Water freezes below 0 °C at ambient pressure ordinarily to ice Ih, with hexagonal stacking sequence. Under certain conditions, ice with a cubic stacking sequence can also be formed, but ideal ice Ic without stacking-disorder has never been formed until recently. Here we demonstrate a route to obtain ice Ic without stacking-disorder by degassing hydrogen from the high-pressure form of hydrogen hydrate, C2, which has a host framework isostructural with ice Ic. The stacking-disorder free ice Ic is formed from C2 via an intermediate amorphous or nano-crystalline form under decompression, unlike the direct transformations occurring in ice XVI from neon hydrate, or ice XVII from hydrogen hydrate. The obtained ice Ic shows remarkable thermal stability, until the phase transition to ice Ih at 250 K, originating from the lack of dislocations. This discovery of ideal ice Ic will promote understanding of the role of stacking-disorder on the physical properties of ice as a counter end-member of ice Ih.
Water freezes below 0 °C at ambient pressure, ordinarily to ice Ih with a hexagonal stacking sequence. However, it is also known to produce "ice Ic" nominally with a cubic stacking sequence under certain conditions, and its existence in Earth’s atmosphere, or in comets is debated. "Ice Ic", or called as cubic ice, was first identified in 1943 by König, who used electron microscopy to study the condensation of ice from water vapor to a cold substrate. Subsequently, many different routes to "ice Ic" have been established, such as the dissociation of gas hydrates, warming amorphous ices or annealing high-pressure ices recovered at ambient pressure, freezing of or nano-confined water (see ref. 1). Despite the numerous studies on "ice Ic", its structure has not been fully verified, because the diffraction patterns of "ice Ic" show signatures of stacking disorder, and ideal ice Ic without stacking disorder had not been formed until very recently. This is the reason why "ice Ic" is double-quoted, and it is recently proposed that the stacking-disordered ice should not be termed as ice Ic, but as ice Ia.8

"Ice Ic" (ice Ia) is known as a metastable form of ice at atmospheric pressure. But, recent computer simulations suggest that even ice Ia could be the stable phase for crystallites up to sizes of at least 100,000 molecules. The stability of stacking-disordered ices is extremely important because of the ubiquitous nature of ice. Stacking-disordered ice can be characterized by the degree of ice cubicity, \( \chi \), which is defined as the fraction of cubic stacking. Untill very recently, the highest cubicity was limited to ~80%8,14, but it has been reported that ideal ice Ic with 100% cubicity has been obtained by annealing ice XVII.10

Recently new ice polymorphs, ice XVI15 and ice XVII16,17 are obtained by degassing gas molecules from neon and hydrogen hydrates, respectively. From these findings, we hypothesized that ideal ice Ic could be obtained by degassing hydrogen from hydrogen hydrate, C2. Five different phases in the H2–H2O system have been reported to date (see ref. 18): Among them, neutron diffraction experiments have never been conducted for the high-pressure phases, C1 and C2, probably due to the technical difficulty in loading hydrogen into a pressure vessel, or compressing it to pressures in the giga-pascal range. To synthesize ideal ice Ic, decomposition under low-temperature conditions for degassing is necessary, which is also not straightforward using conventional pressure-temperature controlling systems. We have developed a Mito system, and have overcome these technical difficulties (see details in Methods).

Here we present the neutron and X-ray diffraction results showing ice Ic without stacking disorder, obtained from degassing hydrogen hydrate C2. We also report an unexpected amorphous-like state in the transformation from C2 to ice Ic, and the thermal stability of ice Ic.

Results

The route to obtain ice Ic. We started by using a mixture of D2O and MgD2, which is an internal deuterium source, to synthesize hydrogen hydrate, C2. After loading the mixture into a pressure-temperature controlling system, MgD2 was decomposed by heating at 403 K and at ca. 0 GPa for 1 h through a nominal reaction of MgD2 + 3D2O → Mg(OHD)2 + 2D2 + D2O (at b in Fig. 1, the observed neutron diffraction patterns are shown in Supplementary Fig. 1). Then, the samples were cooled to room temperature (at c in Fig. 1) and typically compressed up to ~3 GPa until a C2 phase was observed (at d in Fig. 1).

The neutron diffraction pattern for the C2 phase obtained at 3.3 GPa and 300 K (at d in Fig. 1) was analyzed by the Rietveld method. We adopted a splitting site model for guest D atoms located at the 48f site (x, y, z), and the host structure was identical to ice Ic (Fd3m, O at the 8b site (3/8, 3/8, 3/8), D at the 32e site (x, x, x)). The calculated diffraction pattern was in good agreement with the observed one, as shown in Fig. 2a. The refined structural parameters are listed in Supplementary Table 1.

The sample was then cooled from 300 K to 100 K at around 3 GPa (path d → e). In the diffraction pattern taken at e in Fig. 1, peaks from solid deuterium (phase I) appeared at around 200 K (Supplementary Fig. 2), which is consistent with the known melting curve of hydrogen. This observation indicates that fluid deuterium coexisted with C2 through the path from b to d.

