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Discovery of a low-density filled-ice phase in nitrogen hydrate at high pressure



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Nitrogen, Earth's most abundant atmospheric component, in the presence of water, is known to form clathrate hydrates, that are relevant to model the evolution of water-rich planets and satellites. Here, we map the high-pressure phase diagram of nitrogen hydrate up to 16 GPa at room temperature by combining neutron diffraction, Raman spectroscopy, and crystal structure prediction. We reveal a rich sequence of structural transformations, from sI/sII clathrates to hexagonal (sH) and tetragonal (sT) phases, culminating in a previously unknown orthorhombic filled-ice structure above 1.8 GPa. This new phase cannot be indexed to any known ice frameworks and exhibits a density approximately 30% lower than that of stable ice VII, pointing to distinctive water-nitrogen interactions. Our results refine the understanding of nitrogen hydrate behavior under extreme conditions and demonstrate the propensity of N₂ and H₂O to form stable filled-ice structures up to 16 GPa, with important implications for planetary science.

Water exhibits an exceptional diversity of crystalline and amorphous phases depending on thermodynamic conditions, including at least 20 distinct ice polymorphs^{1,2} and several metastable amorphous forms³. In the presence of guest molecules, water forms complex inclusion compounds—gas hydrates—where small guest species are encapsulated within a hydrogen-bonded lattice⁴. Among these, clathrate hydrates adopt cage-based architectures stabilized by a delicate balance of van der Waals forces, hydrogen bonding, and hydrophobic interactions. These materials are of interest not only for fundamental studies of intermolecular interactions but also for their roles in geophysics, planetary science, and gas storage technologies^{5–8}.

Nitrogen (N₂), Earth's most abundant atmospheric component, is known to form clathrate hydrates with water under pressure^{9–13}. These inclusion compounds are relevant to paleoclimate reconstructions from ice cores, to models of volatile inventories on icy moons such as Enceladus and Titan^{14–16}, in water-rich exoplanets^{17,18} and to energy research through guest-exchange processes with methane hydrates¹⁹. In large icy moons²⁰ and ocean-planets^{17,18}, the pressure in the hydrosphere can exceed 1 GPa. Most volatile elements, including N₂, are stable in the form of high-pressure gas hydrates²¹. Understanding the phase behavior as a function of increasing pressure is essential to determine the deep cycle of volatile elements and their consequences for atmosphere generation and evolution for large icy

moons and exoplanets. Nitrogen clathrate hydrate is particularly relevant in the case of Titan, which has a dense atmosphere dominated by nitrogen, whose origin is still debated²².

At low and moderate pressures, nitrogen hydrate crystallizes in both cubic structure I (sI) and structure II (sII), with sII favored at higher pressures and after longer equilibration times^{9,23}. Further compression induces a series of structural transformations: around 0.8 GPa, a hexagonal sH phase emerges, followed by a tetragonal sT phase²⁴. This sequence, reflecting increasing guest-host interactions with pressure, mirrors the behavior seen in other gas hydrates such as hydrogen²⁵ and argon^{26,27}. Furthermore, a chiral channel structure (s_χ), isostructural to the C₀ phase of hydrogen hydrate²⁸, has been obtained by reloading an emptied C₀ hydrogen hydrate with nitrogen^{29–31}.

While the stability of nitrogen clathrate hydrates at moderate pressures is well established, the behavior of the water-nitrogen system at higher pressures (>1.5 GPa), relevant for the deep interiors of large icy moons (Titan, Ganymede and Callisto) and water-rich exoplanets, remains poorly characterized and actively debated. Above 1.8 GPa, the classical clathrate frameworks give way to denser, non-clathrate structures known as filled ices (FIS), in which guest molecules occupy interstitial sites of a hydrogen-bonded water lattice derived from known ice polymorphs^{25,32}. For nitrogen,

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a filled-ice phase, referred to as NH-IV, analogous to methane hydrate III (MH-III) crystallizing in the orthorhombic *Imma* space group, has been proposed²⁴. However, published diffraction data show additional Bragg reflections that cannot be satisfactorily explained by this model, suggesting that the high-pressure behavior of the system could be more complex.

The NH-IV phase exhibits a proton-disordered, ice-like framework comprising four-, six-, and eight-membered rings. Although it bears some resemblance to ice Ih in certain crystallographic projections, its topology is sufficiently distorted to accommodate a high nitrogen content, with a $\text{H}_2\text{O}:\text{N}_2$ ratio of about 2:1. In comparison, the preceding sT phase contains fewer guest molecules ($\sim 3:1$), indicating significant nitrogen enrichment during the transition to the filled-ice state—a behavior also observed in high-pressure hydrogen³² and methane³³ hydrates. Sasaki et al.³⁴, in their Raman spectroscopy study, reported the presence of at least three phases (NH-I, NH-II, and NH-III), while being unable to detect a distinct signature of the sT phase observed in neutron diffraction experiments. The phase labeled NH-III was attributed by the authors to the orthorhombic dihydrate previously identified by Loveday et al.²⁴, and was reported to be stable up to 6 GPa.

Whether stable $\text{N}_2\text{-H}_2\text{O}$ compounds persist to even higher pressures remains controversial. Zhang et al.³⁵ proposed that above 6 GPa, the nitrogen-water system becomes immiscible, in contrast to the remarkable stability of hydrogen and methane hydrates up to megabar pressures^{25,36}. In this regime, nitrogen was observed as fine-grained aggregates embedded in the ice matrix, rather than as a crystalline compound. To date, no Rietveld refinements have been reported above 1.5 GPa, leaving open the question of whether well-defined molecular $\text{N}_2\text{-H}_2\text{O}$ structures exist beyond the clathrate regime.

In this work, we present a comprehensive study of the high-pressure phase diagram of nitrogen hydrate, combining neutron diffraction, Raman spectroscopy, and structural prediction to probe pressures up to 16 GPa at room temperature and down to 80 K at 2.1 GPa. Our results uncover a rich sequence of structural transitions, clarifying the stability and coexistence domains of known phases and revealing a previously unreported filled-ice phase above 1.8 GPa, which cannot be indexed within the NH-IV framework. We designate this new phase NH-V and show that it remains stable up to 5.2 GPa at both room and low temperatures, before transforming into the known NH-IV phase at higher pressures.

The pressure-temperature stability field of NH-V is particularly relevant to the interiors of icy moons such as Titan, Ganymede, and Callisto, with implications for their volatile budgets, redox conditions, and potential habitability. Furthermore, structural analogies among O_2 -, H_2 -, and N_2 -filled ices suggest possible surface co-localization and enhanced reactivity of these species, linking hydrate physics to planetary geochemistry.

Figure 1 summarizes the current understanding of the nitrogen hydrate phase evolution up to 16 GPa at room temperature, combining previous studies^{24,34} with our new data. This diagram provides a reference framework for the discussion that follows, where we detail the structural nature of the newly observed NH-V filled-ice phase and the transition region between clathrate and filled-ice regimes.

