High Density Amorphous Ice from Cubic Ice

Thomas Loerting,*[a, c] Ingrid Kohl,[a]
Werner Schustereder,[b] Katrin Winkel,[a] and
Erwin Mayer[a]

Supercooled water does not behave like a simple liquid, but instead shows a number of anomalous properties.[1] These include the diffusion coefficient [2] or the kinematic viscosity [3] which show anomalous pressure dependencies on compression up to ≈ 200 MPa, whereas beyond ≈ 200 MPa the expected behaviour is observed. To explain these anomalies the second critical point hypothesis has been put forward,[4] in which a first-order-like phase transition between a low- (LDL) and high-density liquid (HDL) is thought to occur. LDL and HDL become indistinguishable above the second critical point, which is postulated to be in the "no man's land" around 180–220 K and 100–340 MPa,[5–8] where only crystalline ice has been observed experimentally. This model is supported by the observation that there are (at least) two different phases of amorphous water called low-(LDA) and high-density amorphous ice (HDA),[9, 10] which have been found to show a first-order like transformation in compression/decompression experiments.[11, 12] On heating, LDA and HDA experience a glass-transition to the highly viscous, supercooled liquids denoted low-(LDL) and high-density liquid (HDL), respectively.[13–17] The role of HDA in this model has become unclear since the discovery of a further distinct structural state called very-high density amorphous ice (VHDA).[18] It has lately been argued that only VHDA and LDA are homogeneous disordered structures, whereas HDA does not constitute a particular state of the HDA network.[19] This issue is still under debate, since the transition from HDA to VHDA on isothermal compression at 125 K has been found recently to be similar to the transition from LDA to HDA.[20] The detailed structures of recovered HDA and VHDA have been determined at ambient pressure and 77 K by means of neutron diffraction with isotope substitution.[21, 22] These two studies contain the first experimental determination of the three site-site distribution functions (H–H, O–O, O–H). For both HDA and VHDA there is no evidence in the diffraction pattern to show that it is microcrystalline rather than a genuinely amorphous structure.

[a] Dr. T. Loerting, Dr. I. Kohl, K. Winkel, Prof. Dr. E. Mayer
Institute of General, Inorganic and Theoretical Chemistry
University of Innsbruck (Austria)
Fax: (+ 43) 512-507-2925
E-mail: thomas.loerting@uibk.ac.at

[b] Dr. W. Schustereder
Max-Planck-Institute for Plasma-Physics, EURATOM Association
Boltzmannstr. 2, 85748 Garching (Germany)

[c] Dr. T. Loerting
Institute of Physical Chemistry, University of Innsbruck
Innrain 52a, A-6020 Innsbruck (Austria)

Herein, we show that HDA produced by pressure-induced amorphization of cubic ice (Ic) at 77 K is not the same material as "traditional" HDA produced by pressure-induced amorphization of hexagonal ice (Ih) at 77 K.[23, 24] The density of both amorphous states recovered at ambient pressure is very similar; however, the X-ray structure factor as well as the phase transition characteristics in differential scanning calorimetry scans, differ in the onset temperature, enthalpy and sharpness of the exotherms.