The C2 phase persisted at pressures at least as low as 0.5 GPa on decompression at 100 K (path e → f). However, surprisingly, the Bragg peaks of C2 mostly disappeared at 0.2 GPa (Fig. 3). This phenomenon is totally unexpected, because the host structure of gas hydrates retains its framework in the previous cases with ice XVI15 and XVII16. The sample was further decompressed to 0 GPa and evacuated using a turbo-molecular-pump. The broad peaks corresponding to ice Ic appeared at this stage. The peak disappearance of C2 before the appearance of ice Ic was reproducibly observed in at least two separate neutron runs and one X-ray diffraction run for a hydrogenated sample (Supplementary Fig. 3). In the neutron diffraction pattern at 0.2 GPa, except for the Bragg peaks from Mg(OHD)2, only a broad peak was observed at around d = 3.75 Å, which was between the peak positions of 111 of C2 and that of Ice Ic (Fig. 3). This fact implies that this state does not have long-range periodicity like a normal crystal, but has only local-ordering like an amorphous or nanocrystal. Considering the observed d-spacing, this amorphous-like form would be an intermediate transition state from C2 to ice Ic, which forms while hydrogen molecules are partially degassed. It is highly likely that this apparent amorphization is derived from the...
The peaks of ice Ic sharpened with increasing temperature. This sharpening is dependent not only on temperature but also on lattice mismatch between C2 and ice Ic, originating from the relatively small cage in the host framework of the ice Ic structure.

From the X-ray diffraction run, ice Ic, which may partially include molecular hydrogen, even appeared at 0.1 GPa through the transition from the C2 phase to the amorphous-like state, even under pressure (Supplementary Fig. 3). This also represents a difference from the previous cases of ice XVI and XVII; ice XVI is formed under evacuation15, and hydrogen molecules can be refilled into ice XVII at an order of 10 bar of pressure16. It is worth noting that the partially degassed states are allowed in the cases of both ice XVI and XVII, so that the guest molecules can be continuously degassed from a fully occupied state to an empty state. The observed phase-separation behavior even under pressure in the ice H2O system indicates that the partially degassed C2 phase would be unstable compared to the fully occupied or empty phases, probably due to the lattice-mismatch.

The Bragg peaks in the neutron diffraction pattern for ice Ic obtained at 100 K were still broad, probably due to the small crystallite size and/or the remaining guest hydrogen molecules. The peaks of ice Ic sharpened with increasing temperature. This sharpening is dependent not only on temperature but also on time, which indicates that it is kinetic behavior.

### Structure refinement for ice Ic

We conducted a separate run in order to obtain a neutron diffraction pattern for the structure refinement of the ice Ic. In this run, the neutron diffraction pattern was obtained at 130 K, which is well below the temperature at which the nucleation of ice Ih occurs21. We confirmed that the peak width did not change in the temperature region from 130 K to 180 K, such that the peak sharpening was almost complete, even at 130 K. The obtained neutron diffraction pattern was well fitted using the ice Ic structure model9, as shown in Fig. 2b and Supplementary Table 1. We also conducted the Rietveld analysis using C2 structure model, and found that the occupancy of the D2 site is zero, within experimental error (occ (D2) = −0.001(1)). This shows that the guest hydrogen molecules are below the detectable limit at 130 K under evacuation. The peak profile around 111 peak of ice Ic has neither the feature of stacking disorder nor the peaks from ice Ih, as shown in the diffraction pattern in the region at around d = 3.9 Å, where the strongest 100 reflection of ice Ih is expected (see inset in Fig. 2b, and more detailed discussion for the peak broadening for ice Ic is described in Supplementary Note, Supplementary Table 2 and Supplementary Fig. 4). This should be a clear indication of the presence of ideal ice Ic without stacking disorder (χ = 100%)13, as clear as the recent discovery of ideal ice Ic by annealing ice XVII10.

### Thermal stability of ice Ic

It is also noteworthy that the ice Ic surprisingly persists up to at least 240 K until ice Ih started to appear at 250 K (Fig. 3). The temperature of 240 K corresponds to the upper limit of the reported metastable region of “ice Ic” (ice Ic). However, in stacking-disordered ice, the cubic stacking sequence starts to change into a hexagonal stacking sequence at a much lower temperature, and the phase transition to ice Ih is completed at 240 K. The notable stability of the ice Ic would be derived from the lack of stacking disorder. The stacking-disordered ice has more dislocations, which promote the phase transformation from ice Ic to ice Ih by reducing the activation energy required to change the stacking sequence22. This is also supported by a recent mesoscopic-size calculation23. Note here that the critical temperature of 240 K has been identified as the temperature above which ice Ih without cubic stacking faults...
forms spontaneously, which is the reason for the anomalous self-preservation regime of natural gas hydrates. The diffraction pattern observed at 250 K looks a mixture of bulk ice Ic and Ih, rather than stacking-disordered ice with many stacking faults, judging from “stackogram” reported in the literatures. At 250 K, crystal growth would be dominant, rather than crystal nucleation. Therefore, once a crystallite nucleates, it quickly grows before other crystallites nucleate, resulting in the mixture of ice Ic and Ih, rather than stacking-disordered ice. This observation also suggests a smaller number of dislocations in the ice Ic observed in this study. On the contrary, the remarkable stability of the ice Ic and the bulk mixture of ice Ic and Ih at 250 K strongly support the conclusion that the obtained ice is not stacking-disordered, and it can therefore be called ice Ic without the need for quotation marks.