Results and discussion

In order to follow the pressure evolution of nitrogen hydrate, hydrogenated $\text{N}_2\text{-H}_2\text{O}$ samples (prepared as described in the Methods section) were cryoloaded into a diamond anvil cell and cycled between 0.4 and 16 GPa while collecting in situ Raman spectra. The pressure cycling of the DAC between 0.4 and 16 GPa served two purposes. First, after initial compression and a holding period at 16 GPa, the hydrate was observed to partially decompose. The sample was therefore decompressed until all components were in the liquid state and subsequently recompressed in order to reform the clathrate hydrate under controlled conditions. Second, the decompression path proved to be spectroscopically informative: upon decompression, it was possible to observe the pure sT phase without the coexistence of the sH phase. This procedure thus allowed both the regeneration of the hydrate and a clearer identification of the sT phase.

Figure 2 shows representative Raman spectra of the $\text{N}\equiv\text{N}$ stretching band across the various hydrate phases (left), the pressure evolution of the Raman shift (center, right), and comparison with literature data for pure nitrogen³⁷ and previously measured nitrogen hydrates³⁴. Spectral features were assigned based on phase-specific trends and cross-validated with diffraction data.

At ambient temperature and 0.3 GPa, diffraction data (Fig. 3, top left) confirm the presence of the cubic sII clathrate ($Fd\bar{3}m$), with refined lattice parameter $a = 17.117(1)$ Å. Raman spectra in this range display two $\text{N}\equiv\text{N}$ stretching bands at 2324.5 and 2325.5 cm^{-1} , attributed to nitrogen molecules in large and small cages, respectively. Below 1 GPa, spectra in some parts of the samples showed only a single stretching band consistent with Sasaki et al.³⁴, likely reflecting incomplete crystallization or local disorder during nucleation. Neutron diffraction (Figure SI-1 and Supplementary Note 1) also detected metastable sI-type clathrate ($a = 11.824(2)$ Å) after loading at 0.6 GPa, suggesting sI-to-sII conversion may not have been fully complete. The coexistence of sI ($Pm\bar{3}n$) and sII ($Fd\bar{3}m$) and nonuniform cage filling may account for anomalies in the low-pressure Raman spectra, including deviations from the expected large-to-small cage intensity ratios.

Upon compression to 0.8 GPa, diffraction and Raman data indicate a transition to the hexagonal sH phase ($P6/mmm$), with refined lattice parameters $a = 11.993(2)$ Å and $c = 9.936(5)$ Å (Fig. 3, top right). The broad diffraction feature indicates residual excess water present among the loaded clathrate hydrate as ice Ih. Its presence is due to incomplete transformation of water ice Ih into sI clathrate during the ex situ synthesis. Raman spectra at this pressure exhibit three bands ($\sim 2328\text{--}2329.5$ cm^{-1}), assigned to nitrogen in distinct cage sites: L, S, and S' cages (i.e. large, small with radius 3.91 Å, and small with radius 4.06 Å, respectively³⁴).

At 0.9 GPa, a tetragonal sT phase ($P4_2/mnm$) appears, coexisting with sH and ice VI (Figure SI-2, Supplementary note 2). Raman spectra were acquired both upon compression and decompression. During compression, the sH phase persists metastably together with sT, probably due to kinetic limitations (Raman measurements are relatively fast and may not allow sufficient time for the sH-sT transformation to fully complete). On the contrary, during decompression, the system evolves from the filled-ice phase directly into the sT phase, thereby avoiding the formation of sH and resulting in a single-phase sT sample. The sT phase, better identified upon decompression in the Raman spectra due to the absence of coexisting sH phase, exhibits a sharp single $\text{N}\equiv\text{N}$ Raman band around 2329 cm^{-1} , consistent with its single-cage topology (see pink dots in Fig. 2). Le Bail refinement at 1.4 GPa yields $a = 6.312(1)$ Å, $c = 10.578(10)$ Å.

The apparent differences in the reported sH-sT transition pressures arise from the use of different experimental probes and compression protocols, as well as from kinetic effects that are common in high-pressure studies of water-rich compounds. In the neutron diffraction experiments, the sH phase is first observed at 0.84 GPa, followed by clear sH/sT coexistence at 0.9 GPa, and the appearance of a single sT phase at 1.4 GPa. In contrast, in the Raman experiments performed upon compression, the sH structure is identified over a broader pressure range, from 0.9 up to 1.6 GPa, with sH/sT coexistence observed between 1.6 and 1.8 GPa. Slightly different transition pressures were also observed upon decompression. These discrepancies can be attributed primarily to differences in compression rate and equilibration time. Raman measurements are relatively fast, whereas neutron diffraction patterns were collected over 2–3 h at each pressure point, allowing the system to approach equilibrium more closely. Under these quasi-equilibrium conditions, the transformation from sH to sT proceeds more completely, resulting in the earlier appearance of pure sT in the neutron experiments. Small hysteresis effects and modest variations in transition pressures between compression and decompression are therefore expected, and similar variations are reported in the literature for related hydrate systems. The small differences with respect to references^{24,34} likely originate from the same kinetic and protocol-dependent factors.

Above 1.8 GPa, the clathrate framework collapses, and diffraction patterns collected at 2.1 GPa (Fig. 3, bottom right) show a transition to a new phase. Initial fits using the orthorhombic *Imma* model (NH-IV) reported by