Hexagonal ice was prepared by either pipetting 0.300 mL of deionized water directly into the piston-cylinder apparatus lined with an indium container kept at 77 K, or by heating HDA close to ambient pressure to ≈ 260 K and recovering to 77 K and 1 bar, or by Johari's procedure of decompressing HDA to 0.06 GPa and heating to 235 K.[25] Cubic ice was prepared by hyperquenching small liquid droplets of ≈ 3 µm diameter on a cryoplate kept at 190 K in the same way reported earlier.[26] The deposit was then transferred to the piston–cylinder apparatus and filled into the indium–lined cylinder by spooning, under liquid nitrogen. Alternatively, cubic ice was prepared by heating HDA to 185 K at 0.025 GPa and recovering to 77 K and 1 bar. HDA was produced by compressing 300 mg of Ih to 1.5 GPa at 77 K in a similar way to our previous studies.[27–29] These starting materials for the pressure-induced amorphization process have been characterized using powder X-ray diffractograms, which are depicted in Figure 1. The posi-
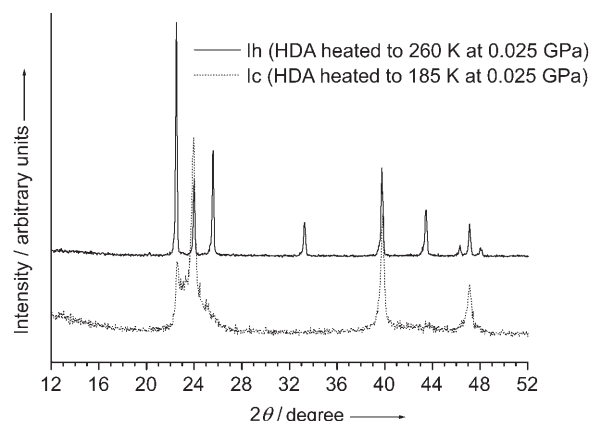

Figure 1. X-ray diffractograms of hexagonal ice after heating of HDA to 260 K and cubic ice after heating HDA to 185 K, both at 0.025 GPa.

tions of the sharp reflexes agree perfectly with the literature values both for Ic and Ih,[30] which confirms the quality of our starting material. It does not make a difference whether Ic and Ih are prepared directly from the liquid or by crystallizing HDA; in both cases we find the X-ray diffractograms to be almost indistinguishable in peak positions and full width at half height (FWHH) within experimental uncertainty. The only exception is that cubic ice, obtained on hyperquenching small liquid droplets, contains also a tiny amount of hexagonal ice (less than 5%), which possibly condensed in humid air during sample transfer or which was formed during the hyperquenching procedure.[31] It is not possible to grow single crystals of Ic, for

even though it has similar crystallographic properties to Ih,[32,33] it is metastable by ≈ 10–$50\,\mathrm{J\,mol^{-1}}$.[34] So far it has not been possible to prepare Ic without glide-type stacking faults and disorder.[35] Ih and Ic are not distinguishable by means of Raman or infrared spectroscopy.[36]

Figure 2 shows the compression and decompression curves obtained on pressurizing and depressurizing Ic and Ih samples at a rate of $1000\,\mathrm{N\,min^{-1}}$ in a cylinder of 8 mm bore diameter
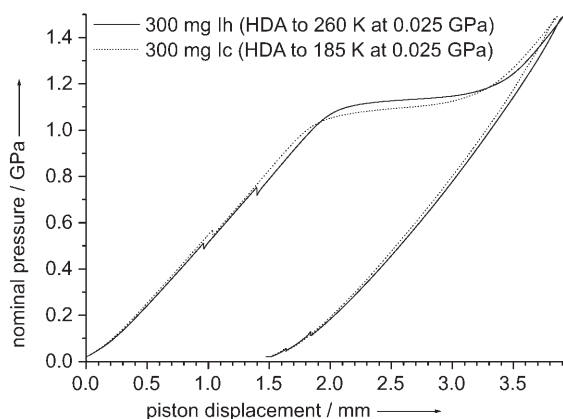

Figure 2. Compression/decompression curves for pressure-induced amorphization of Ih and Ic, obtained on pressurizing/depressurizing 300 mg of H_2O uniaxially.

