Supplementary Material for:

Pressure-annealed high-density amorphous ice made from vitrified water droplets: A systematic calorimetry study on water's second glass transition

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Content

The supplementary material shows thermograms of LDA made from d-HGW (Fig. S1), of d-HGW heated with different rates (5 to 100 K min^{-1}, Fig. S2), and of HDA made via pressure-induced amorphization of ice I (Fig. S4). Furthermore, data on latent heat release during the polyamorphic transition are displayed (Fig. S3).

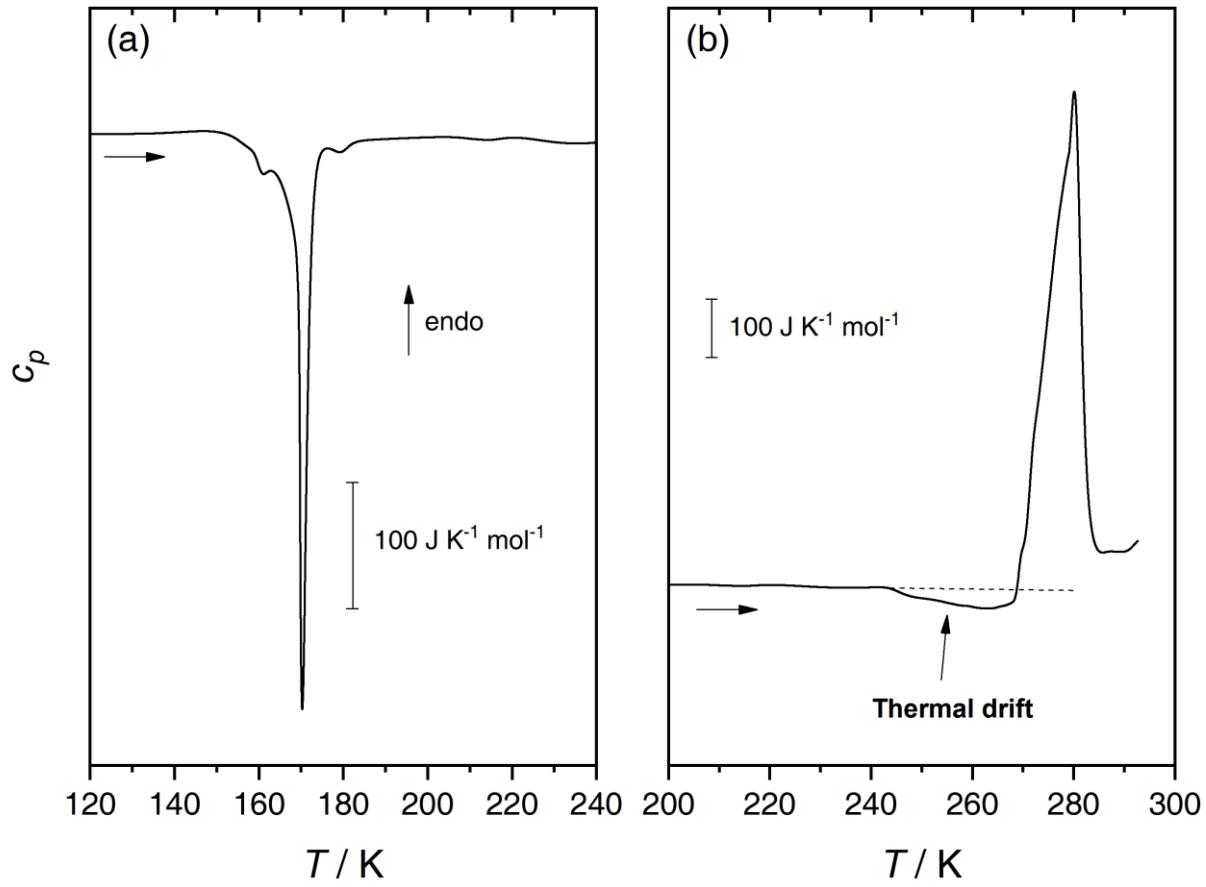

Fig. S1. Thermal behavior of samples after their transition to LDA. In panel (a) the exothermic transition from LDA to ice I_{sd} is encountered around 160 K. Just like found in our earlier work,[1] this transition proceeds in two steps as indicated by the shoulder before the pronounced peak. Another weak exotherm is located around 180 K and probably related to the polytypic conversion of ice I_{sd} to I_h. This conversion is known to occur somewhere between 170 and 250 K.[2] Panel (b) shows the melting endotherm of ice that was used for normalization of the associated DSC trace. In addition to the intense melting peak, we observe a thermal drift just before the melting onset. We speculate that this could be due to the release of gas, which alters the He heat flow in the instrument. A similar effect was observed by Hallbrucker and Mayer[3] during decomposition of gas clathrate hydrates upon heating. This effect impedes the integration of the melting peak and leads to a higher calculated integral. Consequently, we estimate that the values we extract for Δc_p and ΔH are too high by 10-15% as reflected by the large error bars in Fig. 8 and Fig. S3.

