

Amorphous Ices: Stepwise Formation of VHDA from LDA at 125 K

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On compressing low-density amorphous ice (LDA) at 125 K up to 1.6 GPa two distinct density steps accompanied by heat evolution are observable in pressure-density curves. Samples recovered to 77 K and 1 bar after the first and second step show the X-ray diffraction pattern of high-density amorphous ice (HDA) and veryHDA (VHDA), respectively. The compression of the once formed HDA takes place linearly in density up to 0.95 GPa, where non-linear densification and HDA→VHDA conversion is initiated. This implies a stepwise formation process LDA→HDA→VHDA at 125 K, which is to the best of our knowledge the first observation of a stepwise amorphous-amorphous-amorphous transformation sequence. We infer that the relation of HDA and VHDA is very similar to the relation between LDA and HDA except for a higher activation barrier between the former. We discuss the two options of thermodynamic vs. kinetic origin of the phenomenon.

The process of pressure induced amorphization of crystalline material and the term polyamorphism was coined on the example of water, when Mishima et al. pressurized hexagonal ice I_h at 77 K to above 1.0 GPa to yield high density amorphous ice (HDA)^[1]. On pressurizing low density amorphous ice (LDA) at 77 K in excess of 0.6 GPa the same authors observed a transition to HDA comparable in sharpness to the I_h →HDA transition, which they called “apparently first-order”^[2]. This apparent first order nature seemed confirmed when Mishima observed the LDA↔HDA transformations to be reversible with hysteresis and accompanied by heat production in a compression/decompression experiment while the apparatus warmed from 130 K to 140 K^[3]. Stal’gorova et al. challenged this view by showing that the density-increase (as well as the travel time of an ultrasonic pulse) during the LDA→HDA transformation varies linearly with time, whereas an exponential variation would be expected for a first-order transition^[4]. On the other hand Klotz et al. reported that the transformation between LDA and HDA is consistent with a first-order transition by *in situ* neutron diffraction studies at ~0.3 GPa and 130 K which show that all states in the conversion process can be expressed as a linear combination of LDA and HDA^[5]. However, Tse et al. recently emphasized that X-ray rather than neutron structure factors are required to answer the

question unambiguously^[6]. Thus the case of a first-order transition between LDA and HDA is still under debate.

On increasing the temperature in I_h pressure amorphization experiments Mishima noticed a crossover from equilibrium melting to the supercooled liquid (above 190 K) to an amorphization process induced by a mechanical instability of the crystals (below 140 K)^[7]. “HDA” obtained on pressurizing I_h at 140 K in this study shows a X-ray pattern with a halo-peak at 2.75 Å ($2\theta=32.5^\circ$), which is in fact typical of very high-density amorphous ice (VHDA). VHDA was later shown to be a recovered state distinct from HDA^[8]. Annealing of HDA under pressures of ~1 GPa up to ~140 K results in a switch of the first X-ray halo peak in the recovered state from ~3.0 Å (HDA) to ~2.75 Å (VHDA).

Probably the main issue in the current debate on polyamorphism of water is how these three different amorphs relate to each other. Lately some effort has been put into studying transformations of amorphous ices *at ambient pressure*^[9, 10]. It has e.g. been shown that HDA transforms to LDA in a sequence of amorphous ices of intermediate density on heating^[10]. While studies at ambient pressure are certainly important, it was pointed out^[11,12] that it is difficult to judge from these experiments on the nature of phase boundaries between amorphous ices at elevated pressures. A direct observation of the phenomena linked to polyamorphism of ice *at elevated pressures* provides, therefore, more direct insight into the nature of the transitions.

In order to investigate the relationship between the amorphs at elevated pressures we employed LDA as the starting material for the pressurization experiments shown in Figure 1. LDA was produced directly in the material testing machine by compressing I_h at 77 K up to 1.5 GPa, recovering HDA at 77 K and subsequent isobaric heating at 0.025 GPa to 141 K (cf. Fig 7 in Salzmann et al.^[13]). The powder X-ray diffractogram of the recovered sample at 1 bar and 77 K is shown in Figure 2 (trace A^{77K}) and clearly shows the pattern of LDA with the first broad diffraction maximum at 3.70 Å ($2\theta=24^\circ$). The sample was then brought to 125 K at 0.025 GPa and compressed up to a nominal pressure of 1.5 GPa at a rate of 20 MPa/min in a piston-cylinder apparatus of 8 mm bore diameter. The density of the sample during this process (black dashed line in Figure 1) experiences two pronounced steps of 20% (from 0.94 to 1.13 g cm⁻³) at 0.45 GPa and of 5% (from 1.22 to 1.28 g cm⁻³) at 0.95 GPa, respectively. Both density steps are accompanied by heat production (counterbalanced by increasing the

coolant flow), which ceases in the plateau regions following the density jumps. The temperature is generally constant within ± 0.5 K of 125 K and to within ± 2 K during transformations.

