Electron Beam Induced Transformation in High-Density Amorphous Ices

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1. Experiment

1. A Sample Preparation

The amorphous ice samples were made by pressure induced amorphization using a material testing machine (ZWICK, model Z100 TN) as outlined earlier.\textsuperscript{1, 2, 3} In brief, unannealed HDA (uHDA) is made by compression of hexagonal ice Ih (300 μm ultrapure H\textsubscript{2}O (Milli-Q)) inside a steel-piston-cylinder setup\textsuperscript{4}, as depicted in the TOC graphic and Figure S1 (inner bore diameter of 8 mm, outer dimension of steel cylinder d = 56mm) at liquid nitrogen temperature to 1.6 GPa. This is followed by an annealing step at 1.1 GPa to 160 K in order to form very-high density amorphous ice (VHDA).\textsuperscript{5} Through immediate cooling (quenching) back to liquid nitrogen temperature, the metastable VHDA can be extracted from the cell in a liquid nitrogen bath, and further transferred to the cryo-TEM-sample holder. The eHDA sample is made inside the piston-cylinder setup by decompression of VHDA at 140 K from 1.1 GPa to 0.07 GPa and immediate cooling at the final pressure of 0.07 GPa to liquid nitrogen temperature.\textsuperscript{1} This is, high-density amorphous ices at ambient pressure are kinetically arrested, non-equilibrium states.\textsuperscript{3, 6}

1. B Loading Procedure to EM-Sample Holder

After extracting the amorphous ice samples from the piston cylinder setup, they were ground to a fine powder inside a bath of liquid nitrogen. Ice flakes were collected by dipping a TEM grid (Qantifoil R2/1, Cu, 300 mesh) into the ice-powder. Prior to particle collection, the grid was glow discharged (PELCO easiGlow) at 20 mA for 40 seconds. Finally, the grid was transferred onto a cryo-transfer tomography holder (Gatan type-914) and inserted into a JEOL 2010 TEM with LaB\textsubscript{6} filament. Note that this type of cryo-holder
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does not have the full cryo-shielding like in those purposely built cryo-TEMs, which gives rise to a non-optimal thermal environment. We also suspect that the ice flakes are in less optimal thermal contact with the grid/cryo-holder. However, from other studies we know that the HDA – LDA transformation is accompanied by a volume change of 20-25% \(^7\), still we observe that the sample does not fall off the grid, demonstrating that the thermal contact might not be optimal but sufficient.

**Figure SII**: As the TOC graphic the sketch shows preparation of high-pressure ice phases using a piston-cylinder setup. Flakes of the samples get transferred after the preparation-cycle to the EM-grid at liquid nitrogen temperature. Images show diffraction patterns of amorphous ices.

1.C Electron Diffraction and TEM Image Collection

Electron diffraction experiments were performed under a parallel electron illumination with acceleration voltage of 200 kV. We used an electron beam of 6 \(\mu\)m in diameter with an estimated dose rate of 0.1 e\(^{-}\) s\(^{-1}\) Å\(^{-2}\). TEM imaging mode was used for particle searching. As soon as suitable particles are located, the electron beam is blanked to avoid unnecessary
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electron dose. We used a selective area aperture of 2 μm in diameter to choose the region from which diffraction patterns were collected. Before un-blanking the beam, the TEM was switched to diffraction mode. Electron diffraction patterns were collected continuously using an ultra-fast hybrid pixel detector (Timepix, Amsterdam Scientific Instrument, 8 ms deadtime, 512 x 512 pixels). The pixel size of the electron diffraction pattern has been carefully calibrated for each camera length that was used in the experiment.

TEM images were collected using a side entry Gatan Orius SC200 detector. The heating of the specimen, as e.g. necessary for the experiment in Figure 4, was performed with the same cryo-transfer tomography holder (Gatan type-914).

