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LETTERS

Pure Ice IV from High-Density Amorphous Ice

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High-density amorphous ice (HDA), made by compression of hexagonal ice at 77 K, was heated at a constant pressure of 0.81 GPa up to 195 K and its phase transition followed by displacement-temperature curves. The crystalline phases recovered at 77 K and 1 bar were characterized by X-ray diffraction. Pure D_2O ice IV and nearly pure H_2O ice IV were formed on slow heating at a rate of $\approx$0.4 K min^{-1}, whereas pure H_2O and D_2O ice XII were formed on fast heating at $\geq$15 K min^{-1}. On heating HDA at rates inbetween, a mixture of ice IV and ice XII is obtained, where their relative yields depend in a systematic manner on the heating rate. Conversion of HDA into either ice IV or ice XII is an example of a "parallel reaction" where the relative yields of ice IV and ice XII can be controlled by temperature, that is in our approach by the rate of heating. It is conceivable that a similar behavior occurs on crystallization of the related pressure-amorphized silica.

Introduction

Ice IV is a metastable high-pressure phase of ice,[1−8] and according to Figure 1 in ref. 7, it can be formed from the liquid under suitable conditions between 0.2 and 1.0 GPa which covers most of the pressure range of the stability domains of stable ices III, V, and VI. Its formation from the liquid can be induced by appropriate nucleating agents,[3,4] but the effect of the nucleating agent or of the pressure on formation of ice IV is erratic. Engelhardt and Whalley[4] reported that even with the most efficient nucleating agent, "nucleation of ice IV was by no means consistent, and only about 1 freezing in 10 yielded ice IV." They further found that "in these experiments, ice IV exists for only a few seconds to several minutes at about −25 °C before transforming spontaneously to a more stable phase". Of the various high-pressure ice phases obtainable on cooling the liquid, ice IV is probably the most difficult one to form. Ice IV can be recovered by quenching to 77 K and releasing the pressure.[4] This recovered ice IV is fully proton-disordered according to diffraction,[9] infrared,[10] and calorimetric[4] measurements. Recently Suzuki et al.[11] reported that, on heating high-density amorphous ice (HDA) at 1.5 GPa up to 180 K, a high-pressure ice forms which they tentatively assumed to be either ice IV, ice VI, or ice XII.

Here, we show that pure ice IV can be formed in a reproducible manner on controlled isobaric heating HDA at 0.81 GPa up to ≈195 K. The essential parameter is the heating rate, with slow heating favoring formation of ice IV, whereas faster heating rates lead to formation of metastable ice XII. Thus, recovered ice IV without containing a nucleating agent is now available in gram quantitites for further studies. The kinetics of the phase transition of HDA to either ice IV or ice XII is that of a so-called "parallel reaction" which is for a schematic reaction: $A \rightarrow B$ or $A \rightarrow C$.[12] In isothermal studies, the ratio of rate constants, $k_{A\rightarrow B}/k_{A\rightarrow C}$, determines the product yield and not the equilibrium constants for the two reactions. By suitable choice of catalyst or temperature, one rate can be made much faster than the other.[12] Here, we utilize differences in heating

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rate to produce either pure ice IV or pure ice XII. This is to our knowledge the first example of a parallel reaction on crystallization of an amorphous solid, and possible implications for the polymorphism in silica are discussed.[13]

We note that several other high-pressure ice phases form on heating HDA under pressure[5,11,14,15] and on compression of ice Ih at various temperatures.[16–19]

Results and Discussion

Koza et al.[18] showed that on compression of ice Ih at 77 K up to 1.8 GPa not only HDA can form but also ice XII. According to Kohl et al.,[15] this formation of ice XII is caused by pressure drops and apparent shock-wave heating on compression of HDA. This can be avoided by using indium linings.[15,20–22] Therefore, we first show that only HDA forms on compression of ice Ih at 77 K, without contamination by ice XII.

HDA was made by compression of either H_2O or D_2O ice Ih at 77 K up to 1.6 GPa in a self-made piston-cylinder apparatus with 8 mm diameter piston, by using a computerized “universal testing machine” (Zwick, model BZ100/TL3S) for compression at a controlled rate of 7000 N min^{-1}. Its positional reproducibility is ±5 μm, and the spatial resolution of the drive is 0.01 μm. Pressure-displacement curves were recorded with the TestXpert V 7.1 Software of Zwick. Indium linings were used as decribed in refs 15 and 23 to avoid pressure drops during compression, and 0.300 cm^3 of water were pipetted into the precooled piston-cylinder apparatus. The pressure-displacement curves (cf. Figure 1a) had the same shape as those reported for example by Mishima et al.[20,21] and as that shown in Figure 1a of ref 15, with a pronounced decrease in volume on compression above ≈1.1 GPa because of the phase transition of ice Ih to HDA. Curves without pressure drops are characteristic for formation of HDA without ice XII.[15,23] HDA recovered after compression under liquid N_2 at 1 bar was characterized by X-ray diffraction (cf. Figure 1b), and its diffractogram is that reported in the literature,[15,17,20,21,24] with the maximum of the intense broad peak at 3.0 Å. The pressures given in the following are nominal pressures, and the effective pressures at the sample are expected to be slightly lower. Temperature was measured with a Pt-100 inserted firmly in the piston cylinder apparatus or with a thermocouple attached to the outside. For slow heating, the temperature accuracy is estimated as ±3 K, and for rapid heating, the error is expected to be larger.

