How stable is high-density amorphous ice against crystallization?

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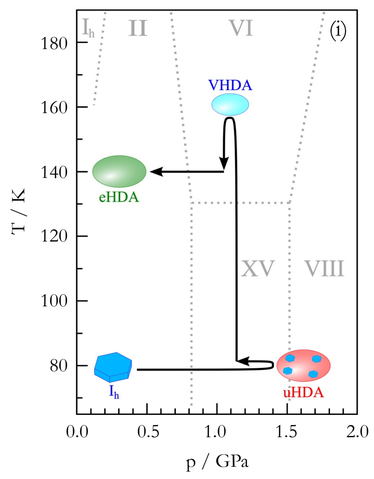
European Research Council
Established by the European Commission

Der Wissenschaftsfonds.

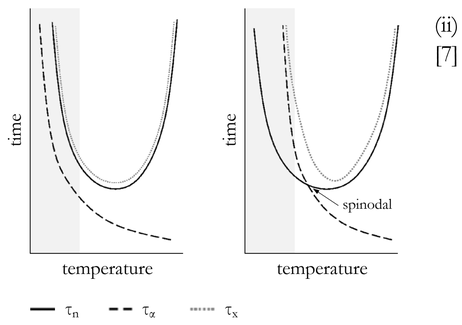
Introduction

Several thermodynamic routes were reported to produce high-density amorphous ice (HDA): uHDA is formed upon compression of hexagonal ice I_h at 80 K [1], while eHDA is formed upon decompression of the very high-density state VHDA [2], see Figure (i).

It has been argued that uHDA perhaps contains small crystals stemming from the starting material ice I_h [3–6]. Here, we provide experimental evidence for this hypothesis and show that, in contrast, eHDA is free of such nanocrystals. The crystalline remnants in uHDA seem to be annihilated during its transformation to VHDA.

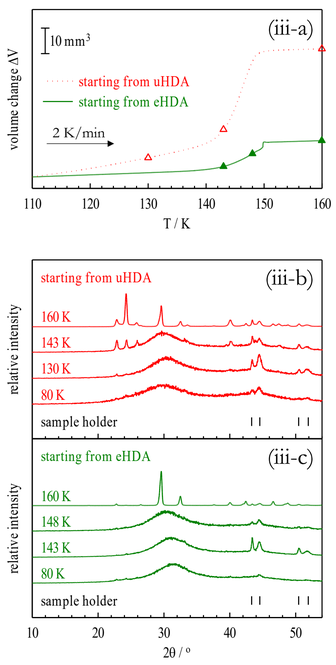


The presence and absence of nanocrystals, resp., is expected to influence HDA's stability against crystallization: In general, at low temperature the transformation curve $\tau_x(T)$, where τ_x is the time the system takes to develop a detectable amount of crystalline material, is either related to the nucleation time $\tau_n(T)$ or to the structural relaxation time $\tau_\alpha(T)$, see Figure (ii).



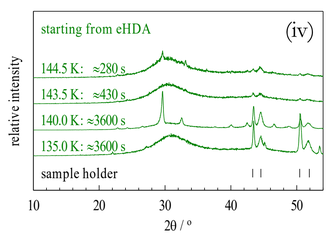
Thus, we also show results on HDA's relaxation behavior and derive a figure in which we compare the characteristic time scales of crystallization τ_x and structural relaxation τ_α. In this context, we also discuss the crystallization behavior of both uHDA and eHDA.

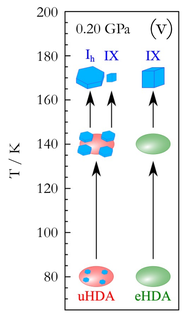
Experiments at 0.20 GPa



Crystallization [8]:

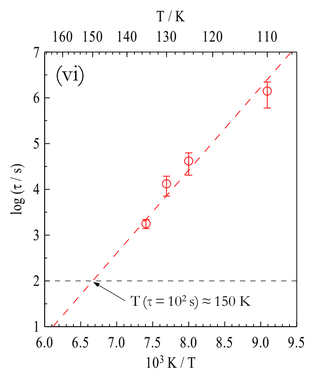
eHDA crystallizes to a single ice phase only, see Figures (iii) and (iv). In comparison, uHDA crystallizes to a mixture of ice phases and shows much lower thermal stability, see Figure (iii). Unexpected from Ostwald's step rule, at low temperatures ice I_h grows first from uHDA, whereas this phase never crystallizes from eHDA. This leads us to conclude that nanocrystals are present in uHDA, triggering growth of ice I_h, see Figure (v). By contrast, these crystals are absent in eHDA, making it more stable against crystallization and structurally homogeneous.





