COMMUNICATIONS

(Meta-)stability domain of ice XII revealed between ≈158–212 K and ≈0.7–1.5 GPa on isobaric heating of high-density amorphous ice

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High-density amorphous ice was heated 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 (meta)stability domain of ice XII thus revealed extends between ≈158–212 K from ≈0.7 to ≈1.5 GPa. We further discuss whether ice XII has a low-temperature region of stability within the ice VI domain. Our (meta)stability domain of ice XII is in a different region of water's phase diagram than that shown by Koza *et al.* [Phys. Rev. Lett. **84**, 4112 (2000)].
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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 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] Subsequent to its formation from the liquid phase, Koza *et al.*[5] 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)[6–9] at 77 K on compression of hexagonal ice (ice Ih) up to 1.8 GPa. Kohl *et al.*[10] 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 ≈≥1.1 GPa. It has been proposed that shock-waves generated by the pressure drops cause transient local heating, and that this induces nucleation and crystal growth of ice XII.[10,11] Thus, the apparent observation of a ''second regime of metastability'' of ice XII postulated by Koza *et al.*[12] between 77 to ≈150 K and 1.0 to 1.8 GPa in order to account for its unexpected formation at low temperatures (see Fig. 1 in Ref. 12) could be an effect of pressure drops and shock-wave heating during compression of ice Ih. Ice XII is metastable with respect to ice V,[13] like metastable ice IV which is also found within the stability region of ice V,[2,14–16] and its density is similar to that of ice IV.[3]

Here, we show that HDA kept at pressures between ≈0.7–1.5 GPa transforms at ≈158 K, on heating from 77 K to 173 K, into ice XII directly, and that ice XII has an extended region of (meta)stability before its phase transition to other high-pressure phases. Thus, ice XII can now be made in a reproducible manner, without contamination by HDA and low-density amorphous water (LDA), and this opens up new possibilities for its detailed characterization. The transition of HDA to ice XII and its subsequent phase transition to other high-pressure ices is followed by isobaric volume–temperature curves, and the phases are characterized by x-ray diffractograms from recovered samples. The basic difference to the experiments described by Koza *et al.*[12] is that conversion of HDA into ice XII occurs without pressure drops and shock-wave heating.[10] The ''second regime of metastability'' originating from the experiments presented here is in a different region of the phase diagram compared with that postulated by Koza *et al.*,[12] and it does not have the ambiguities associated with pressure and temperature changes on pressure drops during compression of ice Ih. We further discuss the possibility that at low temperatures ice XII could have a *p,T* region of stability within the ice VI domain.

To clarify our findings, and the difference to the approach applied by Koza *et al.*,[12] we first present in Fig. 1 our results within the relevant part of water's phase diagram and give the experimental evidence subsequently. 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 K min^{-1}. Formation of ice XII is indicated by full circles, and its phase transition to other high-pressure ices on further

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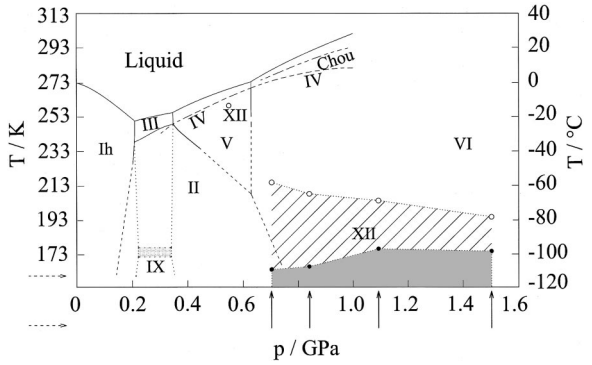

FIG. 1. The medium pressure range of the phase diagram of water–ice. The empty circle in the ice V domain denotes the region where ice XII formed from the liquid (Ref. 3). The hatched region indicates the *p,T* region where ice XII was observed in this study on heating HDA (shaded region). Vertical arrows below the pressure axis indicate the pressures used for isobaric heating of HDA. 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. Horizontal broken arrows indicate for comparison the temperatures used by Koza *et al.* (Ref. 12) for isothermal compression of ice *Ih* (from Ref. 2, with changes).

heating by empty circles. The hatched region in between thus constitutes the *p,T* area where (meta)stable ice XII was observed in this study, above the shaded region for HDA. For comparison Koza *et al.*'s[12] approach, which they presume to be isothermal, is indicated on the temperature axis by horizontal broken 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.*[12] 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 cannot be determined unambiguously, and their postulated ''second regime of metastability'' of ice XII lies below the temperature scale of Fig. 1.