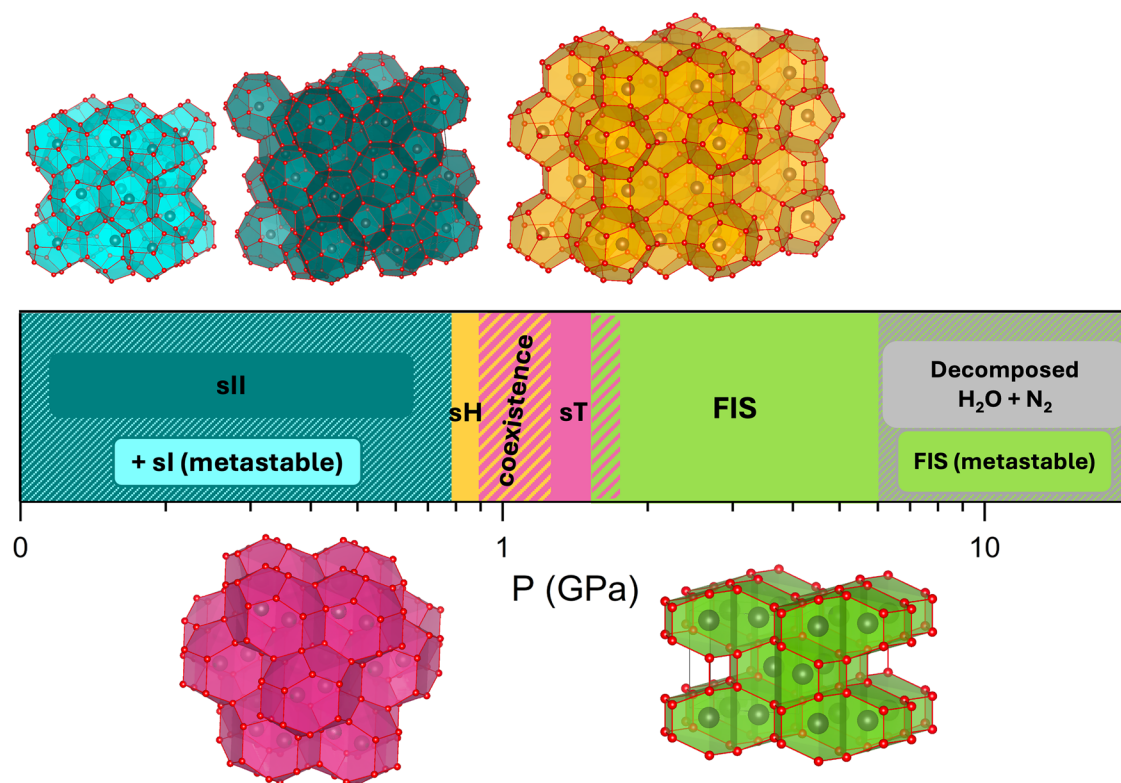


Fig. 1 | Structural transition sequence of nitrogen hydrate at 295 K as a function of pressure. Structural transition sequence of nitrogen hydrate at 295 K as a function of pressure, as observed in this work *via* high-pressure neutron diffraction and Raman spectroscopy.

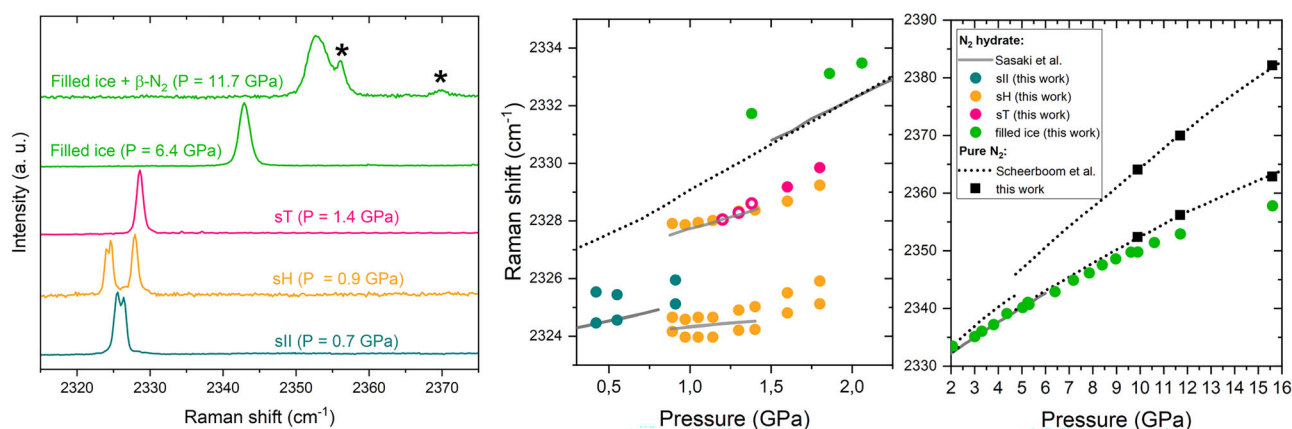


Fig. 2 | Raman spectroscopy data acquired at 295 K. Left: Raman spectra of the N≡N stretching bands of nitrogen hydrate. The pressure at which the spectra were acquired is reported beside each spectrum. All spectra were acquired upon compression except for the sT phase one at 1.4 GPa and the filled ice one at 6.4 GPa, both acquired upon decompression. Figure SI-8 shows a spectrum of sT phase coexisting with sH acquired upon compression and with a higher resolution spectrometer. In the top spectrum, the pure N₂ present in some parts of the samples together with N₂-filled ice is marked with two asterisks. Center and right: Raman shifts of pure and hydrated N≡N stretching bands. The data represented by circles and squares are

from this work. As indicated in the legend, data from the sII phase are reported in blue, sH phase in yellow, sT phase in pink, and the filled-ice phase in green. The full circles are from data acquired upon compression, while the empty ones come from acquisitions upon decompression. With black squares we reported the pure N₂ present in some parts of our samples together with N₂-filled ice. The pressure evolution of pure nitrogen stretching bands is from Scheerboom et al.³⁷ and are reported with small dots, while the full gray lines are relative to the trend of the nitrogen hydrate studied by Sasaki et al.³⁴

Loveday et al. did not fully account for an extra Bragg peak at $d \sim 2.7$ Å, also observed in prior studies²⁴. Previous works on methane hydrate (largely isostructural to nitrogen hydrate at high pressure) also reported the occasional presence of a metastable primitive orthorhombic phase upon compression to 1.8 GPa³⁸. This suggests a distinct polymorph, here designated as NH-V. Refinement using a primitive orthorhombic cell (*Pnma*) gives $a = 8.594(2)$ Å, $b = 5.097(5)$ Å, $c = 7.543(2)$ Å. Evolutionary structure search calculations support a *Pnma* model, within 1 meV/atom from the *Imma*

phase at 2.1 GPa, with a 2:1 H₂O:N₂ ratio and hydrogen bond motifs similar to high-pressure methane hydrates³⁸. Structural analysis reveals a collapse of the 4²5⁸6⁴ (see ref. 39 for notation explanation) sT cages into octagonal, nitrogen-filled 1D channels constructed from cross-linked water hexamers and windowpane-like tetramers, highlighting the topological relationship between clathrate and filled-ice structures (Fig. 4). The NH-V (*Pnma*) phase remains stable up to ~ 5.2 GPa before transforming into the more symmetric NH-IV (*Imma*) phase, which persists under further compression.

