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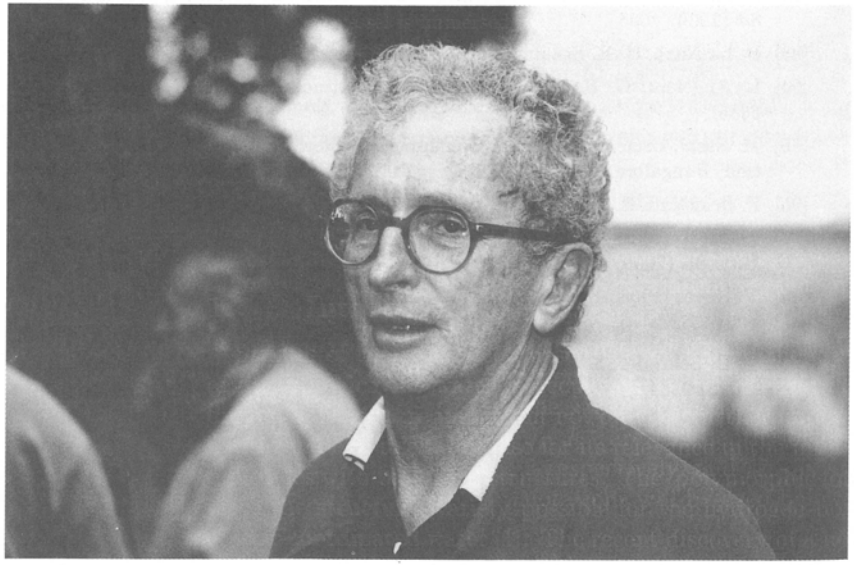

Erwin Mayer.

HIGH-DENSITY AMORPHOUS ICE AND ITS PHASE TRANSITION TO ICE XII

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Abstract

High-density amorphous ice, HDA, was heated in a pressure vessel with indium linings at constant pressures of between 0.52 to 1.9 GPa from 77 K up to 240 K. The formed phases were characterized by X-ray diffractograms of samples recovered under liquid N_2 at 1 bar. The metastable domain of ice XII thus revealed extends between $\approx$ 158–212 K from $\approx$ 0.7 to $\approx$ 1.5 GPa, and is in a different region of water's phase diagram than that shown by Koza et al. [Phys. Rev. Lett. **85**, 334 (2000)]. When HDA, or hexagonal ice, is compressed without using indium linings, ice XII can form even when the pressure vessel is immersed in liquid N_2, but it requires a pronounced apparent pressure drop at pressures $\gtrsim\approx$ 1.1 GPa. These apparent pressure drops can be caused by buildup of friction. We propose that shock-waves generated by apparent pressure drops cause transient local heating up to the temperature range of the ice XII metastable domain, and that this induces nucleation and crystal growth. Pressure-displacement curves obtained on compression of ice Ih are consistent with formation of ice XII from HDA only, and not from ice Ih.

1. Introduction

Studies of the water/ice phase diagram and of the crystalline phases of ice, in which the water molecules form tetrahedral networks by hydrogen bonding, are important not only for further understanding of the hydrogen bond itself, but also for its relevance in the interaction of water molecules with biological structures. The polymorphic forms of ice illustrate the structural variety possible for the hydrogen-bonded polymers of four-coordinated water [1]. The recent discovery of a new phase of ice, crystallizing in the much investigated medium pressure range [2], came as a surprise. This new high-pressure phase of ice, called ice XII, was

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first prepared by Lobban et al. [3], 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 [2]. Ice XII "contains only seven- and eight-membered rings and is the first example of a 4-connected net of this type" [4]. Ice XII is metastable with respect to ice V [5], like metastable ice IV which is also found within the stability region of ice V [2, 6, 7, 8], and its density is similar to that of ice IV [3].

Subsequently to its formation from the liquid phase, Koza et al. [9] reported 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) [10, 11, 12, 13] at 77 K on compression of hexagonal ice (ice Ih) up to 1.8 GPa. However, the decisive conditions favoring ice XII or HDA formation were not clear. In their study the relative amounts of HDA and ice XII were scattered more or less randomly. They concluded that they "have been unsuccessful in identifying a route that would predictably allow to separate the production of HDA from the production of ice XII." Similar findings were later reported in an abstract by Hallbrucker [14]. In retrospect Bragg peaks of ice XII had been observed and reported before in samples prepared on compression of ice Ih for formation of HDA [15, 16, 17] and attributed to "some metastable form of high-pressure crystalline ice" [17], but they have not been assigned to a new phase of ice. 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 apparent pressure drop at pressures $\approx\geq$ 1.1 GPa. They further proposed that shock-waves generated by the apparent pressure drops cause transient local heating, and that this induces nucleation and crystal growth of ice XII.

