

Pure ices IV and XII from high-density amorphous ice

Christoph G. Salzmann, Ingrid Kohl, Thomas Loerting, Erwin Mayer, and Andreas Hallbrucker

Abstract: High-density amorphous ice (HDA), made by compression of hexagonal ice at 77 K, was heated at a constant pressure of 0.81 GPa up to 183 K and its phase transition followed by displacement–temperature curves. The crystalline phases, recovered at 77 K and 1 bar, were characterized by X-ray diffraction. Pure D₂O ice IV and nearly pure H₂O ice IV were formed on slow heating at a rate of 0.4 K min⁻¹, whereas pure H₂O ice XII and D₂O ice XII were formed on fast heating at ≥ 15 K min⁻¹. On heating HDA at rates in between these two values a mixture of ice IV and ice XII was obtained, where their relative yields depended in a systematic manner on the heating rate. Conversion of HDA into either ice IV or ice XII is an example of a “parallel reaction” where the relative yields of ice IV and ice XII can be controlled by temperature, i.e., by the rate of heating, in our approach. It is conceivable that a similar behaviour occurs on crystallization of the related pressure-amorphized silica.

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Résumé : En comprimant de la glace hexagonale à 77 K, nous avons fabriqué de la glace amorphe de haute densité (HDA) que nous avons chauffée à une pression constante de 0,81 GPa jusqu'à 183 K et sa transition de phase suivie par courbes de déplacement de température. Les phases cristallines recouvrées à 77 K et 1 bar ont été caractérisées par diffraction de rayons X. Nous avons fabriqué des glaces IV pures de D₂O et presque pure de H₂O par réchauffement lent à 0,4 K min⁻¹ et des glaces XII pures de D₂O et de H₂O par réchauffement rapide à ≥ 15 K min⁻¹. Chauffer des échantillons de HDA à des taux intermédiaires produit des mélanges de glace IV et XII selon des proportions qui dépendent systématiquement du taux de chauffage. La conversion de HDA en glace IV ou XII est un exemple de réaction parallèle où le taux relatif de glace IV et XII peut être contrôlé par la température, dans notre approche par le taux de chauffage. Il est concevable qu'un même comportement apparaisse dans la cristallisation de la silice rendue amorphe par pression.

[Traduit par la Rédaction]

1. Introduction

Ice IV is a metastable high-pressure phase of ice [1–8], and according to Fig. 1 in ref. 7, it can be formed from the liquid under suitable conditions between 0.2 and 1.0 GPa, which covers most of

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C.G. Salzmann, I. Kohl, T. Loerting, E. Mayer, and A. Hallbrucker,¹ Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria.

¹ Corresponding author (e-mail: Andreas.Hallbrucker@uibk.ac.at).

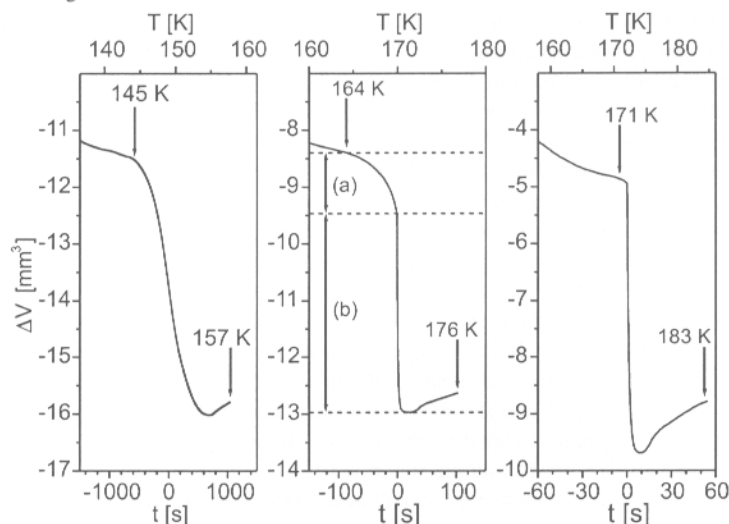
the pressure range of the stability domains of stable ices III, V, and VI. Its formation from the liquid can be induced by appropriate nucleating agents [3,4], but the effect of the nucleating agent or of the pressure on the formation of ice IV is erratic. Engelhardt and Whalley [4] reported that even with the most efficient nucleating agent, "nucleation of ice IV was by no means consistent and only about 1 freezing in 10 yielded ice IV". They further reported: "in these experiments, ice IV exists for only a few seconds to several minutes at about -25°C before transforming spontaneously to a more stable phase". Of the various high-pressure ice phases obtainable on cooling the liquid, ice IV is probably the most difficult one to form. Ice IV can be recovered by quenching to 77 K and releasing the pressure [4]. This recovered ice IV is fully proton-disordered according to X-ray diffraction [9], infrared [10], and calorimetric [4] measurements.

