of type II collapsed CHs at 1 GPa.

Finally, we note that the values for κ of the homogenized, or relaxed, collapsed CHs show indication of the previously reported glass transition near 140 K.[31] Previously reported data for heat capacity show an increase typical of a glass transition at 139 K on both heating and cooling at 1 GPa. The unfrozen states, as compared to the glassy states, have excess heat capacities of $(3.9 ± 0.4)$ J $(H_2O\text{-mol})^{-1}$ K^{-1} and $(3.7 ± 0.4)$ J $(H_2O\text{-mol})^{-1}$ K^{-1} for collapsed DXL-CH and THF-CH at 1 GPa,[31] respectively, which is the same as for vHDA.[33] The heat capacity increase at the glass transition was observed independent of heat treatment at 1 GPa, i.e., the heat capacity is unaffected by the irreversible processes. This is not the case for κ. As shown in Figure 5a, it is possible to detect a weak decrease in the temperature derivative of κ near 140 K on cooling and second heating, i.e., after the sample has been relaxed. Such a change in temperature slope of κ is typically observed at glass transitions, and it is normally attributed to the change in the thermal expansion coefficient at T_g. A similar, but more pronounced, change from positive slope below T_g to negative above has been reported for HDA ice.[33] The dynamic hot-wire method used here to measure κ typically shows glass transition features at temperatures where the relaxation time is slightly less than 1 s.[43] Thus, the change of slope in κ at 140 K is in good agreement with the dielectric loss data. These show a loss peak at ∼140 K for measurements using a probe frequency f of 0.3 Hz, which give a dielectric relaxation time τ_d of about 0.5 s at 140 K ($\tau_d = 1/2\pi f$).

■ CONCLUSIONS

As shown here, it is possible to detect the HDA to LDA type of transitions in collapsed CHs after heat treatment at high temperatures and pressures. This means that collapsed CHs mimic exactly the low temperature transition behavior of water, i.e., pressure induced amorphization/collapse and the further transformations of the collapsed state: a glass transition and an HDA to LDA type of transition. Moreover, the heat capacity step at the glass transition of collapsed CHs is the same as that of pure water, and occurs at the same temperature. Furthermore, the transition coordinates of the HDA−LDA type of transition of collapsed CHs are almost the same as those of pure water.

We have identified two features that can occur during treatment of collapsed CHs above T_g at 1 GPa and explain the change from a transition behavior where the as-made CH is partially recovered on depressurization to one which gives an LDA type of state. The initial process during heating at 1 GPa is likely a homogenization and densification process in which all crystalline remnants that survive the collapse are destroyed,[29] i.e., a process very similar to that observed when HDA is heated near 1 GPa.[2,3] This means that subsequent recrystallization requires nucleation, and therefore the stability of the collapsed state increases. On further heating to above ∼170 K at 1 GPa, or prolonged heat treatment above the glass transition, another process occurs which eventually leads to an HDA to LDA type of transition on depressurization. We attribute this to a partial phase separation into water enriched and guest enriched domains, respectively, where the enrichment refers to the nominal THF CH composition of 17 H_2O per guest molecule. This seems to be a sluggish process, which is enabled by the increase of the diffusivity above T_g. However, despite this

process, the collapsed CHs can remain stable up to 190 K. This means that large domains of pure water cannot arise because pure water crystallizes at 153 K at 1 GPa.

The most significant interest in HDA and LDA ices has been devoted to the possibility of two liquid counterparts, and their coexistence in equilibrium, as suggested in models put forward to explain the abnormal properties of supercooled water.[21] The results here suggest that the collapse of CHs produces amorphous water solutions in which the HDA–LDA type of transitions arise in a similar manner as in pure water. The states show much (HDA) and somewhat (LDA) higher stability against crystallization than those of collapsed ice. We can thus conclude that pressure-amorphization provides a path to form a mixture of amorphous water and solute molecules in low concentration (<6 mol %), and that this state shows identical transition properties as pressure-produced amorphous water in its stable range.

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Notes

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■ ABBREVIATIONS

CH, clathrate hydrate; DXL, 1,3-dioxolane; HDA, high density amorphous ice; LDA, low density amorphous ice; p–T, pressure–temperature; THF, tetrahydrofuran

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