We note that several other high-pressure ice phases form on heating HDA under pressure,[17–19] and on compression of ice Ih at various temperatures.[9,12,20,21] For example, Suzuki *et al.*[19] 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.

We first prepared HDA by compression of ice Ih at 77 K up to 1.2 GPa in a commercially available piston-cylinder apparatus with 10 or 8 mm diameter piston (from Specac Company), by using a computerized ''universal testing machine'' (Zwick, Model BZ100/TL3S) for controlled compression at a rate of 7000 N min^{-1}. Indium linings were used as described in Ref. 10 to avoid pressure drops during compression, and 0.500 (0.250) cm^3 of water were pipetted into the precooled piston-cylinder apparatus with 10 (8) mm diameter piston. The pressure-displacement curves have the same shape as those reported before.[6,7,10] The plateau region is due to the phase transition of ice Ih to HDA. These pressure-displacement curves without pressure drops are characteristic for formation of HDA at 77 K without ice XII.[10] HDA recovered after compression under liquid N_2 at 1 bar was characterized by x-ray diffraction. Its diffractogram, shown in

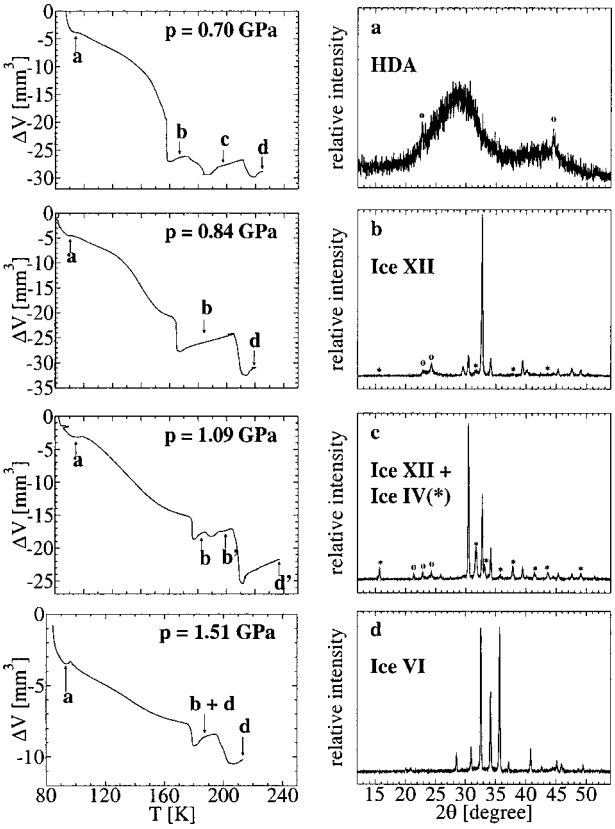

FIG. 2. (Left) Isobaric ΔV vs temperature plots obtained on heating HDA at pressures of 0.70, 0.84, 1.09, and 1.51 GPa. Vertical arrows indicate the temperatures where in subsequent experiments the phase was characterized by heating up to the temperature, cooling thereafter under pressure to liquid N_2, recovering the sample at 1 bar under liquid N_2 and characterizing the sample by x-ray diffraction. The ΔV values of the 1.51 GPa plot have to be multiplied by two for comparison with the other three plots because 0.250 instead of 0.500 cm^3 of water were used. ΔV values were calculated from the displacement by assuming that the diameter of the piston remains constant. The pronounced ΔV increase on heating from ≈80 to 90 K corresponds to the region where liquid N_2 had evaporated and slow warming of the apparatus begins. (Right) x-ray diffractograms (Cu–$K\alpha$) of HDA, and of high-pressure ice phases obtained from HDA, recovered under liquid N_2 at 1 bar and recorded at 88 K. (a) HDA with a small amount of ice Ic (marked by circles); (b) ice XII containing a small amount of ice IV (marked by asterisks) and of ice Ic (marked by circles); (c) ice XII containing a larger amount of ice IV (marked by asterisks) and a trace of ice Ih (marked by circles); (d) ice VI. The relative intensities of the ice XII reflections in (b) and (c) differ, and they further differ from those shown in Ref. 10, which may indicate texture effects. However, their peak positions are identical with those reported for ice XII (Refs. 3, 5, 10, and 12). X-ray diffractograms were recorded on a diffractometer in θ–θ geometry (Siemens, model D 5000), 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 us to use small amounts of sample without distortion of the Bragg peaks.