(i.e. at $20\,\mathrm{MPa\,min^{-1}}$). In agreement with the literature we find for all cases a plateau region, which is indicative of the sharp phase transition to the amorphous state.[23] Ih shows an onset pressure for amorphization of $\approx 1.10\,\mathrm{GPa}$, independent of the preparation route for Ih. The transformation occurs where expected, from linearly extrapolating the melting line of Ih. Therefore, pressure-induced amorphization is interpreted as a thermodynamic melting process followed by immediate vitrification.[23] This is contrary to the mechanical melting hypothesis proposed by Tse et al. where at $T < 160\,\mathrm{K}$ an increase in hydrostatic pressure causes the Ih phonon modes to be softened, ultimately bringing the crystal to a mechanical collapse ("mechanical melting").[37,38] Even though the transition seems to be slightly sharper for hexagonal ice obtained from HDA, compared to hexagonal ice obtained from freezing liquid water, we infer that for our conditions the preparation of Ih does not play a crucial role for the compression/decompression curves. By contrast Johari points out that the onset pressure increases from ≈ 0.68–$0.82\,\mathrm{GPa}$ to ≈ 0.95–$1.02\,\mathrm{GPa}$ for micrometre and millimetre sized crystals of Ih respectively, since sites of elastic instability at grain boundaries lower the onset pressure for amorphization in polycrystalline samples.[25]

For Ic, pressure-induced amorphization has originally been thought to be impossible under similar conditions since Ic is a metastable crystalline phase which shows, by contrast to Ih, no solid-liquid phase boundary.[39] However, this hypothesis had to be refuted since piston displacement curves in compression experiments of Ic are found to be similar to the curves obtained on compressing Ih. We find that, for cubic ice obtained from HDA and cubic ice from the liquid, a lower nominal onset

pressure of $\approx 1.01\,\mathrm{GPa}$ is attained in accordance with earlier findings. Again, the way of preparing the crystals does not affect the amorphization process. All of the curves reach roughly the same point at a pressure of 1.5 GPa corresponding to a density of $\approx 1.40\,\mathrm{g\,cm^{-3}}$. After decompression all of the starting materials reach a density of $\approx 1.18\,\mathrm{g\,cm^{-3}}$, which agrees well with the value determined by Mishima et al. ($1.17 \pm 0.02\,\mathrm{g\,cm^{-3}}$).[11,23] This density ρ is calculated from the raw uniaxial displacement data Δx shown in Figure 2 corrected by the indium baseline from equating $\rho = 0.92 \cdot 6.49/(6.49 - \Delta x)$. In this formula an initial density of $0.92\,\mathrm{g\,cm^{-3}}$ for pre-compressed Ih at 77 K and 1 bar [33] and an initial sample height of 6.49 mm (corresponding to 0.2995 g sample in a cylinder of 8 mm diameter) and a constant diameter of the piston-cylinder apparatus lined with indium is assumed. At higher temperatures the amorphization pressure is reduced and reaches $\approx 0.80\,\mathrm{GPa}$ at $\approx 147\,\mathrm{K}$ for Ih[40] and $\approx 0.65\,\mathrm{GPa}$ at $\approx 145\,\mathrm{K}$ for Ic.[12]

In Figure 3 the X-ray diffractograms of the recovered samples at 88 K and 1 bar are shown. HDA produced from pressure-amorphization of hexagonal ice shows the maximum at a
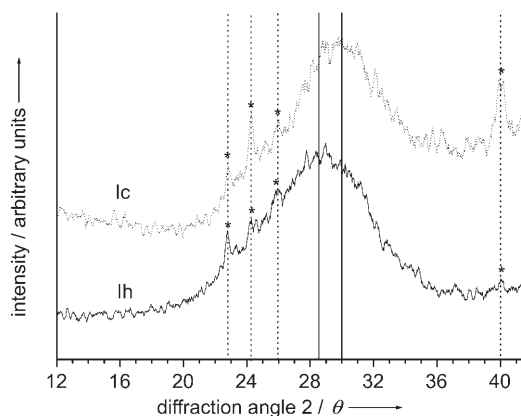

Figure 3. X-ray diffractograms of the recovered HDA states after compression of Ic and Ih from the liquid. The powder diffractogram from Ih made from HDA cannot be distinguished from the diffractogram from Ih made from the liquid.