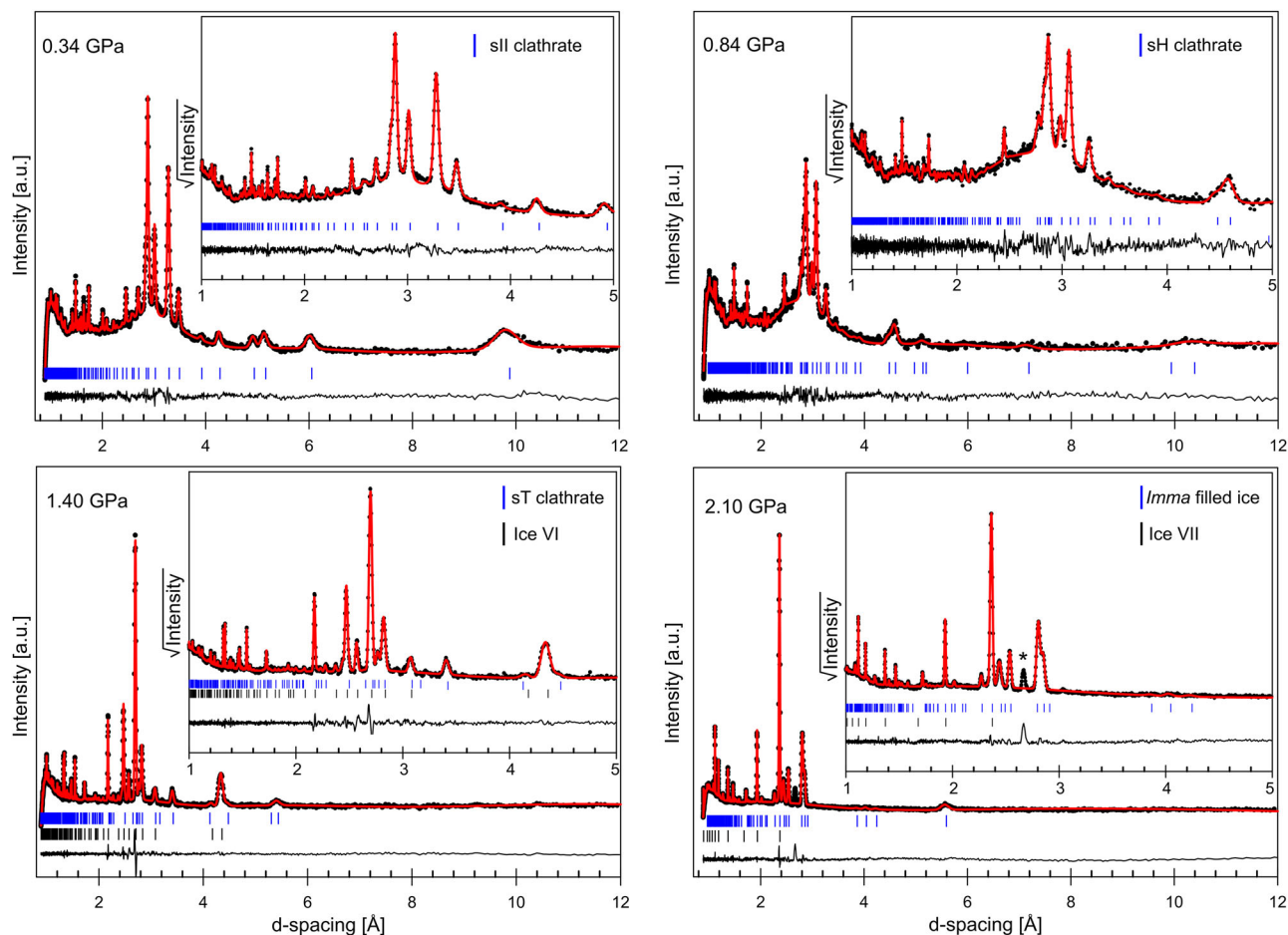


Fig. 3 | Neutron diffraction patterns of a powder sample of deuterated nitrogen hydrate collected upon compression at 295 K. Neutron diffraction patterns of a powder sample of deuterated nitrogen hydrate collected upon compression at 295 K

in a PE press on D20 beamline of ILL ($\lambda = 1.54 \text{ \AA}$). The red line is the refined pattern using Le Bail fit with Topas software, while the data are reported in black.

The NH-IV phase can also be recovered metastably upon decompression to 2 GPa (Figure SI-3, Supplementary note 3).

Table 1 summarizes the crystallographic and compositional data for all identified phases.

Raman spectra confirm that NH-IV (*Imma*) remains stable up to 16 GPa under slow compression (0.1 GPa/h), exceeding previous stability estimates³⁴ and suggesting greater structural adaptability compared to O_2 ⁴⁰ and Ar hydrates⁴¹. After two weeks at 10 GPa and room temperature, however, NH-IV decomposed into pure N_2 (evident from the δ -phase doublet in Raman^{37,42}), and ice VII, indicating its metastability over long timescales—similar to H_2 hydrates²⁵.

To quantify the compressibility of the NH-V phase and assuming the orthorhombic *Pnma* symmetry, we fitted the pressure-volume relationship derived from neutron diffraction data between 2 and 7 GPa with a second-order Birch-Murnaghan isothermal equation of state ($P = 3/2 \cdot B \cdot ((V_0/x)^{2/3} - 1)$)^{43–45}. The resulting fit (Fig. 4 panel g) yielded the bulk modulus $B_0 = (11.6 \pm 0.6) \text{ GPa}$, and a reference volume of $V_0 = (379 \pm 3) \text{ \AA}^3$ ($R^2 = 0.99528$). For comparison, the bulk modulus of the methane hydrate filled ice was reported to be $(15.2 \pm 0.5) \text{ GPa}$ ⁴⁶, $(15.4 \pm 0.5) \text{ GPa}$ ⁴⁷, 16.9 GPa ⁴⁸. As the overall bulk modulus is mainly affected by rigidity of the hydrogen-bonded network, the results support the structural similarity of the water network in MH-III and NH-V. The small variations of the bulk modulus can be ascribed to the different host-guest dispersion interaction in the two substances.

A second hydrate sample was brought above 2 GPa. This time the compression was effectuated more rapidly (0.3 GPa/h instead of 0.1 GPa/h),

and pure sT phase was observed (Fig. 3). Also, in this case, sT showed again a direct transition into the lower symmetry (*Pnma*) NH-V instead of (*Imma*) NH-IV, confirming the sequence of transition. To examine the thermal stability of NH-V, the sample was cooled to 90 K at 2.6 GPa and then heated to 300 K, collecting diffraction patterns throughout (Fig. 4g). The Le Bail refinement of the 91 K data yielded cell parameters of $a = 8.548(39) \text{ \AA}$, $b = 5.039(30) \text{ \AA}$, and $c = 7.382(32) \text{ \AA}$. The thermal expansion behavior was modeled using the semi-empirical expression proposed by Hester et al.⁴⁹, replacing the lattice parameter a_0 with volume V_0 at 91 K ($318.4 \text{ \AA}^3$). The values of the fit, provided in Fig. 4f, resulted in $V_1 = (2.7 \pm 0.5)10^{-5}$, $V_2 = (-4.1 \pm 1.5)10^{-7}$, $V_3 = (6.1 \pm 0.7)10^{-9}$ ($R^2 = 0.9996$). When comparing the relative thermal expansion of NH-V at 2.6 GPa with literature data for ambient-pressure sI N_2 , CH_4 , and CO_2 clathrates (see Fig. SI-4, where volumes normalized to the value at 91 K are plotted as a function of temperature), NH-V appears to expand less than typical clathrate structures, which is likely a pressure effect. However, the thermal expansion of NH-V begins to plateau around 90 K, closely mirroring the behavior of deuterated ice Ih. This similarity is consistent with the structural relationship between NH-V and a distorted hexagonal ice framework⁵⁰.