The new high-pressure phase of ice, called ice XII, was first prepared and characterized by Lobban et al. [11] by slow crystallization from the liquid phase at 260 K at a pressure of 0.55 GPa, which is within the stability region of ice V [8]. Ice XII "contains only seven- and eight-membered rings and is the first example of a 4-connected net of this type" [12]. In the same year Chou et al. [6] reported a new "High-Pressure Phase of H_2O Ice" in the ice VI domain at 0.7–1.2 GPa and 3–26 $^{\circ}\text{C}$. They speculated on the relation of their new phase to the ice XII reported by Lobban et al. [11] but, because of a lack of data, could not confirm it or rule it out (see note 24 in ref. 6). Subsequent to the formation of ice XII from the liquid phase [11], Koza et al. [13] reported the formation of ice XII in a completely different region of water's phase diagram, namely, as an incidental product in the preparation of high-density amorphous ice (HDA) [14–17] at 77 K on compression of hexagonal ice (ice Ih) up to 1.8 GPa. Kohl et al. [18] then showed that in this route ice XII forms on compression of ice Ih at 77 K only *via* HDA, and not directly from ice Ih, and that its formation requires a sudden pronounced pressure drop at pressures $\approx \geq 1.1$ GPa. They further proposed that "shock waves generated by the pressure drops cause transient local heating up to the temperature range of the ice V domain, and that this induces nucleation and crystal growth of ice XII". It follows that the apparent observation of a "second regime of metastability" of ice XII postulated by Koza et al. [19] between 77 and ≈ 150 K and 1.0 and 1.8 GPa to account for its unexpected formation at low temperatures (see Fig. 1 in ref. 19) seems to be an effect of pressure drops and shock-wave heating during compression of ice Ih. Ice XII is metastable with respect to ice V [20], like metastable ice IV that is also found within the stability region of ice V [3,4,8,9] and whose density is similar to that of ice IV [11]. Ice XII can be prepared in a reproducible manner, without contamination by HDA and low-density amorphous water (LDA), by isobaric heating of HDA kept at pressures between ≈ 0.7 and 1.5 GPa [21]. In this pressure range, HDA transforms partially into ice XII on heating from 77 K, and between ≈ 158 and 212 K it has an extended region of metastability before its phase transition to other high-pressure phases (see Fig. 1 in ref. 21).

Here, we show that the pure ices IV and XII can be formed in a reproducible manner on controlled isobaric heating of HDA at 0.81 GPa up to ≈ 183 K [21,22]. The essential parameter is the heating rate, slow heating favouring formation of ice IV, whereas faster heating rates lead to the formation of metastable ice XII. Thus, the recovered pure ices IV and XII are now available in gram quantities for further studies. This approach is complementary to cooling liquid water under pressure and offers a new and reproducible way of preparing ices IV and XII. Raman spectra of recovered ices IV and XII prepared in this manner on heating HDA were recently reported [23,24]. Comparison of the Raman spectrum of ice XII with that of the new high-pressure phase of H_2O ice reported by Chou et al. [6] suggests that their new ice was in fact ice XII (cf. Fig. 4 in ref. 23).

The kinetics of the phase transition of HDA to either ice IV or ice XII is that of a so-called "parallel reaction" which is for a schematic reaction: $\text{A} \rightarrow \text{B}$ or $\text{A} \rightarrow \text{C}$ [25]. In isothermal studies, the ratio of rate constants, $k_{\text{A} \rightarrow \text{B}}/k_{\text{A} \rightarrow \text{C}}$, determines the product yield and not the equilibrium constants for the two reactions. By suitable choice of catalyst or temperature, one rate can be made much faster than the other [25]. Here, we utilize differences in heating rate to produce either pure ice IV or pure ice XII. This, to our knowledge, is the first example of a parallel reaction on crystallization of an amorphous solid, and

