Structural Studies of Several Distinct Meta-stable Forms of Amorphous Ice

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Introduction

Amorphous phases of pure ice are currently partitioned into two distinct amorphous forms: high-density amorphous (HDA) and low-density amorphous (LDA) [1]. The transition between the two forms has been shown to be very sharp (and apparently first order) with infinitesimal changes in pressure. This study investigates the nature of this transition by following the position of the first sharp diffraction peak (FSDP) during an isothermal annealing process. Once the FSDP position had stabilized, the sample was quenched to 40K for structural characterization. We observed at least three distinct meta-stable forms of amorphous ice, all produced from a continuous structural transformation of pressure-amorphized ice *I* at low pressure. It is likely that an infinite number of meta-stable forms are possible, depending on the annealing conditions.

Methods and Materials

Samples used for the x-ray experiments were transferred from liquid nitrogen storage into a cryostat mounted on the high-energy x-ray diffractometer at the ID-11-C beamline at the APS [2]. The sample was loaded into an aluminum holder with thin Kapton® windows. The x-ray measurements were made in transmission geometry with an incident beam energy of 98 keV and scattering from 4-mm-thick samples. The procedure for correcting the data has been outlined in detail in previous work [3]. The x-ray data presented were analyzed with ISOmer-X [4]; corrected for detector dead time, container scattering, and varying detector distance and polarization; and normalized to the sum of the elastic plus Compton scattering with a Klein-Nishina correction. Multiple scattering and attenuation corrections were found to be negligible (~1%) at this energy.

Results

The x-ray structure factor in Fig. 1 shows a shift of the FSDP position toward lower momentum transfer, from 2.25 to 2.16 to 2.09 and finally to 1.71 Å^{-1}, for the phases shown. Also shown is an initial decrease in the x-ray FSDP intensity, followed by an increase in intensity and significant sharpening in the final LDA phase. This is accompanied by a significant increase in the intensity of the peaks at 3.05 and 4.75 Å^{-1}. On the basis of this direct structural evidence, we suggest that amorphous ice can exist in a series of meta-stable forms, from the high-density form to the low-density form.

Discussion

These data are likely to have a very significant impact on the current understanding of the proposed continuous structural relationship between low-density liquid (LDL) water and LDA ice and between high-density liquid (HDL) water and HDA ice. In addition, an understanding of the structural variations in amorphous water, particularly the predominant length scales over which these variations occur, is likely to have a significant impact on the understanding of biomolecular hydration and cryopreservation.

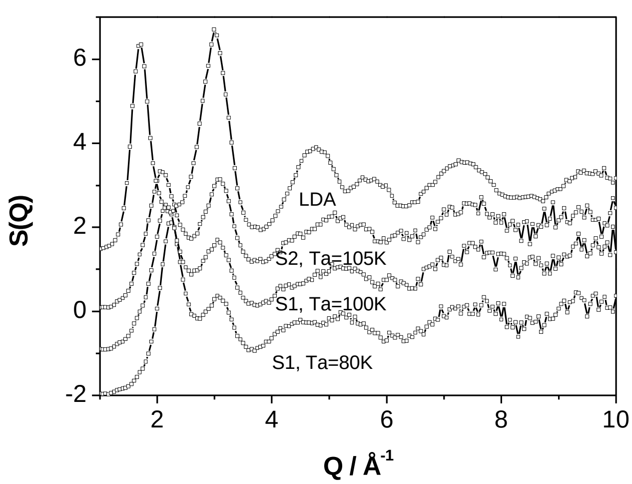

FIG. 1. Total and x-ray S(Q) of temperature-quenched amorphous ice states. All data were recorded at T = 40K. Each x-ray data set was recorded over 3 h. The open squares represent the recorded data, and the solid lines are the smoothed functions.

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