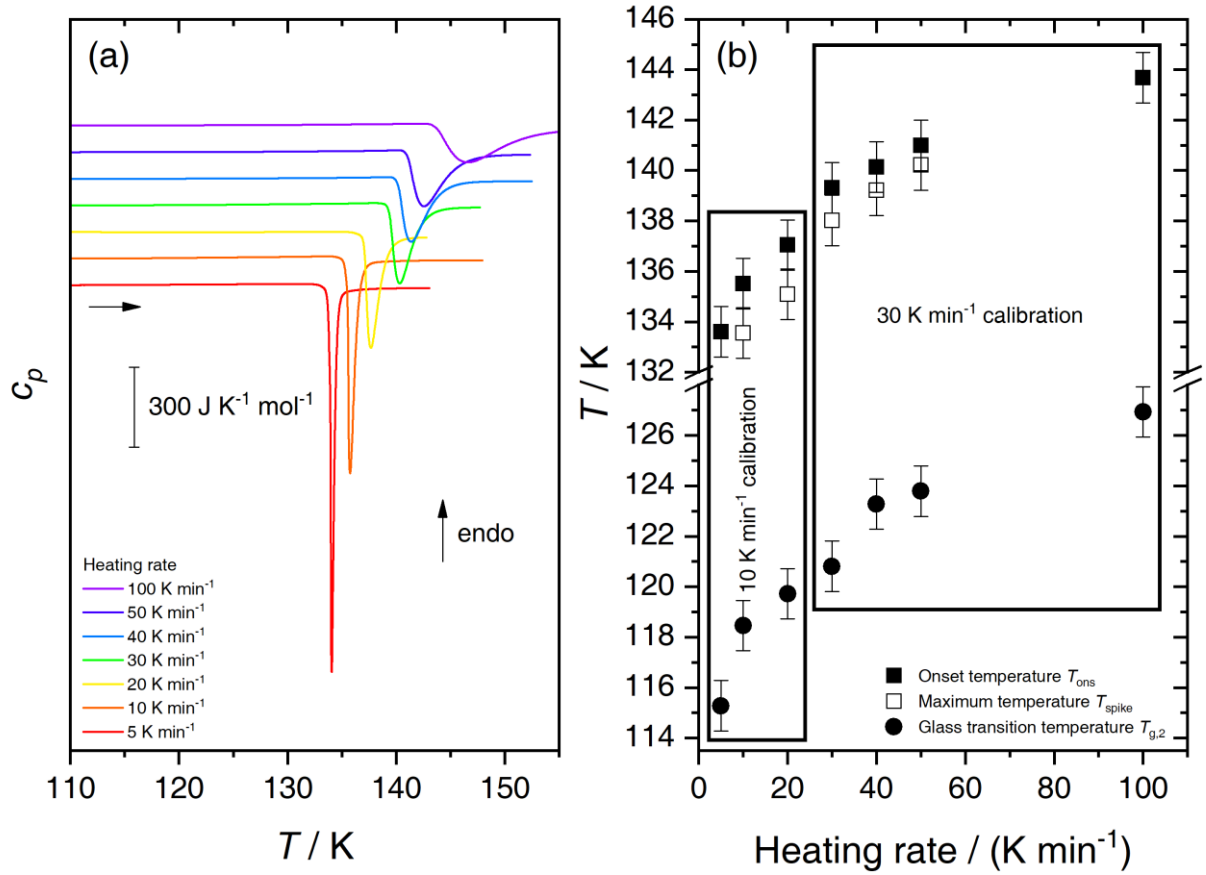

Fig. S2. Effect of heating rate on the HDA → LDA transition in one sample batch. Here, HDA has been prepared by pressure-annealing at 1.9 GPa and decompression to 0.15 GPa at 140 K. (a) Thermograms recorded at 1 bar with 30 K min^{-1}. Curves are shifted vertically for clarity. (b) Onset temperatures T_{ons} of the HDA → LDA transformation (filled symbols) and corresponding spike temperatures T_{spike} (empty symbols) following the second glass transition of water $T_{g,2}$ (filled circles). The former is just like a first-order transition highly rate-dependent where high rates shift the transition to higher temperatures. The latter two are similarly rate-dependent where especially T_{spike} appears to be strongly correlated with T_{ons}. This is consistent with the assumption that the spike is associated with LDL nucleation, which initiates the polyamorphic transition. Interestingly, no spike is observed for 5 and 100 K min^{-1}, i.e., the lowest and highest rates. For 5 K min^{-1}, this is most likely due to sensitivity of the instrument. For 100 K min^{-1}, this could be because HDA is strongly superheated so that nucleation and growth take place instantaneously.