Fig. 1. ΔV vs. temperature (top) plots on isobaric heating of H_2O HDA at 0.81 GPa at three heating rates, showing two types of kinetic and phase transition of HDA to two different high-pressure ices. The heating rates were (left) 0.4 K min^{-1} , (middle) 4.0 K min^{-1} , and (right) 15 K min^{-1} , respectively. The lower temperature in each plot indicates the onset of crystallization, the upper temperature indicates where the heating was stopped and the pressure vessel with the sample was cooled with liquid nitrogen for subsequent recovery of the samples. The time scale at the bottom of each plot indicates the time at which each phase transition has taken place, with $t = 0$ as the maximal volume change.



its possible implications for the polymorphism in silica are discussed in ref. 26.

We note that several other high-pressure ice phases form on heating HDA under pressure [5,18,27,28] and on compression of ice Ih at various temperatures [13,17,19,29].

2. Experimental procedures

The procedure for preparing ices IV and XII on isobaric heating of HDA is described in refs. 22 and 21. Briefly, 0.300 cm^3 of either D_2O water (from Aldrich company, No. 15, 188-2, 99.9 atom% D) or of deionized H_2O water was pipetted into a precooled piston-cylinder apparatus with a 8 mm diameter piston. HDA was then made by compression of ice Ih at 77 K up to 1.6 GPa by using a computerized universal testing machine (Zwick, Model BZ100/TL3S) for compression at a rate of 7000 N min^{-1} . Its positional reproducibility was $\pm 5 \text{ }\mu\text{m}$ and spatial resolution of its drive was $0.01 \text{ }\mu\text{m}$. Pressure-displacement curves were recorded with the TestXpert V 7.1 Software of Zwick. Indium linings were used as described in ref. 18 to avoid pressure drops during compression. The pressure-displacement curves produced had the same shapes as those shown in Fig. 1a of ref. 18, and those reported, for example, by Mishima et al. [14,15]. HDA was then transformed into pure ice IV on isobaric heating up to $\approx 180 \text{ K}$ at a pressure of 0.81 GPa and at a rate of 0.4 K min^{-1} [22], or into pure ice XII on heating at a rate of $\geq 15 \text{ K min}^{-1}$ [21]. The samples were quenched to 77 K, the pressure was released at 77 K, and ice IV or XII was recovered under liquid N_2 and 1 bar. Recovered ices IV and XII were characterized by X-ray diffraction as shown (Fig. 2).

X-ray diffractograms were recorded in θ - θ geometry on a diffractometer (Siemens, model D 5000, Cu-K α) equipped with a low-temperature camera from Paar. The sample plate was in a horizontal position during the whole measurement. Installation of a "Goebel mirror" allowed recording of small amounts of sample without distortion of the Bragg peaks. Calculation of X-ray diffractograms was performed with the "PowderCell" Software (BAM, Bundesanstalt für Materialforschung, Berlin, Ger-

many). This software also allows us to calculate the percentages of ices IV and XII in the mixtures.

3. Results and discussion

Figure 1 displays the change in volume, ΔV , with temperature (top) on heating HDA (made from H_2O) from 77 K to upper temperatures marked in the plots for three different heating rates. The onset of phase transition to a high-pressure ice phase is recognizable by a pronounced ΔV decrease in a small temperature range. The ΔV - T curve recorded on heating at 0.4 K min^{-1} (left) shows the onset of crystallization at 145 K (marked) and a gradual ΔV decrease on further heating. The ΔV - T curve recorded on heating at 15 K min^{-1} (right) shows the onset of another crystallization process at 171 K (marked) and a very fast ΔV decrease on further heating. The ΔV - T curve recorded on heating at 4.0 K min^{-1} (middle) contains both crystallization processes: first a slow process sets in with an onset temperature of 164 K (marked as region (a)), and on further heating the rapid crystallization process takes over (marked as region (b)). The time necessary for the phase transition can be calculated from the heating rate and the temperature region of the phase transition. These times are inserted at the bottom of Fig. 1, with $t = 0$ as the maximal volume change. This shows that the slow crystallization process (left) requires $\approx 1400 \text{ s}$, whereas the fast one (right) is finished after $\approx 15 \text{ s}$.