In order to characterize the structural state formed after the second density jump we quenched the sample to 77 K at 1.5 GPa (point ^{77K}C in Figure 1), released the pressure at a rate of 20 MPa/min fully and recorded the X-ray diffractogram of the recovered phase, which is shown as the green curve in Figure 2. This pattern with the first broad maximum at 2.75 \AA ($2\theta=32.5^\circ$) is indistinguishable from the VHDA pattern reported by us previously^[8]. The same recovery procedure initiated at 0.7 GPa after the first density jump causes an X-ray pattern (red curve) with a maximum located inbetween LDA and VHDA, which resembles HDA on pressurizing I_h at 77 K. Consistent with the LDA→HDA transformation study in ref. 3 the LDA sample does not crystallize to cubic or hexagonal ice at temperatures of 125 K during compression up to 0.7 GPa.

The densities of the phases recovered after the first and second density jumps (cf. legend of Fig. 1) amount to 1.17 g cm^{-3} and 1.30 g cm^{-3} , respectively, which is close to the bulk densities of HDA and VHDA at 77 K and 1 bar^[1, 8]. The increase of densities of the recovered states of 27% and 11% is exactly the increase expected for the LDA→HDA and HDA→VHDA transformations, respectively. We conclude, therefore, that VHDA formation at 125 K occurs according to the stepwise sequence LDA→HDA→VHDA^[25]. At lower temperatures, e.g. 100 K, the HDA→VHDA transformation does not take place as also observed previously^[2]. At higher temperatures, e.g. 140 K, LDA crystallizes. This is, to the best of our knowledge, the first observation of a stepwise amorphous-amorphous-amorphous transformation sequence for all systems known to show polyamorphism including besides water e.g., SiO_2 , GeO_2 , Si, Ge, triphenyl phosphite or aluminates^[14].

In order to check whether these changes depend on the rate of compression we conducted additional sets of experiments at rates of 6 MPa/min, 600 MPa/min (matching the compression rate employed by Mishima in his studies of the LDA/HDA transformation^[3]) and 6000 MPa/min. In Figure 3 the corresponding pressure-density curves are shown in the top panel together with the slopes of these curves in the bottom panel. In all cases the pressures at the density steps are found to be 0.45 ± 0.02 GPa and 0.95 ± 0.05 GPa with no dependence on compression rate. Whereas the densification step of $\sim 20\%$ for the first step is almost

independent of compression rate, the second step drops to ~1% at compression rates of ≥ 600 MPa/min. Despite this drop, the samples recovered after compressing at 600 MPa/min are VHDA as evidenced by the X-ray diffractogram (not shown) and the density of 1.30 ± 0.02 g cm^{-3} after decompression. From the change of the second density step and the broader pressure range of densification in going from rates of 20 MPa/min to 600 MPa/min, we estimate that the time required to transform HDA to VHDA is on the order of 10 minutes at 125 K, which corresponds to the time required to sweep the transformation pressure range at 20 MPa/min. On the other hand the transformation time from LDA to HDA is at least an order of magnitude faster at 125 K since the first density step barely changes even at the highest compression rate employed. The transformation from LDA to HDA, and also that of HDA to VHDA, is best described as “thermally activated process, whose rate increases with increase in the pressure”^[28], and thus our finding implies that the activation barrier between LDA and HDA is considerably lower than the activation barrier between HDA and VHDA. A similar conclusion, namely that the activation energy for HDA→LDA is at least 20 kJ/mol lower than for VHDA→LDA, was recently presented by Koza et al.^[30] This higher activation barrier was also found by differential thermal analysis (Fig. 4 in Mishima^[7]): ~125 K are required to transform HDA annealed under pressure (“VHDA”) to LDA, whereas only ~115 K are required to transform unannealed HDA (“HDA”) to LDA. The much faster kinetics of HDA→LDA implies for the reverse transformation sequence VHDA→HDA→LDA that it is very difficult to isolate and characterize HDA simply because it rapidly transforms to LDA once formed from VHDA. On decompressing HDA at 77 K (produced by compressing LDA at 77 K) the reverse HDA→LDA transformation does not take place (Fig. 2 in ^[2]). The reverse HDA→LDA transformation takes place on decompression only for temperatures above ~130 K (Figs. 2 and 3 in ^[3]) with a hysteresis of up to a factor of 10 in conversion pressure. On decompressing VHDA in the material testing machine isothermally at e. g. 135 K we can easily recover LDA, whereas we are unable to quench to 77 K at the HDA stage because of the much faster HDA→LDA kinetics. However, by isochoric heating of VHDA up to ~141 K we are able to recover an amorphous state that has the same density as HDA and a HDA-like X-ray pattern (Fig. 1D in ^[8]). Koza et al. (Fig. 1 in ^[30]) succeeded to demonstrate the reversibility by recording an intermediate HDA structure factor using the fast *in situ* neutron scattering technique during isobaric annealing of VHDA at 113 K. That is, both the HDA↔VHDA and LDA↔HDA transformations are reversible in principle – still they are difficult to observe together because of the low temperatures and the different activation energies.