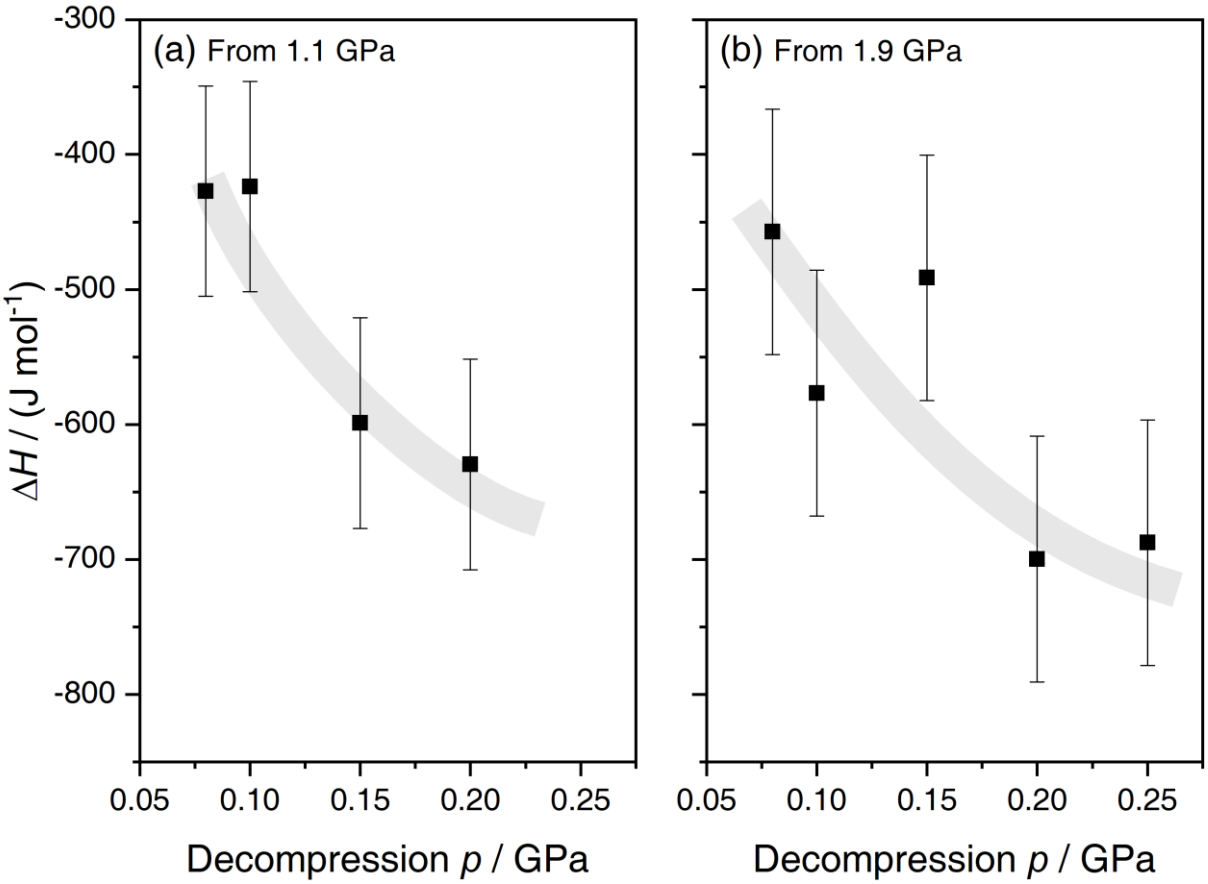

Fig. S3. Latent heat ΔH released during the HDA → LDA transition at 1 bar. Similarly to T_{ons}, the magnitude of ΔH reflects the degree of HDA relaxation where unrelaxed samples release more enthalpy than relaxed samples. A significant effect on enthalpy is found for samples subjected to path (c) and (d) shown in Fig. 1 and plotted here in panel (a) and (b), respectively. The broad lines are guides to the eye. The shape of the lines in panel (c) and (d) was established in ref. [4] where a broader pressure range was covered. Note that considerable error bars result from the normalization procedure as outlined in Fig. S1. Still, there is a trend to more stable samples at lower end pressures of decompression as was already suggested by Winkel et al.[5] Samples decompressed to >0.20 GPa are less relaxed than ones decompressed to 0.15, 0.10 and 0.08 GPa. We speculate that relaxation rate is picking up upon crossing the glass transition pressure of HDA at 140 K upon decompression. This pressure was estimated to be around 0.15 GPa,[6] which is consistent with results from this study.