Fig. 2 as curve a, is that reported in the literature,[6–9] with the maximum of the intense broad peak at 3.0 Å. The pressures given in the following are nominal pressures, and the pressures at the sample are expected to be slightly lower. The temperature was measured with a thermocouple firmly attached to the outside of the piston cylinder apparatus, and its accuracy is estimated as ±2 K by following the glass–liquid transition of glycerol at ambient pressure.

Figure 2 shows four plots of the change in volume, ΔV, with temperature on heating HDA from 77 K up to 240 K at

constant pressures of 0.70, 0.84, 1.09, and 1.51 GPa. Heating rate was $\approx 6\ \mathrm{K\,min^{-1}}$ at 110 K, and it decreased linearly to $\approx 1.5\ \mathrm{K\,min^{-1}}$ at 240 K. Phase transitions become apparent by pronounced decrease in volume. The phases were characterized by x-ray diffraction in subsequent experiments, e.g., HDA was heated from 77 K at constant pressure up to the temperature marked by an arrow, the sample cooled to liquid N_2 and recovered under liquid N_2 at 1 bar. This assumes that the formed phase survives on cooling and decompression at 77 K, and it is the standard procedure for investigating high-pressure ices at 1 bar. The letters at the arrows refer to the x-ray patterns of the formed high-pressure ice phases.

The ΔV versus temperature plot obtained on heating HDA (marked a) at 0.70 GPa up to ≈150 K (Fig. 2, top) thus indicates first its gradual densification. We note that Mishima reported annealing effects on heating HDA at 1.0–1.5 GPa up to 130–150 K.[9] On further heating a phase transition is indicated by the abrupt decrease in volume. To characterize this a new HDA sample was heated up to 177 K, that is to the arrow marked as b, and recovered subsequently under liquid N_2 at 1 bar. Its x-ray pattern is shown as curve b. It contains mainly the Bragg peaks of ice XII.[3,5,10,12] Additional weak peaks indicate ice IV (marked by asterisks)[16] and cubic ice (marked by circles) as minor impurities. A new HDA sample heated to ≈200 K, that is to the arrow marked c, was characterized as ice XII containing a significantly larger amount of ice IV (curve c). Phase transition of the ice XII/ice IV mixture starts at ≈212 K, and the sample characterized after heating to ≈224 K, the arrow marked d, is ice VI (curve d). We note that the relative intensities of the ice XII peaks vary (curve b versus c) which may indicate texture effects, but the peak positions are the correct ones.[3,5,10,12]

In the same manner isobaric ΔV versus temperature plots were obtained on heating HDA at other pressures, and Fig. 2 shows three further isobaric plots obtained with increasing pressures of 0.84, 1.09, and 1.51 GPa. On heating HDA at a pressure of 0.84 GPa, it first densifies similar to heating at 0.70 GPa. Phase transition to ice XII starts at a higher temperature of ≈165 K which is consistent with Mishima's[8] report of the dependence of the onset of crystallization of HDA on pressure. Points b and d in the ΔV versus temperature plot were characterized as ice XII with a small amount of ice IV (similar to curve b), and as ice VI (curve d).

The ΔV versus temperature plot in Fig. 2 obtained on heating HDA (a) at 1.09 GPa shows that the onset of crystallization at ≈175 K is shifted further to even higher temperatures. The phase formed on heating a new HDA sample to 183 K, to the arrow marked b, was characterized as ice XII containing a small amount of ice IV (similar to curve b). On heating a new HDA sample up to 200 K, that is to the arrow marked as b′, the x-ray pattern of the sample recovered at 77 K and 1 bar (not shown) contained also the peaks of ice XII and ice IV, but the relative intensity of the ice IV peaks had increased slightly. A further phase transition is indicated by the volume decrease between 205–212 K. The phase formed was characterized as ice VI on heating another HDA sample up to 235 K, to the arrow marked d′. The Bragg peaks in its x-ray diffractogram (not shown) are at the positions reported for ice VI (Ref. 22) and shown in curve d, but deviations in its relative intensities may indicate a texture effect.