Apparent pressure drops and shock-wave heating can be avoided by using indium linings [10, 11, 12, 13]. This allowed us to determine the metastable domain of ice XII by heating HDA at constant pressures of between 0.52 and 1.9 GPa from 77 K up to 240 K. The metastable domain of ice XII thus revealed lies in the ice VI domain and extends between $\approx$ 158–212 K from $\approx$ 0.7 to $\approx$ 1.5 GPa [19]. Thus, the observation of a "second regime of metastability" of ice XII, postulated by Koza et al. [20] between 77 to $\approx$ 150 K and 1.0 to 1.8 GPa in order to account for its unexpected formation on compression of ice Ih at low temperatures (see Fig. 1 in Ref. [20]), seems to be an effect of apparent pressure drops and shock-wave heating.

We note that several other high-pressure ice phases form on heating HDA under pressure [21, 22, 23], and on compression of ice Ih at various temperatures [13, 20, 24]. For example, Suzuki et al. [23] recently

reported that on heating HDA at 1.5 GPa up to 180 K, a high-pressure ice forms which they tentatively assumed to be either ice IV, ice VI or ice XII.

2. Experimental methods

HDA samples were prepared by compression of ice Ih at 77 K in a commercially available piston-cylinder apparatus with an 8 mm (up to 1.8 GPa) or 10 mm (up to 1.3 GPa) diameter piston (from Specac Company), and pressure-displacement curves were recorded with the TestXpert V 7.1 Software. Controlled compression was achieved with a computerized "universal testing machine" (Zwick, Model BZ100/TL3S). Samples were recovered after compression from the piston-cylinder apparatus under liquid N_2 and characterized by X-ray diffraction. The characterized HDA samples were thereafter reloaded under liquid N_2 into the piston-cylinder apparatus and compressed for a second time. The compressed samples were further characterized by differential scanning calorimetry. As reported recently [5], this allows to determine the relative amounts of HDA and ice XII more accurately than by evaluation of X-ray diffractograms. The isobaric HDA $\rightarrow$ ice XII phase transition was studied in a controlled manner by using indium linings as described in Ref. [18] to avoid pressure drops and transient shock-wave heating. X-ray diffractograms were recorded on a diffractometer in θ-θ geometry (Siemens, model D 5000, Cu-$K\alpha$), equipped with a low-temperature camera from Paar. The sample plate was in horizontal position during the whole measurement. Installation of a "Goebel mirror" allowed to record small amounts of sample without distortion of the Bragg peaks.

3. Results and discussion

We first show that compression of HDA without indium linings can lead to formation of ice XII even when the pressure vessel is immersed in liquid N_2, and that this requires an apparent pressure drop presumably causing transient shock-wave heating [18]. We then proceed to the HDA $\rightarrow$ ice XII phase transition and the metastable domain of ice XII which was determined by isobaric heating of HDA at pressures of between 0.52 and 1.9 GPa in the absence of apparent pressure drops by using indium linings [19]. Thus, indium has a pronounced effect because its malleability is high even at 77 K.

Figure 1 shows that HDA can transform on compression into ice XII. Figure 1a is the pressure-displacement curve obtained on compression of ice Ih at 77 K which is similar to curves reported, e.g., by Mishima et al. [10, 11] The plateau region between 1.11 and 1.35 GPa is due to the