The discovery of ideal ice Ic will allow us to research the real physical properties of ice Ic, without stacking disorder. For example, accurate heat capacity or vapor pressure measurements from low temperature will provide the free energy of ice Ic, which settle the long-standing argument for the stability of ice Ic compared to ice Ih. The physical properties of the ideal ice Ic are also important to understand how stacking disorder plays a role in the physical properties of ice Ic. For instance, since the thermal conductivity of ice Ic is significantly smaller than ice Ih, the difference of thermal conductivities between ice Ih and Ic will emboss the effect of stacking disorder. It is also interesting what will be happened when ice Ic is compressed under low temperature; whichever ice Ic will be transformed into HDA (High Density Amorphous ice) or not?

In any case, it is worth conducting what we previously did for ice Ih, to this ideal ice Ic as well.

Methods

Synthesis of MgD2. MgD2, used as the starting material in this study, was synthesized from reagent-grade MgH2 as follows. MgH2 powder (Wako pure chemical industries, Ltd.) was purchased and further ground in an agate mortar to increase the surface area, after which it was placed in a copper tube with a diameter of 4 mm and a length of 40 mm. The tube was mechanically sealed and but not welded, allowing the transfer of hydrogen gas. The copper tube was inserted into a 1/4” Inconel tube and connected in parallel to a deuterium gas cylinder and a turbo-molecular pump (TMP) with 1/16” stainless tubes and stop bulbs. The Inconel tube, including the sample copper tube, was heated to 773 K for 1 h using a tube furnace under hydrogen gas. Under these conditions, MgH2 completely decomposed into Mg and D2, and the degassed H2 was evacuated. Then, the D2 gas was introduced up to 4 MPa, and the temperature was cycled at the rate of 1 K/min between 673 K and 773 K while keeping the pressure at 4 MPa, which represents stable and unstable conditions for MgH2, and this temperature cycle was repeated for 20 times. This activation process is necessary for the reaction 2Mg + D2 –→ Mg2D2. Finally, the p-T conditions were maintained at 673 K and 4 MPa for 3 days to complete the reaction. The recovered sample was analyzed by powder X-ray diffraction (MiniFlex-II, Rigaku) and identified to be MgD2 with a trace amount of MgO. Both MgD2 and MgO react with D2O and produce Mg(OH)2, so this small amount of MgO does not affect the conclusion of this study.

Neutron diffraction and p-T control. Neutron powder diffraction experiments were conducted at the beamline PLANET in the Material and Life Science Experiment Facility (MLF) of J-PARC, Ibaraki, Japan. The incident beam consists of D2 gas was introduced up to 4 MPa, and the temperature was cycled at the rate of 1 K/min between 673 K and 773 K while keeping the pressure at 4 MPa, which represents stable and unstable conditions for MgH2, and this temperature cycle was repeated for 20 times. This activation process is necessary for the reaction 2Mg + D2 –→ Mg2D2. Finally, the p-T conditions were maintained at 673 K and 4 MPa for 3 days to complete the reaction. The recovered sample was analyzed by powder X-ray diffraction (MiniFlex-II, Rigaku) and identified to be MgD2 with a trace amount of MgO. Both MgD2 and MgO react with D2O and produce Mg(OH)2, so this small amount of MgO does not affect the conclusion of this study. The load was applied by driving the piston by bellows using a He gas cylinder. The bellows allow us to control pressure at a few kbar more precisely than conventionally used membranes.

DFT calculations. Quantum Espresso36 was used for the DFT calculations. We used Perdew-Burke-Ernzerhof (so-called PBE) type nonempirical exchange-correlation functions37 for this study. The pseudopotentials were derived using projector augmented-wave approximation38. The dispersion effects were taken into account using the exchange-hole dipole moment method (XDM), which calculates coefficients for polynomial of DFT-D dispersion energy41 from the exchange-hole dipole moment calculated from simulated electron wave function42,43. XDM damping function parameters are taken from44. The enthalpies of four possible configurations of ice Ih were calculated within a unit cell with a kinetic energy cutoff of 70 Ry and a Brillouin zone k mesh of 8 x 8 x 8. The cell parameters and atomic coordinates were optimized using BFGS-Newtonian methods at atmospheric pressure.

Data availability. The primary data that support the plots within this paper and other finding of this study are available from the corresponding author on reasonable request. The neutron crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1973757, 1973759. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions
K.K. and S.M. conceived and designed the experiments. K.K., S.M., T.H., A.S.-F., R.Y., K.Y., and H.K. conducted the neutron diffraction experiments. K.K., R.Y., K.Y., and H.K. conducted the X-ray diffraction experiments. F.N. carried out the DFT calculations and wrote the corresponding part of the manuscript. K.K. analyzed the data and wrote the manuscript with contributions from all authors.

Competing interests
The authors declare no competing interests.

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