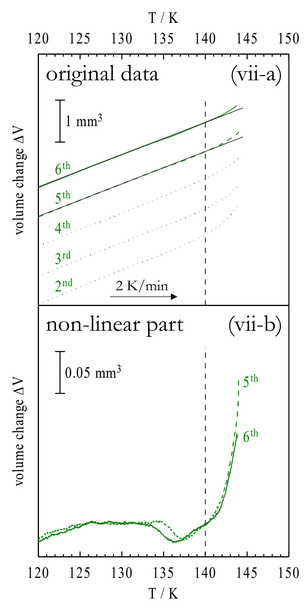
Structural relaxation [9]:

Starting with uHDA, the relaxation state of samples pressure-annealed for certain times can be probed by analyzing the temperature of the transition to low-density amorphous ice at ambient pressure. Utilizing such data, we determine the relaxation time τ_α for different temperatures. The results are presented in Figure (vi).



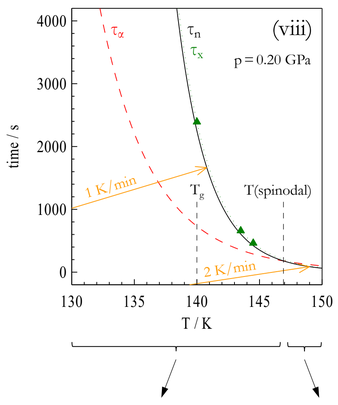
Glass-to-liquid transition [10]:

As shown in Figure (vii), the glass transition temperature T_g of eHDA can be determined from the volume change ΔV upon heating. T_g is indicated by a deviation from linear expansion behavior (vertical lines).



Discussion

Stability against crystallization and separation of time scales at 0.20 GPa:



In Figure (viii) HDA's structural relaxation time $\tau_\alpha(T)$, i. e., the linear fit in Figure (vi), is compared to the crystallization curve $\tau_x(T)$ of eHDA. τ_x is derived from the diffraction patterns in Figures (iii-c) and (iv) as follows:

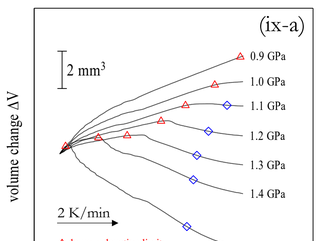
$1500\ s < \tau_x(140.0\ K) < 3600\ s$, since crystalline material isn't found after annealing > 140 K for 1500 s (≙ annealing at 143.5 K for 430 s), but after annealing at 140 K for 3600 s. Analyzing patters from similar annealing experiments, we find $\tau_x(143.5\ K) > 430\ s$ and $\tau_x(144.5\ K) \approx 280\ s$.

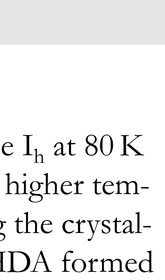
Upon heating with 2 K/min from 80 K, eHDA crystallizes abruptly close to 150 K, while uHDA starts to crystallize already below 143 K, see Figure (iii). From this it follows that τ_x of pure HDA (= eHDA) is limited by the nucleation time τ_n, see Figure (viii), while τ_x of seeded HDA (= uHDA) is limited neither by τ_n nor by τ_α. Thus, HDA shows diffusionless crystal growth after nucleation. Below T(spinodal) relaxation is faster than nucleation ($\tau_\alpha < \tau_n$) and HDA can be equilibrated. However, for $T \geq T(\text{spinodal})$ HDA is instable – there's no corresponding minimum in the free energy surface any more. Since $T(\tau = 10^2\ s) = 150\ K > T(\text{spinodal})$ compared to $T(\tau = 10^2\ s) < T(\text{spinodal})$ at 1 bar [11], HDA's stability decreases with increasing pressure.

Transformation of uHDA to VHDA:

At high pressures ice I_h is less stable than HDA. Therefore, compressing ice I_h at 80 K results in formation of uHDA, see Figure (i). However, for kinetic reasons higher temperatures are expected to be necessary for full transformation by dissolving the crystalline remnants present in uHDA [5, 6]. Since eHDA formed upon decompression of VHDA is purely glassy, the nanocrystals indeed seem to be annihilated during the transformation of uHDA to VHDA [12], cf. Figure (x).

Therefore, we studied this temperature-induced process at several pressures ≥ 0.9 GPa, providing the volume change ΔV upon isobaric heating in Figure (ix-a). ΔV exhibits two characteristic features, even though it changes continuously with temperature [13]. Linear expansion behavior is found from 80 K to a pressure-dependent temperature indicated by △, where densification starts. At another temperature indicated by ◇, ΔV(T) starts to flatten again. We speculate that these temperatures indicate the lower and upper limit of uHDA's relaxation towards VHDA, respectively; the nanocrystals are expected to dissolve in-between, see Figures (ix-b) and (x).





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