diffraction angle 2θ of ≈ 28.5–$28.8°$ (obtained from four samples of differently prepared Ih) corresponding to an interplanar spacing of $\approx 3.1\,\text{Å}$. This is in agreement with earlier X-ray and neutron diffraction studies on HDA[22,41–43]. The diffracted maximum, after recovery of pressure-amorphized cubic ice, is reproducible at an angle of ≈ 29.6-$30.0°$ ($\approx 3.0\,\text{Å}$), that is, a shift of $\approx 1.1°$ compared to HDA obtained from Ih. For comparison LDA, HGW and ASW show a maximum at $24.0°$ ($3.7\,\text{Å}$), and VHDA at $33.0°$ ($2.7\,\text{Å}$).[18,23] These results for LDA[11,22,44] and VHDA[21,45,46] are also consistent with earlier measurements of the structure factors. To eliminate the possibility that this shift in diffraction angles is related to the equipment rather than to the ice samples, a small amount of hexagonal ice condensed onto the samples during transfer serves as internal standard. The three sharp hexagonal peaks between 22° and 26° as well

as the sharp peak at 40° are found within 0.1° in all three diffractograms, which confirms that the shift of the maximum is indeed a sample property. In general, different X-ray structure factors imply different radial density functions, that is, different structures. We conclude, therefore, that HDA prepared from Ih and HDA prepared from Ic show subtle differences in their respective O-O radial density functions. Such structural differences are also expected to affect the phase transition behaviour.

Hence, we report in Figure 4 differential calorimetry scans of these HDA samples. Both samples show the well known two exotherms related to the transitions from HDA→LDA and from
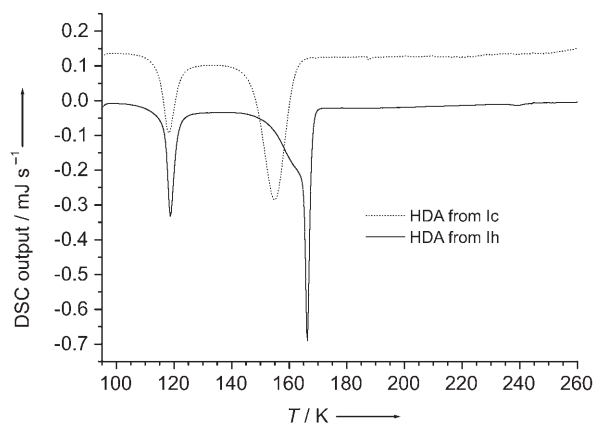

Figure 4. Differential scanning calorimetry scans of the recovered HDA states after compression of Ic and Ih.

LDA→Ic.[47] Whereas Handa et al.[47] used a Tian-Calvet heat-flow calorimeter with ≈ 2.7 g of amorphous sample, we employ a highly sensitive differential scanning calorimeter, which requires only ≈ 10–20 mg of amorphous sample. Due to the better heat transfer associated with heating a relatively small mass, the sample and reference capsules were heated at much higher rates than by Handa et al., namely 10 K min^{-1} instead of 10 K h^{-1}. We determine the small sample mass by measuring the melting enthalpy of hexagonal ice, whereas Handa et al. determine the sample mass by weighing. The first exotherm related to the HDA→LDA transition shows an enthalpy of -426 ± 33 J mol^{-1} and peaks at a minimum temperature of 117.5 ± 0.5 K (3 scans, 2 batches) for HDA prepared from Ic. When prepared from Ih the exotherm releases -513 ± 45 J mol^{-1} and is centered at a minimum temperature of 118.8 ± 1.7 K (9 scans, 6 batches). This shows that HDA prepared from Ic behaves slightly different from HDA prepared from Ih. Even more pronounced is the difference for the conversion of the resulting LDA-state to Ic, the onset and minimum temperatures, the FWHH and the enthalpies of conversion show pronounced differences even though all samples were treated in the same way at a heating rate of 10 K min^{-1}. The minimum temperatures are 165.9 ± 0.4 K for HDA from Ih (24 scans, 6 batches) and 156.5 ± 1.5 K (5 scans, 2 batches) for HDA from Ic. Possible explanations for the ≈ 10 K difference of the transition to cubic ice (for samples prepared from cubic ice) are that small clusters of cubic ice survive the whole proc-