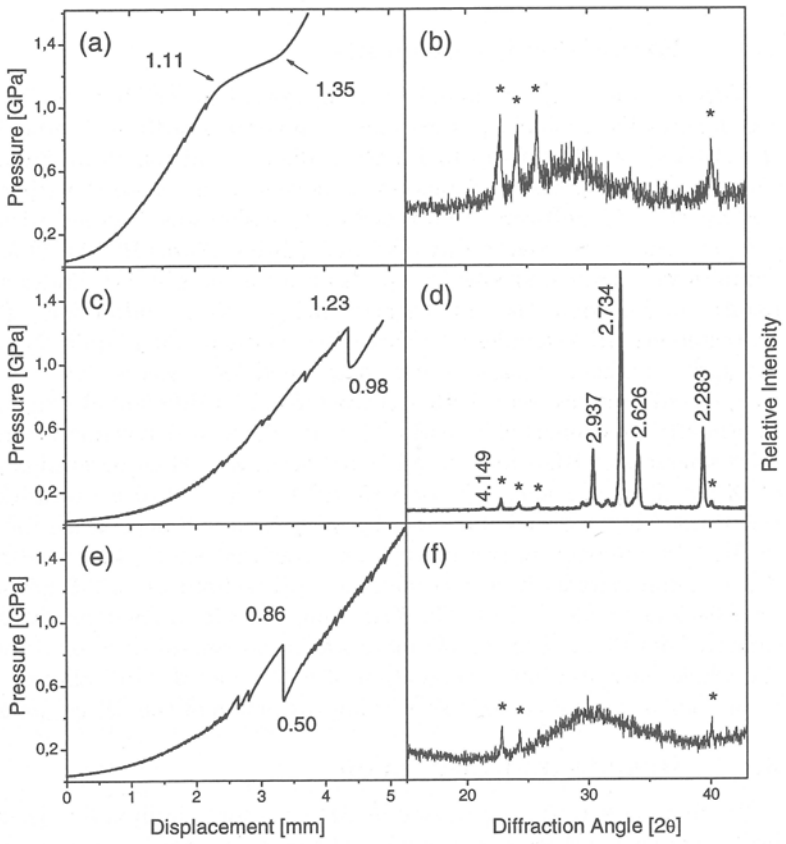

Figure 1. Ice XII formation on compression of HDA at 77 K. (a) Formation and characterization of HDA as shown by the pressure-displacement curve of ice Ih and (b) X-ray diffraction pattern (Cu-$K\alpha$) of recovered HDA recorded at 1 zero pressure; (c) is the pressure-displacement curve of HDA compressed up to 1.8 GPa, and (d) the X-ray diffraction pattern of ice XII recovered after (c). Note the pressure drop at 1.23 GPa. (e) Pressure-displacement curve of HDA, with pressure drop at 0.86 GPa, and (f) X-ray diffraction pattern of HDA recovered after compression. Ice Ih peaks are marked by the asterisks. HDA was compressed without indium linings. (From Ref. [18].)

phase transition of ice Ih to HDA. Figure 1b shows the characteristic X-ray diffraction pattern of a HDA sample which was recovered after compression under liquid N_2 at 1bar. Bragg peaks marked with asterisks are from a small amount of ice Ih condensed onto the sample during the transfer. The diffraction curve is shown only up to $2\theta = 43°$, because intense peaks from the substrate interfere at higher 2θ values. Therefore, the shoulder on the HDA peak at high 2θ values is not observable [10, 11, 15]. This HDA sample was subsequently compressed and Fig. 1c shows the pressure-displacement curve, with a pronounced pressure drop at 1.23 GPa. The compressed material was thereafter identified by its X-ray diffraction pattern as nearly pure ice XII (Fig. 1d), contaminated only with a small amount of ice Ih (marked with asterisks). In a further experiment, a pressure drop on compression of HDA up to 1.5 GPa occurred at 0.86 GPa, but the recovered phase was unchanged HDA (cf. Figs. 1e and 1f). Apparently it requires not only a pressure drop, but also a minimum pressure for inducing formation of ice XII.

The curvature at the beginning of all three pressure-displacement curves is due to densification of ice Ih on first compression (Fig. 1a) or of the HDA pieces filled into the piston cylinder apparatus (Figs. 1c and 1e). These curvatures are followed by fairly straight lines: for Figure 1a this indicates compression of ice Ih until its phase transition to HDA starts at 1.11 GPa, for Figs. 1c and 1e it indicates compression of HDA.

In Fig. 2 we show that pressure-displacement curves of ice Ih samples are also consistent with formation of ice XII from HDA, and not directly from ice Ih. In the pressure-displacement curve of ice Ih shown in Fig. 2a the second, intense, pressure drop occurs at 1.08 GPa. The recovered phase characterized by X-ray diffraction is some untransformed ice Ih (Fig. 2b, marked with asterisks) and HDA. In the pressure-displacement curve of another ice Ih sample shown in Figure 2c the pressure drop occurs at 1.29 GPa. The recovered phase now is nearly pure ice XII (cf. Fig. 2d) containing only a small amount of ice Ih. Thus ice XII is formed on pressure drop only when conversion of ice Ih to HDA had already occurred. From the shape of these pressure-displacement curves we conclude that for Fig. 2c the ice Ih→HDA transition had been nearly completed when the pressure drop occurred at 1.29 GPa. However, for Fig. 2a the pressure drop at 1.08 GPa occurred at the beginning of the transition, and further compression without pressure drop resulted in formation of HDA and not of ice XII.