The slopes of the pressure-density curves at 125 K (bottom panel Fig. 3) yield information whether the compression process takes place elastically or inelastically. By elastic compression we mean that $dp/d\rho$ is constant within experimental error, whereas on inelastic compression it increases largely. Elastic densification of VHDA^[26] corresponds to a slope of $\sim 0.10 \text{ g cm}^{-3} \text{ GPa}^{-1}$, whereas HDA^[27] is expected to show a slope of $\sim 0.14 \text{ g cm}^{-3} \text{ GPa}^{-1}$ in the elastic case^[2]. We find slopes in the range from 0.13-0.17 $\text{g cm}^{-3} \text{ GPa}^{-1}$ at 0.55-0.80 GPa after the first density step and 0.10-0.13 $\text{g cm}^{-3} \text{ GPa}^{-1}$ at >1.10 GPa after the second step. This is very close to elastic compression of HDA and VHDA, respectively. So we conclude that inelastic compression only takes place in the grey shaded areas in Fig.3.

This finding has implications on the current debate on the relation between HDA and VHDA. Whereas Mishima infers a continuous crossover from the slope dp/dT of the melting/amorphization curves, which “shows that the different HDA ices are all in the same HDA ‘megabasin’ on the potential-energy surface”^[7], Debenedetti and Stanley on the other hand called this an open question by asking “whether VHDA is a distinct phase separated from HDA by a first-order transition or whether it is simply very dense HDA”^[15, 16]. For the interpretation of the conversion from HDA to VHDA shown here there are basically two options: a) a true thermodynamic phase transition or b) a kinetic densification process that takes place in a non-linear, accelerating and decelerating, fashion, so that steps in density result. In terms of structure LDA, HDA and VHDA can be distinguished by the number of water molecules in the first coordination shell, which increases from 4 to 5 and 6, respectively^[17, 18]. This implies that the number of interstitial water molecules has to increase by one molecule to produce HDA from LDA and by another molecule to produce VHDA from HDA. Since these two changes in structure are quite similar, it seems plausible that the LDA/HDA relation should be similar to the HDA/VHDA relation. The observation of two steps on isothermal compression seems to confirm this idea even if the second step is less sharp. Some theoretical calculations on supercooled and amorphous water suggest that a thermodynamic transition between HDA and VHDA is possible by showing that several metastable liquids separated by first-order phase transitions and critical points can be found for various water potentials^[19a,b]. However, there are models for which there is no unique correspondence between a metastable liquid, an amorphous phase and a crystalline phase^[20]. In case of SPC/E water this correspondence has been established^[21], but there are also simulations suggesting rather a kinetic densification^[22a,b]. It is intriguing to think that the two

steps between LDA, HDA and VHDA observed here are analogs in the glassy state for phase transitions between a low-, high- and very-high density liquid, respectively. Our finding that at slow compression rates the inelastic conversion from LDA to HDA (0.35-0.55 GPa) develops into elastic compression of HDA (0.55-0.80 GPa), then into inelastic conversion from HDA to VHDA (0.80-1.10 GPa) and finally to elastic compression of VHDA (>1.10 GPa) points in the direction that densification of amorphous ice occurs as two thermodynamically distinct transitions. Nevertheless, we can not presently exclude the alternative option of a kinetically controlled densification process in amorphous ice that accelerates and decelerates in specific pressure ranges corresponding to the two lynch pin sites being filled with a first and second water molecule.