To further investigate the nature and thermodynamic stability of the newly observed high-pressure phase NH-V, we performed a combination of fixed- and variable-composition structure prediction calculations using the evolutionary algorithm as implemented in the USPEX code, constrained to H_2O and N_2 molecules⁵¹ and enthalpies were computed using Quantum ESPRESSO. Structure prediction calculations were performed at 2 and 4 GPa for the 2:1, 4:1, 5:1, 6:1 and 5:3 compositions. The most stable crystal

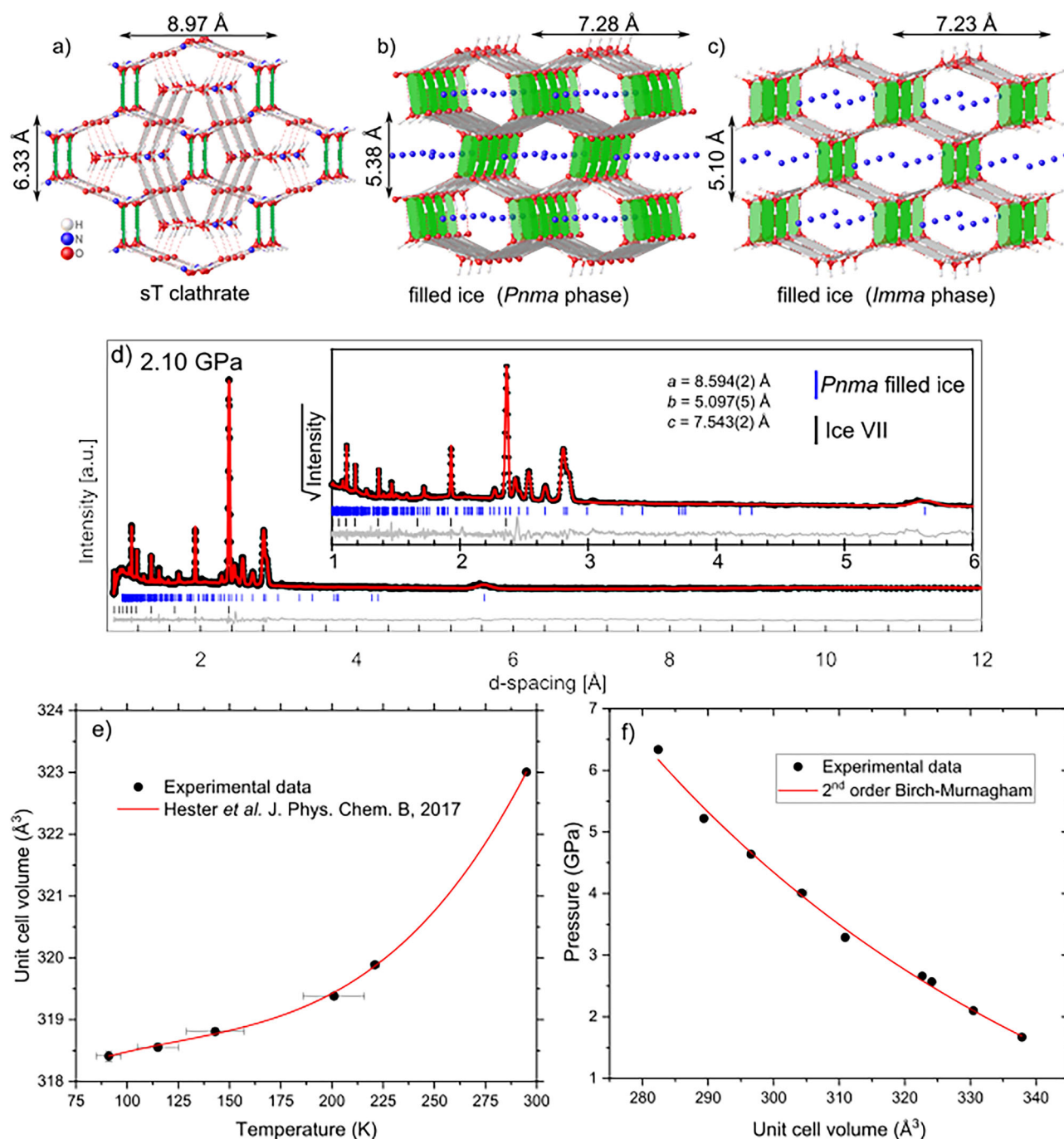


Fig. 4 | Structural evolution sequence, Le Bail refinement of *Pnma* structure, unit-cell volume as a function of temperature and unit-cell volume as a function of pressure. Top panel: structural evolution sequence from (a) sT (NH III) to (b) *Pnma* (NH-V) to (c) *Imma* (NH-IV). Medium (d): Example of Le Bail refinement of the diffractogram of the new *Pnma* structure at 2.1 GPa and 295 K. The lattice parameters are indicated in the legend. Some ice VII was also present in the sample

(see text). Bottom panel: (e) Temperature dependence of the unit-cell volume of NH-V at ~2.6 GPa, measured during heating from 91 to 300 K. Data were fitted with the thermal expansion model of Hester et al.⁴⁹. f Pressure dependence of the unit-cell volume of NH-V, obtained from Le Bail refinements of neutron diffraction patterns between 2 and 7 GPa at 295 K. The red line represents the fit using a second-order Birch-Murnaghan⁴³ equation of state^{43–45}.

structures found at each pressure were then relaxed as a function of pressure. The formation enthalpies relative to pure ice and solid nitrogen are reported in the convex hull diagrams at 1, 2, 6, and 10 GPa (Fig. 5), where we only show the structures with compositions 4:1, 3:1 and 2:1, relevant to the discussion. The relative enthalpies were obtained by calculating the enthalpy per atom of each structure and subtracting the weighted sum of the enthalpies per atom of the corresponding decomposition products, namely water ice and solid N_2 . The weights are given by the number of atoms of each

component present in the structure. For example, for the 4:1 composition, the relative enthalpy is defined as $\Delta H_{4:1} = [14H_{4:1} - (12H_{\text{ice}} + 2HN_2)]/14$.

The convex hull diagram (black line in Fig. 5) indicates which structures are thermodynamically unstable with respect to decomposition into other phases, i.e. points lying on the hull. Structures above the hull would decrease their internal energy by decomposing into stable structures, although the diagram does not take into account the system's kinetics, hence the potential for metastability.

Table 1 | Unit-cell parameters and stoichiometry of nitrogen hydrate phases

	sII	sH	sT	<i>Pnma</i> FIS	<i>Imma</i> FIS
Pressure [GPa]	0.3	0.9	1.4	2.1	5.2
Space group	<i>Fd3m</i>	<i>P6/mmm</i>	<i>P4₂/mnm</i>	<i>Pnma</i>	<i>Imma</i>
Lattice parameters [Å]	<i>a</i> = 17.117(1)	<i>a</i> = 11.993(2) <i>c</i> = 9.936(3)	<i>a</i> = 6.312(1) <i>c</i> = 10.578(10)	<i>a</i> = 8.594(2) <i>b</i> = 5.097(1) <i>c</i> = 7.543(2)	<i>a</i> = 7.840(2) <i>b</i> = 4.852(2) <i>c</i> = 7.591(2)
Unit-cell volume [Å ³]	5015.1(8)	1237.9(6)	421.5(8)	330.5(1)	289.3(3)
Unit-cell composition	24 N ₂ · 136 H ₂ O	7 N ₂ · 34 H ₂ O	4 N ₂ · 12 H ₂ O	4 N ₂ · 8 H ₂ O	4 N ₂ · 8 H ₂ O
H ₂ O to N ₂ ratio	≈ 5.66: 1	≈ 4.85: 1	3:1	2:1	2:1
Reference	Chazallon et al. ¹⁰	Loveday et al. ²⁴	Manakov et al. ²⁷	This work	This work

Unit-cell parameters and stoichiometry of the different phases of nitrogen hydrate identified at high pressure.