In our experience the decisive factor for formation of ice XII on compression of HDA at 77 K is a massive apparent pressure drop at a sufficiently high pressure. This pressure drop is caused by sudden release of friction. Build-up of friction between the piston and the pressure vessel

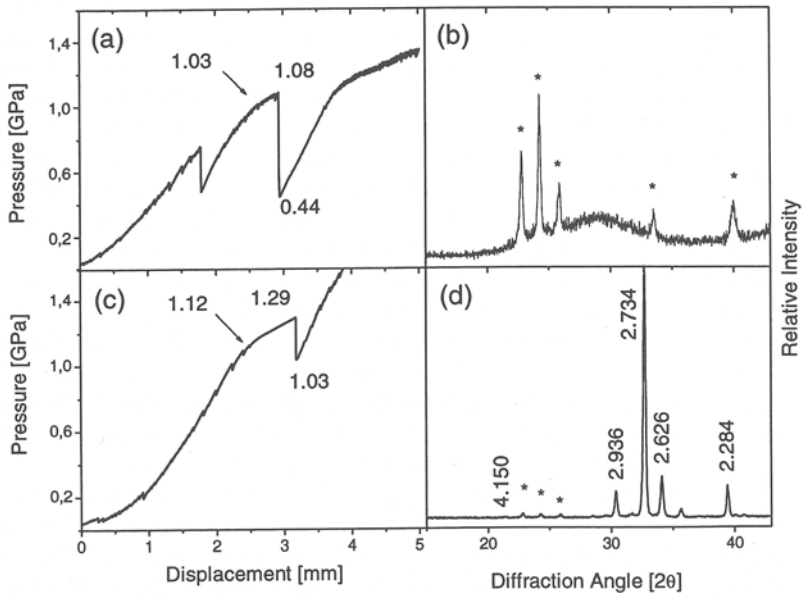

Figure 2. Ice XII formation on compression of ice Ih at 77 K. (a) and (c) Pressure displacement curves of two ice Ih samples, with pressure drop at 1.08 GPa for (a) and 1.29 GPa for (c); (b) is the X-ray diffraction pattern (Cu-Kα) of recovered HDA recorded at zero pressure after (a), (d) is the pattern of nearly pure ice XII recovered after (c). Ice Ih peaks are marked by the asterisks. Ice Ih was compressed without indium linings. (From Ref. [18].)

containing ice Ih and/or HDA can occur because the sample creeps on compression between piston and pressure vessel [25]. To minimize or avoid this friction build-up, Mishima et al. [10, 11, 12, 13] held samples enclosed in an indium cup. Sudden release of friction generates a shock-wave which causes the enormous bang and presumably heating of the sample. Johari [26] reported that in his studies of compression of ice Ih "the sudden release of the mechanical energy also produces a spike of temperature from 77 K up to $\approx$ 170 K, lasting for only a few seconds, as indicated by the thermocouple inserted into the plug and kept $\approx$ 1 mm away from the ice sample." This temperature then is within the metastable domain of ice XII shown in Fig. 3.

Shock wave generation is a necessary requirement for formation of ice XII at 77 K bath temperature on compression of ice Ih, or HDA, but it is not sufficient: Figs. 1e and 1f show that HDA has to be com-