The ΔV versus temperature plot obtained on heating HDA at 1.51 GPa (Fig. 2) shows further increase of the onset of crystallization. Abrupt decrease of volume started at 178 K, and the phase characterized subsequently on heating to 189 K (to the arrow marked b and d) was a mixture of ice XII and ice VI. The second transition starting at 195 K is from the ice XII→ice VI transition, as characterized after heating a sample to 214 K (arrow marked d).

Thus, the pronounced changes in volume with increasing temperature can be assigned to specific phase transitions. The ΔV versus temperature plot shows that the HDA to ice XII transition occurs within a very narrow temperature range, i.e., within ≈1 K, whereas the further transition of ice XII ice IV to ice VI occurs over a wider range of ≈7 K. Therefore, as upper temperature range for the (meta)stability region of ice XII inserted in the phase diagram of Fig. 1, the temperature of the beginning of the rapid volume decrease was chosen. Estimates of the high- and low-pressure boundary of ice XII formation from HDA were obtained for 1.91 and 0.52 GPa (not shown in the figures). On heating HDA at 1.91 GPa, ice VI was formed directly at ≈182 K, whereas on heating HDA at 0.52 GPa, ice V was formed at ≈158 K.

Thus, the metastability region of ice XII revealed by our isobaric ΔV versus temperature plots obtained on controlled slow heating of HDA (Fig. 1) lies in a very different p,T region of water's phase diagram than that reported by Koza *et al.*[12] This is easily explained as follows. First, since ice XII forms on compression of ice Ih only from HDA, and not directly from ice Ih,[10] Koza *et al.*'s observation of ice XII formation on compression of ice Ih only at pressures exceeding 1.0 GPa in fact reflects the pressure necessary to form HDA, and not the low-pressure boundary of the ice XII region. Second, according to Koza *et al.*[12] the ice XII region lies below 150 K whereas in our study ice XII formation from HDA starts at ⩾158 K. The reason for these different results can be explained by the difference in experimental approaches. In our experiments ice XII is produced by controlled slow heating of HDA, whereas Koza *et al.*'s temperature values are misleading because pressure drops necessary for ice XII formation are accompanied by transient local heating.

The rapid transition from HDA to ice XII and the relatively slow transition of ice XII to the other high-pressure ice phases is surprising. Rapid transition from HDA to ice XII could be caused by crystalline nuclei of ice XII present already in HDA providing nucleation sites or seeds, as pointed out by one of the reviewers, and we can not discard or confirm this possibility.

We finally discuss the possibility that at *low* temperatures ice XII could be more stable than ice VI. When both ice VI and XII are proton-disordered, entropy difference is relatively small and, according to the Clapeyron relation, the VI–XII phase boundary would be nearly parallel to the temperature axis. On the other hand, if ice XII is proton-ordered, the VI–XII phase boundary would be rather parallel to the pressure axis. There may be a possibility that ice XII becomes stable at low temperatures in case it becomes proton-ordered. So far both ice VI and ice XII are considered to be

proton disordered.[2,3] However, Kohl[23] recently observed indications for proton-ordering of ice XII, in the same manner reported for ice V by Handa *et al.*[24] On isothermal annealing at 119 K and 1 bar and subsequent reheating, an endothermic peak is observed by differential scanning calorimetry. In line with Handa *et al.*[24] we attribute the effect of annealing to proton-ordering of some ice XII which becomes disordered on subsequent heating. This will be reported separately. Enthalpy favors formation of ice XII from ice VI at 1 bar. The enthalpy of the ice XII→cubic ice transition is $-1.27 \pm 0.05\ \mathrm{kJ\,mol^{-1}}$.[13] For the enthalpy of the ice VI→cubic ice transition, Handa *et al.*[25] have reported lower bound and upper bound values of -1.405 and $-1.760\ \mathrm{kJ\,mol^{-1}}$. Thus, for ambient pressure the enthalpy of the ice VI→ice XII transition calculates either as -0.13 or as $-0.49\ \mathrm{kJ\,mol^{-1}}$. We note that Johari and Whalley[26] had reported evidence for a very slow transformation in ice VI at 123 K and 0.9 GPa for 252 days, and had suggested that probably a wholly new phase was being produced. We speculate that this could have been proton-ordered ice XII. This could be tested experimentally by keeping ice VI at suitable *p,T* conditions for long periods of time and by searching for formation of ice XII by diffraction. We emphasize that the low-temperature boundary of the ice XII region shown in Fig. 1 reflects the kinetics of the HDA→ice XII transition and thus, that even lower temperatures have to be considered in the search for an ice VI →ice XII transition.

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