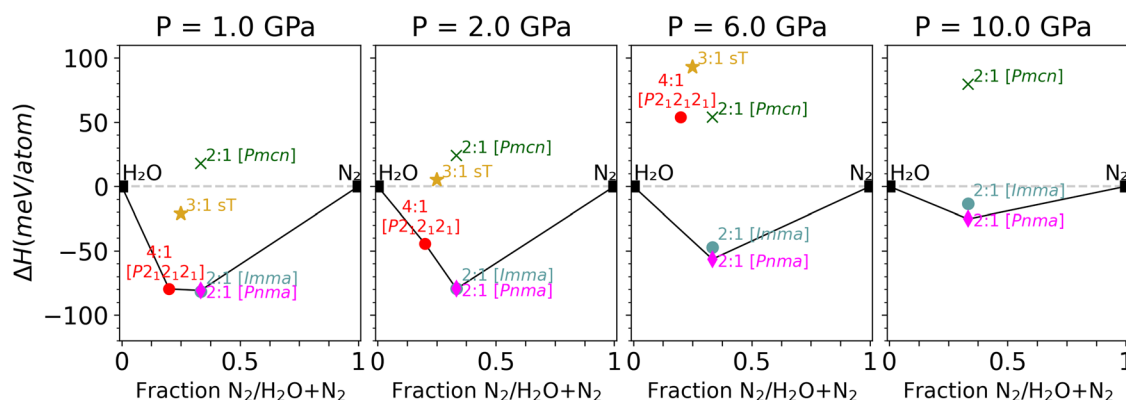


Fig. 5 | Convex hull diagrams of the H₂O–N₂ system at 1, 2, 6 and 10 GPa. Convex hull diagrams of the H₂O–N₂ system at 1, 2, 6 and 10 GPa, showing the formation enthalpy relative to ice and solid N₂ of the most relevant crystal structures, labeled with their space group. Thermodynamically stable phases lie on the convex hull.

At 1 GPa, a structure with *P2₁2₁2₁* space group and 4:1 H₂O:N₂ (denoted NH 4:1) composition was found to lie on the convex hull. However, NH 4:1 becomes unstable above ~ 3 GPa, suggesting it has a narrow stability range. This structure was never observed in our diffraction patterns, even as metastable.

At 2 GPa, we identified two nearly-isoenergetic phases (within 5 meV/atom) with 2:1 H₂O:N₂ composition. One is the *Imma* phase proposed by Loveday et al.²⁴, and the other is a previously unreported phase with *Pnma* space group. This second phase is consistent with our diffraction patterns. The structural information for this phase is given in Table SI-II of the Supporting Information.

The two phases remain nearly isoenergetic between 2 and 5 GPa, and both become progressively less stable at higher pressures. The two structures, NH-IV (*Imma*) and the newly assigned NH-V (*Pnma*), are likely both accessible in the intermediate 1.8–6 GPa range, with the *Pnma* phase probably favored at room temperature and under non-fully hydrostatic compression due to its more distorted framework.

We also manually included two other crystal structures in the convex hull. The first is a *Pmcn* phase with 2:1 H₂O:N₂ composition that is isostructural to MH-IV³⁶. This structure exhibits a positive formation enthalpy, and is over 100 meV/atom above the convex hull—strong evidence that it is unlikely to form. The *sT* structure was obtained from the experimental CIF file of argon hydrate²⁶ by replacing the argon guest with an N₂ molecule positioned at the center of the cages. No further optimization of the N₂ orientation or of the surrounding H₂O framework positions was performed, which may account for the discrepancy between the calculated stability pressure and the experimental observations. Note also that a possible pressure shift can occur between experiments and simulations, where the *sT* phase appears stable at pressures below 0.1 GPa. The structure is unstable at 1 GPa, as is 60 meV/atom above the hull. This may be attributed also to

limitations in DFT accuracy, particularly in the estimation of relative enthalpies under pressure.

At 2 GPa, the compositions on the convex hull remain the same as at 1 GPa, although the 4:1 *P2₁2₁2₁* phase is almost unstable, and it becomes unstable at 6 GPa, leaving only the 2:1 *Pnma* phase on the hull. As pressure further increases, so does the stability of the 2:1 *Pnma* phase, which, according to our calculations, becomes unstable at about 13 GPa. Experimentally, the qualitative trend is similar, although decomposition appears to occur around 6 GPa rather than the 13 GPa predicted by our calculations. This discrepancy may arise from the known limitations of the PBE functional, which tends to underestimate the energy of the strongly bound N–N triple bond and may over-stabilize nitrogen-rich compounds under pressure.

In summary, the *sT* → *Pnma* → *Imma* sequence is maintained, although the transition pressures in the simulations may differ from those observed experimentally. This discrepancy is due in part to the simulations being performed at zero temperature.

The evolution of the density shown in Fig. 6 (based on experimentally derived unit-cell volumes, assuming 100% chemical occupancy of the nitrogen in a given hydrate phase) reflects the progressive densification upon compression, while remaining consistently below the densities of pure ice VI/VII under comparable conditions. The transition from *sII* to *sH* is accompanied by a modest density increase, followed by a sharper jump (~18.5%) at the *sT* transition, consistent with increased nitrogen uptake. However, precise refinement of nitrogen occupancy in the *sT* phase was not possible due to its narrow observation range under compression and peak overlap with coexisting ice VI. As a consequence, a nominal full cage occupancy was assumed. This likely overestimates the true density of *sT*: a slightly lower occupancy (90%) yields densities that better match the expected monotonic densification trend. Notably, the subsequent transition