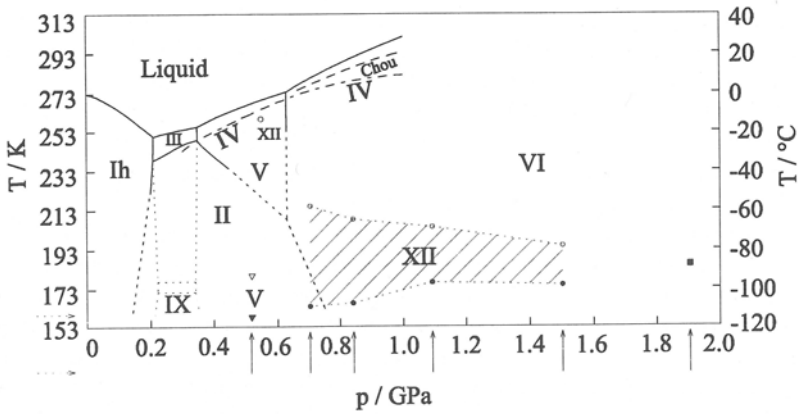

Figure 3. The medium pressure range of the phase diagram of water/ice. The empty circle in the ice V domain denotes the region where ice XII formed from the liquid [3]. The hatched region indicates the p, T region where ice XII was observed in our study [19]. Vertical arrows below the pressure axis indicate the pressures used for isobaric heating of HDA by using indium linings. Full circles characterize the temperature region where ice XII formed from HDA, and empty circles denote the region of its phase transition to another high-pressure phase. Full and empty triangle indicate where at 0.52 GPa ice V and ice II are formed, and the full square indicates formation of ice VI from HDA at 1.91 GPa. Horizontal broken arrows indicate for comparison the temperatures used by Koza et al. [20] for isothermal compression of ice Ih. (From Ref. [19].)

pressed above 0.86 GPa before a pressure drop induces formation of ice XII. The threshold value necessary for ice XII formation estimated from these pressure-displacement curves is $0.86 < \leq 1.23$ GPa. In a further experiment (not shown) HDA was transformed on compression by a pressure drop at 1.1 GPa which narrows the range of the threshold value. On compression of HDA its density increases in a nearly linear manner [10, 11, 25]. Thus, it is really the *density* of HDA which has to be above a threshold value before a shock wave can induce formation of ice XII.

In a next step we determined the (meta-)stability domain of ice XII by isobaric heating of HDA at pressures of between 0.52 and 1.9 GPa in the absence of apparent pressure drops by using indium linings [19]. The experimental evidence is shown in Figure 2 of Ref. [19] in form of isobaric volume change versus temperature plots, and of X-Ray diffractograms of samples recovered at 77 K and 1 bar. Figure 3 shows our

results within the relevant part of water's phase diagram, and the difference to the approach applied by Koza et al. [20]. The empty circle in the ice V domain indicates the region where ice XII was first obtained from the liquid [3]. Vertical arrows on the pressure axis indicate the pressures at which we heated HDA isobarically from 77 K at a rate decreasing from ≈ 6 to ≈ 1.5 Kmin^{-1}. Formation of ice XII is indicated by full circles, and its phase transition to ice VI on further heating by empty circles. The hatched region in between thus constitutes the p,T area where (meta-)stable ice XII can exist. For comparison Koza et al.'s [20] approach, which they presumed to be isothermal, is indicated on the temperature axis by horizontal dotted arrows. At these temperatures, and additional temperatures of 77 and 100 K, samples of ice Ih were pressurized up to 1.8 GPa. Koza et al. [20] report that "the observation of explosive sound accompanied by abrupt loss of pressure indicates the development of shock waves during the compression which could play a major role in the transformation process." Due to the nature of their experiments, transition pressures and temperatures can not be determined unambiguously, and their postulated "second regime of metastability" of ice XII lies below the temperature scale of Fig. 3.

It is intriguing that HDA transforms over such a wide range of pressures first into ice XII before on further heating stable ice VI is formed. Figure 2 in Ref. [19] demonstrates that HDA densifies further on isobaric heating before its phase transition to ice XII occurs. In a similar manner, Figure 1 shows that HDA requires at 77 K a minimal pressure of $\geq\approx 1.1$ GPa, or a minimal density, before pressure drop and shock-wave heating can lead to formation of ice XII. According to Mishima et al. [10, 11] the density of HDA at 77K and 1.0 GPa is 1.31 ± 0.02 g/cm^{-3}, and an even higher density results on isobaric heating of HDA at 1.1 or 1.9 GPa (see Fig. 2 in Ref. [19]). Thus, the density difference between low-density amorphous ice (LDA) and HDA at 77 K and 1 bar is similar to that of the latter and, for example, HDA at 1.0 GPa and 150 K, shortly before its phase transition to ice XII. Therefore, the structural state of densified HDA at a density of ≥ 1.31 g/cm^{-3} has to be considered in attempts to understand the HDA→ice XII phase transition in terms of local structural elements. X-Ray [15, 16] and neutron [17] diffraction studies of the structure of HDA do not seem to be helpful here because they were done at 1 bar, and the density of HDA at this pressure is only 1.17 ± 0.02 g/cm^{-3} [10, 11]. The problems in interpreting the structures of LDA and HDA on the basis of the available diffraction data are lucidly illustrated by Pusztai [27].

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