After heating to the upper temperatures marked in the three plots of Fig. 1, the pressure vessel with sample was quenched under pressure with liquid nitrogen to 77 K, the pressure was released, and the samples were recovered under liquid nitrogen at 1 bar. These recovered samples were characterized by X-ray diffraction. Figure 2 (bottom panel) shows the diffractogram of the recovered sample obtained on heating H_2O HDA at 0.4 K min^{-1} and its comparison with the calculated diffractogram A' confirms that it consists of nearly pure H_2O ice IV, with a minor amount of ice XII (marked by open circles). A small amount of ice Ih is marked by asterisks in this and the other diffractograms. The ice Ih comes from condensation of water vapour during transfer of the sample into the precooled sample plate holder of the diffractometer. The diffractogram of the recovered sample obtained on heating at 15 K min^{-1} is shown as plot C (top) and its comparison with the calculated diffractogram C' shows that it consists of pure H_2O ice XII. The diffractogram of the recovered sample obtained on heating at 4.0 K min^{-1} is shown as plot B (middle); it contains a mixture of ice IV and ice XII, and the calculated plot B' shows that it consists of 58% ice IV and 42% ice XII.

Figure 3 depicts the dependence of these percentages of ice IV and ice XII on heating rate. Additional experiments with other heating rates, and starting with either H_2O HDA or D_2O HDA, are also included. With increasing heating rate, the relative amounts of ice XII increase and at heating rates of $\geq 15 \text{ K min}^{-1}$, pure ice XII can be obtained. It is now possible to assign crystallization kinetics (see the middle panel of Fig. 1) to the formation of (a) ice IV and (b) ice XII.

Whereas pure D_2O ice IV is obtained on heating at 0.4 K min^{-1} , H_2O ice IV made on heating at the same rate contains a minor amount of ice XII (cf. plot A of Fig. 2 and Fig. 3). Engelhardt and Whalley [4] have already remarked that the nucleation of ice IV from liquid water "appears to be more probable for D_2O than for H_2O ", and similar behaviour seems possible for ice IV from HDA. However, we expect that pure H_2O ice IV can also be made from HDA on decreasing the heating rate even further, below the 0.4 K min^{-1} rate used in this work, but, at present it is not possible for us with our pressure vessel.

Careful analysis of the crystallization kinetics of ice IV vs. ice XII formation by the Johnson-Mehl-Avrami relation [30-33] requires isothermal studies, which are, at present, not feasible. Because of this, in the following, we discuss the parameters that control the formation of ice IV or ice XII on heating HDA only in a qualitative manner. The ΔV vs. temperature curves of Fig. 1 show that formation of ice IV starts at a lower temperature than that of ice XII, but that ice XII formation is much faster than that of ice IV once a certain temperature region is reached. It is instructive to compare the times necessary for the phase transitions: this gives $\approx 1400 \text{ s}$ for the formation of H_2O ice IV (see left panel, Fig. 1), and $\approx 15 \text{ s}$ for the formation of H_2O ice XII (see right panel, Fig. 1). Thus, at low temperatures the rate constant for the formation of ice IV ($k_{\text{HDA} \rightarrow \text{iceIV}}$) must be much higher than that of ice XII ($k_{\text{HDA} \rightarrow \text{iceXII}}$), whereas

Fig. 2. X-ray powder diffraction patterns (Cu-K α) of the recovered samples and, for comparison, of the calculated ones recorded at 90 K: Plot A is the diffractogram of the recovered sample obtained on heating HDA at 0.4 K min⁻¹ (Fig. 1, left), and A' the calculated diffractogram of ice IV (structural data from ref. 9); plot B is the diffractogram of the recovered sample obtained on heating at 4.0 K min⁻¹ (Fig. 1, middle), and B' the calculated diffractogram of a mixture of ices IV and XII, with 58% ice IV and 42% ice XII; and plot C is the diffractogram of the recovered sample obtained on heating HDA at 15 K min⁻¹ (Fig. 1, right), and C' the calculated diffractogram of ice XII (structural data from ref. 11). Reflections marked by asterisks indicate a small amount of ice Ih, open circles in plot A indicate a minor amount of ice XII, and an artifact in plot C is marked by a cross.