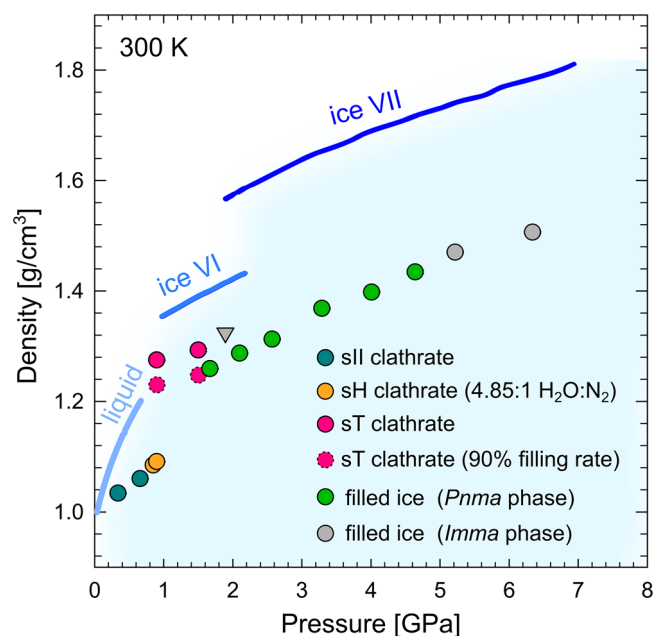


Fig. 6 | Densities of high-pressure phases of nitrogen hydrate based on the unit-cell volumes derived via neutron diffraction at 295 K, assuming full nitrogen occupancy. Blue lines represent experimentally derived densities of liquid water, ice VI and ice VII, respectively (refs. 77, 78). Circles and the triangle denote data collected upon compression and subsequent decompression, respectively.

from a fully occupied sT phase to NH-V phase exhibits a slight density drop (2.8%), which may reflect incomplete cage or channel filling, as observed in other gas hydrates²⁷. Upon decompression, the expected density trend is recovered, highlighting kinetic barriers to achieving full occupancy in the compressed filled-ice channels.

Finally, the low-frequency Raman bands between 2–10 GPa (Figures SI-5, SI-6, SI-7, respectively Supplementary notes 5, 6, 7) exhibit broad phonon features, matching signatures reported for filled-ice methane hydrates⁵². As phonon lattice modes are collective modes reflecting the crystalline structure of a sample, the broadness of these bands is ascribable to a defected crystalline structure.

Conclusions

In conclusion, we have clarified the high-pressure phase behavior of nitrogen hydrate up to 16 GPa using a combined approach of neutron diffraction, Raman spectroscopy, and structure prediction. Our results trace the full sequence of transformations from open clathrate frameworks (sII, sI, sH, sT) to filled-ice structures NH-V (*Pnma*) and NH-IV (*Imma*), revealing how guest-host interactions, structural rearrangements, and density changes are closely interlinked.

A key outcome of this study is the identification and structural characterization of a previously unresolved filled-ice phase in the *Pnma* space group (NH-V), which forms above 1.8 GPa as the sT clathrate collapses into a more compact, channel-based topology. This intermediate structure, less dense than the *Imma* phase that follows, highlights the non-monotonic path of densification in the nitrogen-water system—shaped not only by thermodynamics but also by kinetic and configurational constraints. Although the two orthorhombic phases share the same hydrogen-bonded network topology, the lower-symmetry *Pnma* structure exhibits an inclination of the mean plane of the water tetramers of approximately 1.3° with respect to the crystallographic *a* axis. In the *Imma* polymorph, the tetramer walls are aligned along this axis, further reducing the channel volume. The NH-V topology is interpreted as the result of preserving hexamer motifs through the phase transition, while re-linking them into one-dimensional channels, a similar mechanism common to high-pressure ice polymorphs⁵³.

The stability range of NH-V overlaps with the expected pressure-temperature conditions in the deep interiors of icy moons, suggesting that such metastable nitrogen-rich hydrates could affect internal stratification, volatile storage, and chemical evolution. During the first billion years after accretion, the progressive warming of the deep interiors of these large icy moons, consisting of a mixture of organics, ices and rock²², is expected to result in a progressive release of nitrogen-bearing compounds, first ammonia and then molecular nitrogen as the interior warms up ($T > 500$ K)^{54,55}. On Titan, the generation of a massive N_2 -rich atmosphere has been proposed to result from N_2 production in the refractory core (from thermal degradation of organic matter or ammonia-rich fluids at pressure between 1.5 and 5 GPa). Release of N_2 and H_2O during the differentiation of Titan's deep interior should result in the formation of NH-V, which would imply transient storage and delayed release to the surface to form a N_2 -rich atmosphere. This will provide a mechanism to generate the nitrogen-rich atmosphere after the Late Heavy Bombardment, which has affected all planetary objects during the first billion years of the Solar System. Mass-radius relationships⁵⁶, planet population models⁵⁷ well as recent experiments on the reaction between hydrogen with silicate melts at high pressure⁵⁸ indicate that a large fraction of Earth-size to Mini-Neptune-size exoplanets may contain several percents of water, especially for planets around low-mass stars. This would result in the formation of thick hydrospheres with pressure ranging between 1 and more than 10 GPa (depending on the water fraction and planet size). In such conditions, the transport of volatile elements, in particular N_2 , would be strongly affected by the formation of nitrogen hydrate. The total pressure of N_2 has an impact on the thermal state of the atmosphere⁵⁹ and hence on the definition of the habitable zone. Therefore, determining the partitioning of nitrogen between the solid hydrosphere (in the form of NH) and the atmosphere is essential to constrain the thermal state at its surface and to assess the habitability conditions. Our results show that any produced nitrogen molecule will interact with water molecules as they migrate upward and will be stored temporarily in the form of NH-V, and then progressively transform into the different phases as they decompressed during their transport toward the outer ice shell. The temporary storage of nitrogen in gas hydrates and their subsequent slow transport through the hydrosphere would allow a relatively late formation of Titan's atmosphere. This is consistent with the late formation scenario proposed by refs. 41,60, to explain the presence of a massive atmosphere on Titan despite the strong erosion induced by massive impacts during the Late Heavy Bombardment⁶¹. Future modeling work is needed to quantify the timing of nitrogen production by organic alteration, storage and transport to the outer layer and finally out-gassing at the surface.

By resolving a previously open structural question, this work contributes to a clearer picture of how gas hydrates adapt under pressure and what role they might play in shaping planetary environments.

Methods

Sample preparation

The sI/sII phase nitrogen clathrate hydrate was prepared by means of ex situ synthesis following a well-assessed procedure reported for various clathrates^{10,52,62,63}. The D_2O or H_2O ice powder was produced by nebulization of MilliQ water in a liquid-nitrogen bath using a SinapTec 80 kHz (NexTgen Inside 80 kHz 30 W), known to produce ice grains of 90 μm size. The condensed ice was then sifted through a sieve. In the case of deuterated water, the procedure was performed under nitrogen atmosphere to avoid the condensation of non-deuterated atmospheric water. 2 g of water ice powder were placed in an autoclave kept at -30 °C and inflated with 160 bar of the desired gas. The temperature was slowly increased to $+0.5$ °C, where the enclathration is supposed to take place. Several temperature cycles around 0 °C were performed. The autoclave was opened in a cold chamber (-25 °C). The clathrate was tested by means of Raman spectroscopy with a Qontor Raman spectrometer at ambient pressure in a liquid nitrogen continuous-flow cryostat (Oxford Instruments) with optical access. Samples showing a good amount of enclathrated gas were transferred in vials and stored in dewars under liquid nitrogen.