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Figure captions:

Figure 1: Pressure-density curves for isothermal compression of LDA at a rate of 20 MPa/min at 125 K, subsequent quenching to 77 K and decompression at 20 MPa/min. Density ρ is calculated from the raw data, i.e., uniaxial displacement Δx , from equating $\rho = 0.92 \cdot 6.49 / (6.49 - \Delta x)$ by employing an initial density of 0.92 g cm^{-3} for LDA at 125 K (the density of LDA at 77 K is $0.94 \pm 0.02 \text{ g cm}^{-3}$ and decreases on increasing the temperature^[23]) and an initial LDA sample height of 6.49 mm (corresponding to 0.2995 g sample in a cylinder of 8 mm diameter). The signal due to the piston-cylinder apparatus lined with 0.351 g of Indium (and no ice sample) was subtracted as a baseline from the raw pressure-displacement data. We assumed a constant diameter of the piston-cylinder apparatus on changing the temperature from 125 K to 77 K. All the experiments were done in a computerized (software TestXpert V7.1) “universal testing machine” (Zwick, model BZ100/TL3S) with a positional reproducibility of $\pm 5 \text{ }\mu\text{m}$ and a spatial resolution of $0.01 \text{ }\mu\text{m}$. All samples were kept in a container carefully designed of 0.351 g Indium and of 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^[24].

Figure 2: Powder X-ray diffractograms for the samples A, B and C recovered at 77 K in Figure 1. X-ray diffractograms were recorded on a diffractometer in θ - θ geometry (Siemens, model D 5000, Cu-K α), equipped with a low-temperature camera from Paar at 88 K. 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 Bragg peaks. Curves are shown on same scale, smoothed and offset for clarity. Dashed lines are intended to guide the eye to the location of the maximum of the first broad diffraction peak. The dotted lines indicate positions of reflexes caused by traces of Ih, which had formed by condensation of water vapour during transfer of sample onto the precooled X-ray sample holder (cf. ref 29). The sample itself is fully amorphous.

Figure 3: Top: Effect of compression rate on pressure-density curves for isothermal compression of LDA at 125 K. The protocol is analogous to the procedure described for Figure 1 using compression rates of 6 MPa/min (red), 20 MPa/min (black), 600 MPa/min (green) and 6000 MPa/min (blue). Bottom: Change of density with increasing pressure (first derivative of curves in top panel). Areas of inelastic compression where the change exceeds ca. $0.20 \text{ g cm}^{-3} \text{ GPa}^{-1}$ are shaded in grey.

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- [25] At the compression rate of 20 MPa/min we find that the pressures at the density steps as well as the densities of the recovered states are reproducible to $\pm 0.02 \text{ g cm}^{-3}$. The relative changes caused by the density steps, i.e., the jumps of 5% and 20%, respectively, are accurate to $\pm 1\%$.
- [26] The estimate for elastic densification of VHDA was obtained here both by compressing VHDA slowly to 1.6 GPa at 77 K and from slowly decompressing VHDA from 1.6 GPa to 0.2 GPa at 77 K. At 125 K the slope remains equal to the slope at 77 K within the experimental error.
- [27] The estimate for elastic densification of HDA was obtained from the densities given by Mishima: $\rho(\text{HDA}, 1.0 \text{ GPa}, 77 \text{ K}) = 1.31 \text{ g cm}^{-3}$ and $\rho(\text{HDA}, 1 \text{ atm}, 77 \text{ K}) = 1.17 \text{ g cm}^{-3}$.

This estimate is in good agreement with our own data obtained on compressing HDA slowly at 77 K. A higher compressibility of HDA as compared to VHDA seems plausible in view of VHDA's denser packed structure.