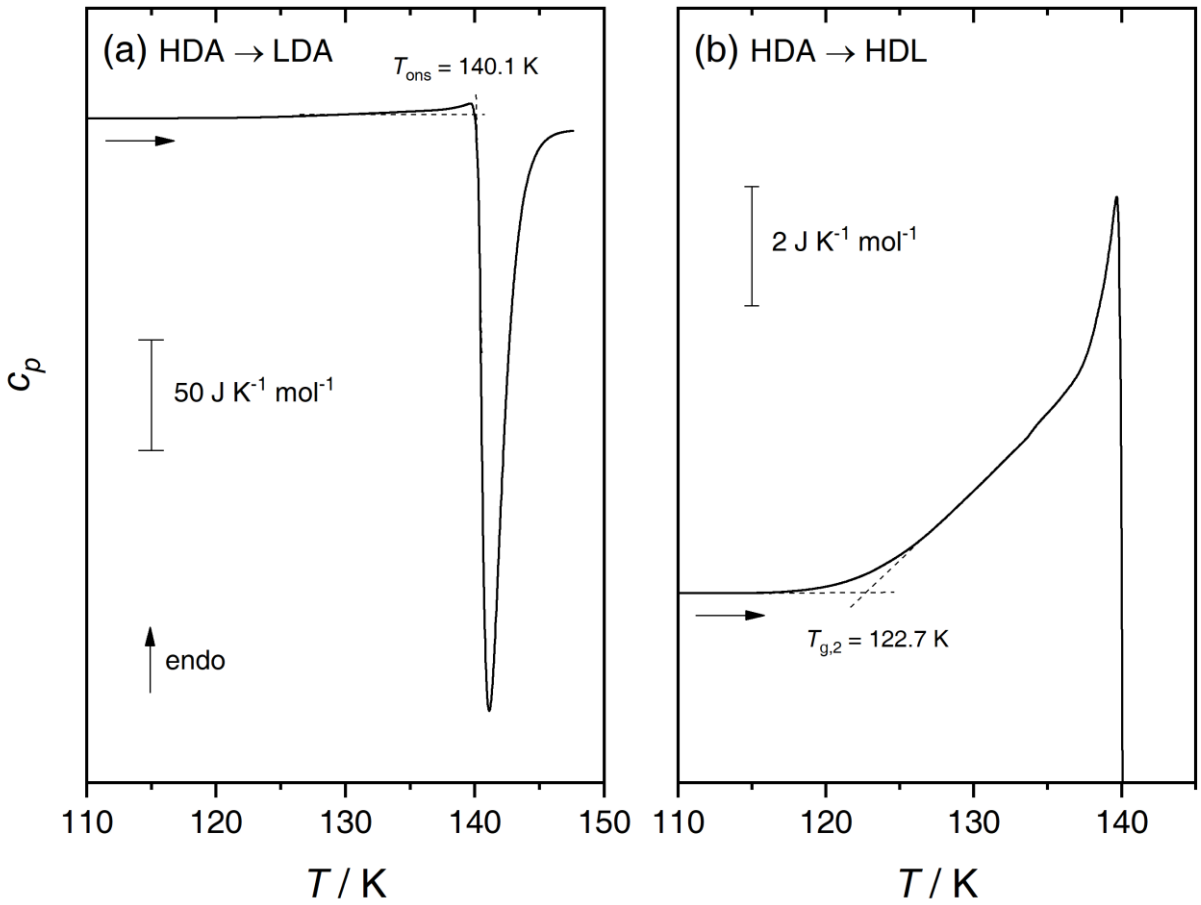

Fig S4. DSC scans of the polyamorphic transition (left) and second glass transition (right) in an HDA sample prepared via pressure-induced amorphization of ice I. The sample was annealed at 1.9 GPa and decompressed to 0.10 GPa. It displays very similar T_{ons} and $T_{g,2}$ (both marked by dashed tangents) as HDA that was made from vitrified droplets and subjected to similar annealing procedures. This strengthens the argument that both types of HDA can be used interchangeably.

Additional References

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