Loading procedures

Concerning spectroscopic characterization, screw-driven diamond anvil cells (Mao-Bell design, DAC) with 500 μm culet diamonds were used to generate pressures of the order of gigapascals. Preindented stainless steel gaskets with 150 μm holes were used to contain the sample. Ruby balls were placed in the sample chamber to probe the pressure using the ruby photoluminescence method⁶⁴. The high-pressure cells were loaded while in a bath of liquid nitrogen. During the loading, the lower part of the high-pressure cells was immersed in a liquid-nitrogen bath to maintain the clathrate in its stable form prior to pressure application. No excess liquid nitrogen was detected in the sample chamber during loading or during the subsequent Raman and diffraction experiments. Once the cell was closed, it was removed from the liquid-nitrogen bath and pressure was applied by tightening the screws.

Raman spectroscopy

Raman spectra of the pressurized samples were collected with LabRaman HR (exciting wavelength of 532 nm, nominal power of 1 W), both with a 600 lines/mm grating and a 1800 lines/mm one (only with the 1800 lines/mm grating it was possible to resolve the splitting of the nitrogen band at low pressure) and fitted with Fityk software⁶⁵ using Voigt functions. Lower wavenumbers Raman spectra were obtained with a *in-house* set-up in back-scattering geometry, equipped with a 660 nm line of a diode laser as an excitation source and using a long working distance 20 $\times$ Mitutoyo microscope. Spectra were collected thanks to an Acton/SpectraPro 2500i monochromator equipped with holographic super notch filters and a CCD detector (Princeton Instruments Spec-10:100BR). Such set-up allowed a spatial resolution on the sample of about 3 μm and a spectral resolution of 1 cm^{-1} .

Neutron diffraction

Around 30 mm^3 of the deuterated sample was cryoloaded in a spherical TiZr gasket and sealed with approximately 3 kbar in the clamp modulus, subsequently transferred to a Paris-Edinburgh (P-E) press coupled with a cryostat⁶⁶. The press was cooled by two-stage closed-cycle refrigerator in an “orange” cryostat. A lead chip was added to the sample to monitor the pressure following its equation of state⁶⁷. Two loadings were performed: the first sample was slowly compressed up to 6 GPa, while the second one was compressed to about 2 GPa and then cooled down to 100 K and slowly heated up to ambient temperature. The neutron diffraction data were collected at the high-intensity diffractometer D20 at the Institut Laue-Langevin (Grenoble, France)⁶⁸, using a wavelength of 1.54 $\text{\AA}$ ⁶⁹. The diffraction patterns used for the compressibility study were acquired two hours after compression. Due to limited acquisition time, measurements for the thermal expansivity study were made during continuous heating; thus, the results reflect non-equilibrated conditions. The sequential refinements tracked unit-cell evolution, and all volumes were normalized to 2.6 GPa using the isothermal equation of state obtained from the compressibility study. The temperature was measured at the top of the anvil cell throughout the acquisition of the diffraction pattern. Unit-cell parameters were obtained by Le Bail fitting of neutron diffraction patterns using TOPAS software⁷⁰, while thermal expansion diffraction data were obtained using GSAS-II software⁷¹. Both neutron and synchrotron X-ray diffraction measurements were carried out on the sample. However, neutron scattering was adopted as the primary structural probe for this study. Indeed, DAC x-ray diffraction measurements suffered from poor grain statistics, resulting in spotty diffractograms, which prevented the collection of a representative powder average in the small illuminated volume. On the contrary, the larger beam size and bulk penetration of neutrons provided significantly improved grain statistics, yielding smooth and representative diffraction patterns across the investigated pressure range. While these measurements do not allow for a full refinement of the deuterium positions, they provide robust lattice parameters, unit-cell evolution, and unambiguous phase identification. The analysis, therefore, relies on Le Bail fits, which are fully appropriate

given the data quality and the scope of this work, namely, establishing the phase sequence, symmetry changes, and compressibility of the filled-ice structures.

Simulation methods USPEX and Quantum Espresso

Structural predictions were carried out using the USPEX (Universal Structure Predictor: Evolutionary Xtallography) algorithm, a powerful evolutionary algorithm capable of identifying stable crystal structures for a given stoichiometry^{72–74}. In this study, the structural exploration on the $\text{H}_2\text{O}-\text{N}_2$ system, treats H_2O and N_2 molecules as unbreakable building blocks from which candidate structures were generated.

USPEX initially produces randomized structures under chemical and physical constraints, including fixed stoichiometry, predefined inter- and intra-molecular distances, to ensure chemically reasonable starting configurations. These candidate structures were then subjected to a multistage relaxation protocol using Quantum ESPRESSO^{75,76}, involving four consecutive relaxation steps with systematically increasing computational accuracy, until forces were lower than 0.5 mRy/atom, and stresses were within 1.0 kbar of the target pressure.

During relaxation, any structure that became chemically unstable, such as through molecular dissociation or violation of the imposed distance constraints, was discarded. At the end of each generation, the structures with the lowest free energy were selected as the basis for the next generation. USPEX employs various evolutionary operators (e.g., heredity, mutation, and substitution) to generate new structures based on these best-performing candidates.

These structural searches were performed on fixed compositions, allowing for direct comparison of structural stability. Final candidate structures were evaluated using the convex hull construction to determine their thermodynamic stability relative to competing phases.

The local structural relaxations and computation of total enthalpies were performed using Quantum ESPRESSO^{75,76}, using progressively tighter constraints on the forces and stresses, and better convergence parameters. The Kohn-Sham wavefunctions were expanded on a plane-wave basis of up to 80 Ry, and integration over the Brillouin zone was performed using a k-space point density of 1.0053 up to 0.8796 $\text{\AA}^{-1}$. We employed the Optimized Norm-Conserving Vanderbilt pseudopotentials (ONCV) from pseudo-dojo. The exchange-correlation functional was treated within the Perdew-Burke-Ernzerhof (PBE) approximation. Chosen crystal structures were then further relaxed as a function of pressure from 0 to 100 GPa. For these calculations we employed a cutoff of 90 Ry, k-point density of 0.185 $\text{\AA}^{-1}$, and a fixed occupation.

Data availability

The experimental data supporting this work phases are available at the ILL-data repository under the following <https://doi.org/10.5291/ILL-DATA.5-22-834>⁶⁹. These datasets are currently under embargo until 2027. However, they are available from the authors upon reasonable request.

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Author contributions

S.B., L.E.B. and G.T. designed the research. S.B. and E.L.M. created the synthesis protocol and synthesized the samples. S.B., S.E. and R.G. performed Raman experiments. S.B. and S.E. analysed Raman data under the supervision of L.E.B. and R.B. S.B., S.E., T.P. and R.G. performed diffraction experiments. T.C.H. provided technical support at D20 beamline. T.P. and S.B. analysed diffraction data under the supervision of L.E.B. and R.B. S.D.C. and S.E. performed structure prediction calculations with T. P. feedback. S.B., T.P., L.E.B., wrote the paper. All authors contributed to correcting and improving the paper writing.

Competing interests

The authors declare no competing interests.

Additional information

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