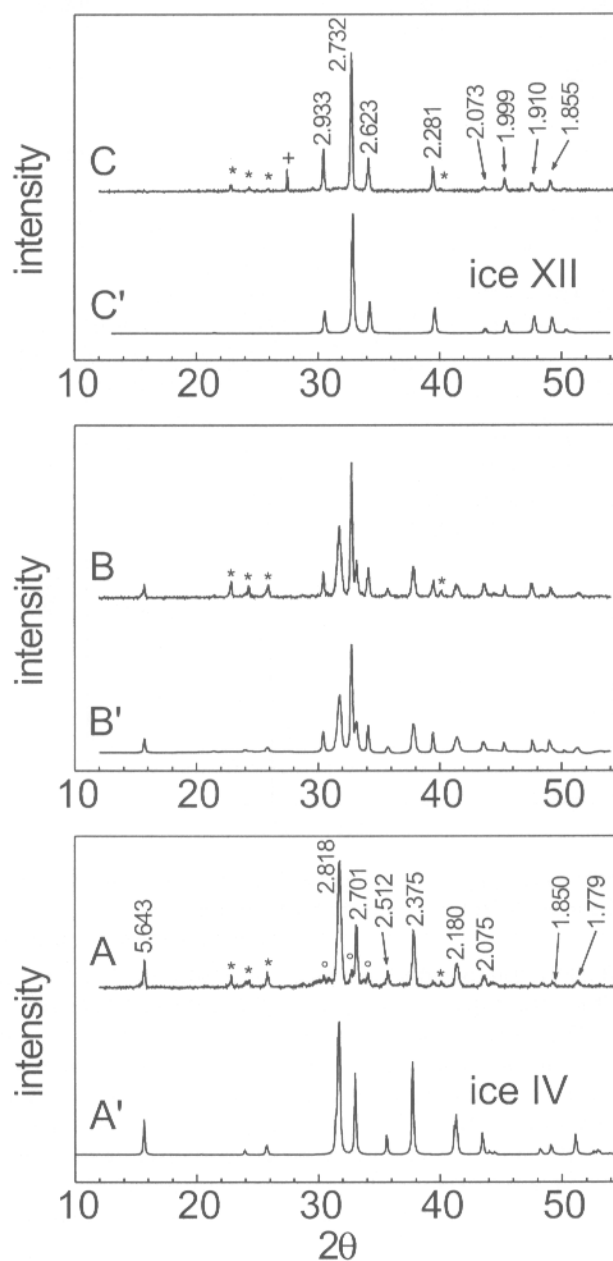


Fig. 3. Percentages of yields of ice IV and ice XII for H₂O and D₂O samples vs. heating rate. Relative amounts were determined by a Rietveld fit provided by PowderCell software (from ref. 22).

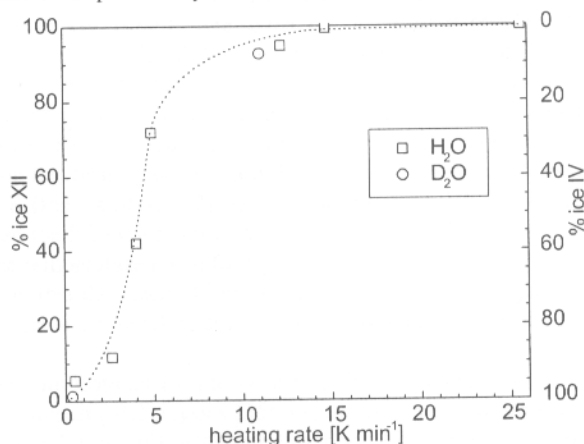
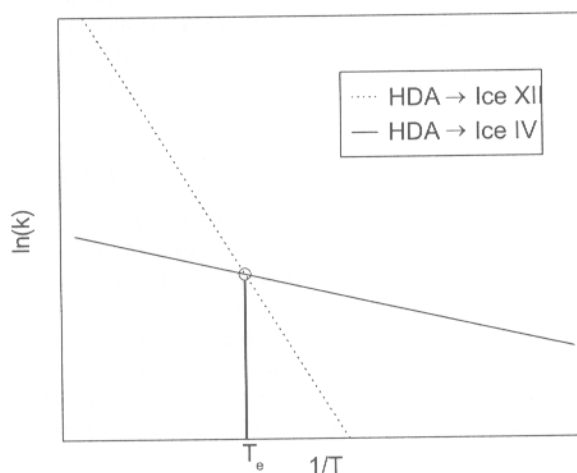


Fig. 4. Schematic picture visualizing the requirement of different temperature-dependent rate constants for the HDA → ice IV transition (continuous line) and the HDA → ice XII transition (broken line). T_e is the temperature where the two rate constants have the same value (from ref. 22).



at *high* temperatures the opposite holds true. This requires that $k_{\text{HDA} \rightarrow \text{ice XII}}$ increases much more with temperature than $k_{\text{HDA} \rightarrow \text{ice IV}}$, and that the activation energy for HDA → ice XII formation is much higher than that for HDA → ice IV formation.