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Fig.1

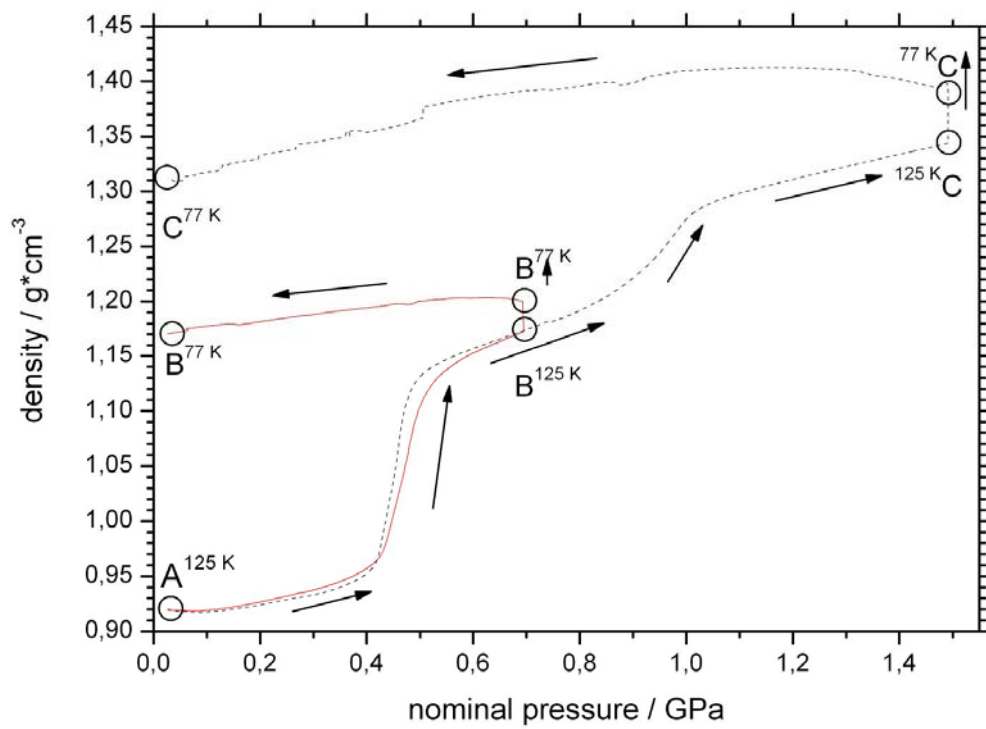


Fig.2

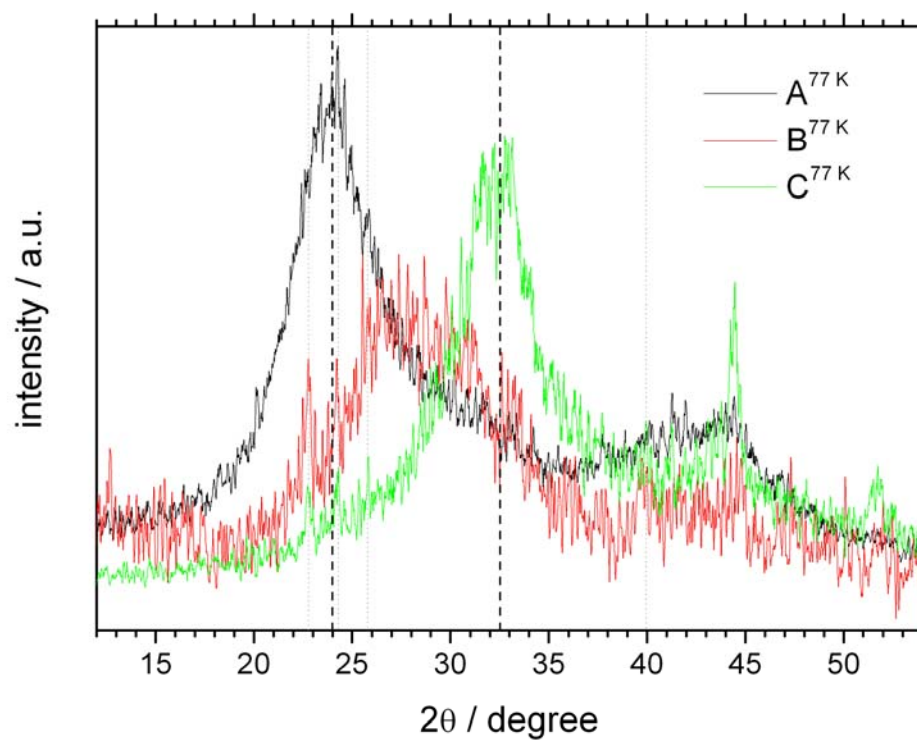


Fig.3