2. Data Analysis

The calibration of the pixel size in ED patterns is closely related to the z-height of the specimen in the TEM. The height of the specimen varies slightly across the TEM grid. In addition the sample height changes during the phase transition, as the high-to-low-density transition involves a volume change of 20-25%. These small variations are then magnified by the projection lens. Therefore, our ED results are less accurate compared e.g. to the X-ray diffraction data shown in Figure 2 and 3. The intensity I(Q) of the ED data in Figures 2-4 are plotted without geometrical corrections, therefore the relative intensities can be misleading.

To evaluate the diffraction data, a Bayesian model was fitted directly against the tif-images using the PyMC3 library in python and Automatic Differentiation Variational Inference (ADVI). The radius r from the central beam of to each pixel was calculated
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using the distance in x and y from the beam center, Pythagoras’ theorem and dividing by the correction for the barrel distortion. $r$ can be treated as a distance in reciprocal space because of the flat Ewald sphere at the resolutions and wavelength of the microscope.

$$r = \sqrt{(x - x_c)^2 + (y - y_c)^2}/\text{dist}$$

Correction for the barrel distortion was done by the method described by Capitani et al.\textsuperscript{10} by refining the azimuth and amplitude of distortion correction function ($\text{dist}$):

$$\text{dist} = 1 + 0.01 \times \text{amplitude} \times \cos\left(2 \times \left(\text{azimuth} + \arctan\left(\frac{y - y_c}{x - x_c}\right)\right)\right)$$

The background was fitted as a straight line with unique parameters $a_0$ and $a_1$ for each frame:

$$\text{background} = a_0 + a_1 \times r$$

The data was modeled as four Gaussian peaks, two peaks per phase.

This is, the parameters derived from ED are obtained by modeling $I(Q)$ and are thus valid within the model. Additionally, due to geometrical reasons and an unknown exact z-height, the accuracy and precision of peak positions are much lower for ED compared to XRD. When determining lattice parameters from a single crystal in ED, the errors (deviation from powder x-ray data) are typically $> 1\%$.\textsuperscript{11} We estimate the error in $Q$ for the here presented data on amorphous ices (see table 1 in main manuscript) to be $\pm 0.04 \text{ Å}^{-1}$ around $Q_1$ and $\pm 0.08 \text{ Å}^{-1}$ around $Q_2$. 

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3. Results – Extended Discussion

Figure S2 compares X-ray scattering measurements on amorphous ice to estimate the maximal temperature rise due to local heating. It is known from calorimetry experiments\textsuperscript{2}, X-ray\textsuperscript{12} and neutron scattering experiments\textsuperscript{13}, that eHDA transforms to the low-density state upon heating above 127 K (heating at 4 K/min, see Figure S2-b), or 134 K (heating at 10 K/min see calorimetric data in ref.\textsuperscript{2}), depending on the heating rate\textsuperscript{12}. In accordance with literature, VHDA is thermally less stable than eHDA\textsuperscript{2}, transforming already occurs around 117 K (if heated with 4 K/min, see Figure S2-b). This is reflected in our ED results, as VHDA starts to transform at a lower dose compared to eHDA. Comparing Figure S2-b with Figure 2c, for the case of VHDA and S2-c with 3c for the case of eHDA, we estimate an increase in temperature from 98 K to at least 117 K after an accumulated dose of 2 e/Å\textsuperscript{2} in the case of VHDA, and to at least 127 K at 3 e/Å\textsuperscript{2} for eHDA, respectively. This comparison can only give rough estimation for the maximal possible temperature rise, since other mechanisms than local heating play an important role, as discussed in the main manuscript.

**Figure S12:** Comparison between ED results with X-ray scattering measurements. Estimated temperature rise due to local heating. Data shown in Figure 5b/c are reproduced from ref.\textsuperscript{12}. VHDA and eHDA were warmed with 4 K/min inside a cryostat while measuring I(Q) with X-ray diffraction.
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