This is visualized in Fig. 4 in a schematic manner for Arrhenius behaviour. Below a certain temperature, T_e , $k_{\text{HDA} \rightarrow \text{ice IV}}$ is much larger than $k_{\text{HDA} \rightarrow \text{ice XII}}$, and consequently, nearly pure ice IV is formed. Above T_e , the opposite holds true and nearly pure ice XII can be formed. This schematic picture also requires that the so-called pure ice IV (ice XII) must contain a minor amount of ice XII (ice IV), and by “pure” we mean that the minor crystalline phase is not detectable in our X-ray diffractograms. T_e is the temperature where $k_{\text{HDA} \rightarrow \text{ice IV}} = k_{\text{HDA} \rightarrow \text{ice XII}}$, and thus where equal amounts of ice IV and ice XII are formed on isothermal reaction. It can be determined by heating HDA very rapidly to a given temperature, holding it at that temperature until complete conversion is achieved, cooling the sample to 77 K, and then determining the relative yields of recovered ice IV and ice XII by diffraction. This is at present not possible.

We have further considered whether, in addition, some metastable ice IV transforms into metastable ice XII, i.e., whether ice IV is more metastable in this p - T region than ice XII. Such an ice IV \rightarrow ice XII transition would be barely recognizable in the ΔV vs. T plots because their densities are nearly identical [11]. We surmise that the ice IV \rightarrow ice XII transition can be ruled out on the basis of ΔV vs. T plots shown in Fig. 1 of ref. 22 where pure D₂O ice IV was formed on slow heating at 0.4 K min⁻¹ either to 162 K (Fig. 1c of ref. 22) or to 195 K (Fig. 1g of ref. 22). Thus, the additional slow heating of ice IV from 162 to 195 K does not lead to the formation of ice XII from ice IV. This further proves that formation of ice XII on fast heating occurs from HDA, and not from ice IV, because ice XII formation had finished at ≈ 172 K (Fig. 1e of ref. 22). The absence of an ice IV \rightarrow ice XII transition could be for kinetic reasons, and an ice IV \rightarrow ice XII transition is still possible at higher temperatures. However, in our experiments the temperature range for that is very small because transition to stable ice VI sets in [21]. We further note that the metastability of ices IV and XII at low temperature and a pressure of 0.7 GPa has also been reported by Klotz et al. in an experimental report of a neutron diffraction study on HDA [34].

We finally discuss implications for the polymorphism of silica that is important in geophysics, materials science, and fundamental physics [35]. Pressure-induced amorphization of crystalline silica occurs at 25–35 GPa and 300 K [36]. Although this amorphization is in a different p - T domain than that of ice I at ≈ 1.0 GPa and 77 K, it demonstrates the remarkable similarity in physical properties of these tetrahedrally bonded compounds [36,37]. Teter et al. [26] point out that it is still unclear what phases of silica are stable at high pressure, what types of metastable phases are possible, and what structural similarities may exist among them. It is conceivable that the effect of heating rate at a given pressure on the type of metastable phase formed as outlined in this study for HDA, is also important for crystallization of pressure-amorphized silica, and that its study clarifies contradictory experimental results.

4. Concluding remarks

Pure D₂O ice IV and H₂O ice XII, and nearly pure H₂O ice IV are now available in gram quantities for further studies. The effect of heating rate on isobaric heating of HDA to produce either pure ice IV or pure ice XII is, to our knowledge, the first example of a parallel reaction on crystallization of an amorphous solid. It is conceivable that similar behaviour can be observed in other systems on crystallization of an amorphous solid. For example, crystallization of pressure-induced amorphous silica gives, depending on the p - T domain, various stable or metastable crystalline phases [26]. Here, the effect of heating rate on the type of crystalline phase formed could be important in the same manner as for HDA transitions to either ice IV or ice XII in this study and in our previous ones [21,22].

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