ess and serve as crystallization seeds and/or different substates in the LDA basin are reached when HDA is prepared from Ic instead of Ih. The enthalpies for conversion are quite similar at -1347 ± 62 J mol^{-1} and -1301 ± 78 J mol^{-1}, respectively. However, the transition is much sharper for HDA from Ih (FWHH = 2 K) compared to HDA from Ic (FWHH = 7 K).

This provides direct evidence that HDA is not a well-defined state on the potential energy hypersurface, but rather depends on the conditions of preparation. Recently, also thermal conductivity[48] and ultrasound velocity[49] measurements have indicated that HDA made on transforming LDA by pressurization above 0.8 GPa and by amorphizing Ih above 1.2 GPa at 77 K, is a different material. Also neutron diffraction[50–52] and adiabatic calorimetry of HDA[47] show that a slow and continuous relaxation process takes place in HDA through a series of potential energy minima even at temperatures below 100 K. In other words, to define the state of HDA it is necessary to define the exact conditions of preparation and the temperature history. By contrast, for VHDA such a definition is not necessary, provided that the fully relaxed state has been obtained by annealing under pressure.[53]

In summary we have shown that pressure-induced amorphization of cubic and hexagonal ice results in states of HDA differing slightly in structure and enthalpy, but which are similar in terms of density. Two slightly different states of HDA are produced implying that the "high-density amorphous ice" megabasin is very shallow, and probably a multitude of structures are produced at 77 K and 1 bar. These results, however, do not clarify whether VHDA is located in the HDA-megabasin or in a different megabasin.

Experimental Section

X-ray Diffractograms: Recorded at 88 K in θ-θ geometry employing Cu-Kα rays ($\lambda = 0.1542$ nm) using a Siemens D-5000 diffractometer equipped with a low-temperature camera from Paar. The sample plate was in the horizontal position during the whole measurement. Installation of a "Goebel mirror" allowed the use of small amounts of sample without distortion of the Bragg peaks. The curves in Figure 3 are smoothed by a gliding average of ten points (software OriginPro7G). The reflexes marked with stars arise from hexagonal ice condensed onto the sample during transfer under liquid nitrogen from the material testing machine to the x-ray diffractometer (see Figure 1 for comparison). This is consistent with our observation that Raman spectra of recovered HDA containing 5% D$_2$O do not show the decoupled O-D stretching band of ice I.[54] If ice I had originated in these recovered HDA samples from incomplete conversion to HDA, it would show the decoupled O-D band. These sharp Ih reflexes serve as an internal standard for the accuracy of the diffraction angle.

Compression/Decompression Curves: Obtained at a controlled rate of 1000 N min^{-1} using a computerized (software TestXpert V7.1) "universal testing machine" (Zwick, model BZ100/TL3S) with a positional reproducibility of ± 5 μm and a spatial resolution of 0.01 μm. Sample containers are designed of 0.231 g indium and are the same shape in order to exclude artefacts produced by different amounts and shapes of indium. Indium is required to prevent sudden pressure drops accompanied by shock-wave heating causing crystallization of HDA to ice XII.[55]

Differential Scanning Calorimetry: All diffractograms are recorded on a Perkin–Elmer differential scanning calorimeter (model DSC-4) at a heating rate of 10 K min^{-1}. After heating each sample from 93 K to $\approx$ 260 K, the sample was cooled back to 93 K and a second DSC scan of Ih was recorded at 10 K min^{-1} as a baseline. The mass of the sample was determined from a DSC scan recording the melting endotherm at 10 K min^{-1} from 250 K to 300 K and using 6012 J mol^{-1} as heat of melting.[56] The mass is determined to be between 10 and 40 mg and all curves are normalized to 1 mg of sample.

Acknowledgements

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