In subsequent experiments, HDA was made by compression of ice Ih at 77 K as described above and then heated isobarically without characterizing it by X-ray diffraction, and the absence of pressure drops in the ΔV versus temperature plots is taken as indication for the absence of shock-wave heating.

Pure ice IV, or pure ice XII, was obtained on isobaric heating of HDA at 0.81 GPa, by varying the heating rate between ≈0.4 K min^{-1} (for ice IV) and ≈25 K min^{-1} (for ice XII). Figure 1c shows the change in volume, ΔV, on isobaric heating of D_2O HDA at 0.81 GPa with a rate of ≈0.4 K min^{-1} up to ≈162 K (marked by the arrow). ΔV values were calculated from the displacement by assuming that the diameter of the piston remains constant. In this and the following ΔV versus temperature plots, only the temperature range from 140 to 200 (190) K is shown for clarity, but heating was always started from 77 K. Controlled slow heating was started at ≈110 K, and fast heating was started at ≈80 K.

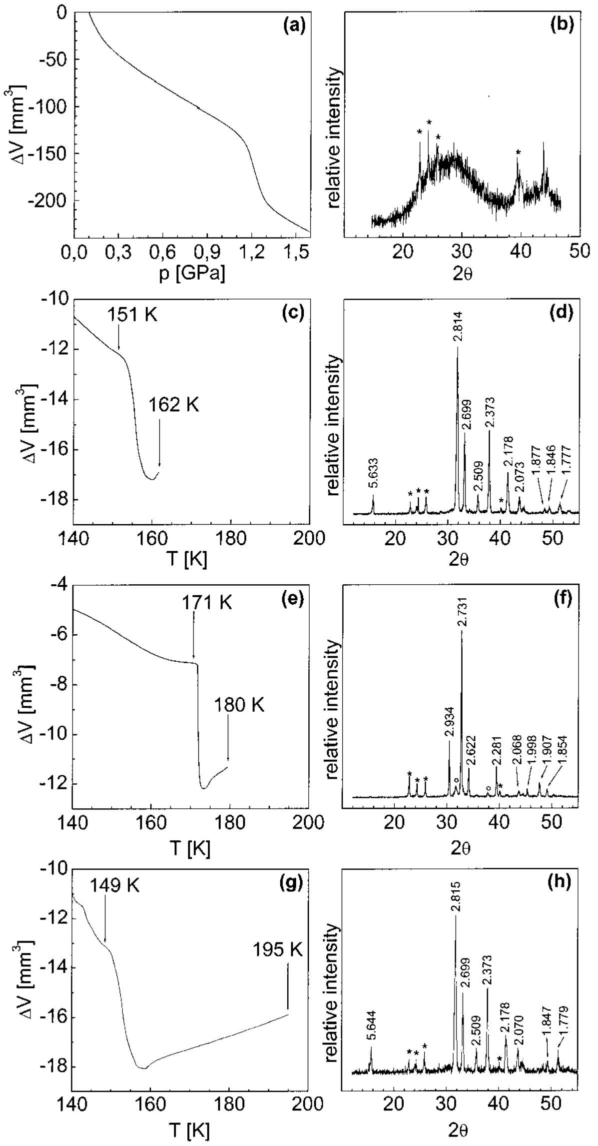

Figure 1. Formation of D_2O ice IV (D_2O ice XII) on isobaric heating of D_2O HDA at 0.81 GPa. (a) The ΔV versus p plot shows the conversion of D_2O ice Ih to HDA on compression at 77 K up to 1.5 GPa and (b) the X-ray diffractogram of the sample recovered at 77 K and 1 bar. (c) The ΔV versus T plot on isobaric heating of D_2O HDA at 0.81 GPa at a rate of 0.4 K min^{-1} up to 162 K and (d) the X-ray diffractogram of recovered D_2O ice IV. (e) The ΔV versus T plot on isobaric heating of D_2O HDA at 0.81 GPa at a rate of 11 K min^{-1} up to 180 K and (f) the X-ray diffractogram of recovered D_2O ice XII containing a small amount of ice IV (marked by empty circles). (g) The ΔV versus T plot on isobaric heating of D_2O HDA at 0.81 GPa at a rate of 0.4 K min^{-1} up to 195 K and (h) the X-ray diffractogram of recovered D_2O ice IV. Reflections of ice Ih are marked by asterisks. X-ray diffractograms (Cu Kα) were recorded on a diffractometer in $\theta-\theta$ geometry (Siemens, model D 5000), equipped with a low-temperature camera of Paar. The sample plate was in horizontal position during the whole measurement. Installation of a “Goebel mirror” allowed us to use small amounts of sample without distortion of Bragg peaks.

HDA first gradually densifies further on isobaric heating at 0.81 GPa (cf. Figure 1c).[17,22,24] A pronounced decrease in volume starts at ≈151 K (marked), indicating phase transition to a denser phase, and it ends at ≈159 K. After heating to 162 K (marked), the sample was cooled to liquid N_2 and recovered under liquid N_2 at 1 bar. Thereafter, it was characterized by its X-ray diffractogram (cf. Figure 1d) as pure ice IV by comparison with the d spacings and intensities reported by Engelhardt and Kamb.[9] A small amount of ice Ih is marked by asterisks in this and the following diffractograms. This ice Ih comes from condensation of water vapor during transfer of the sample into

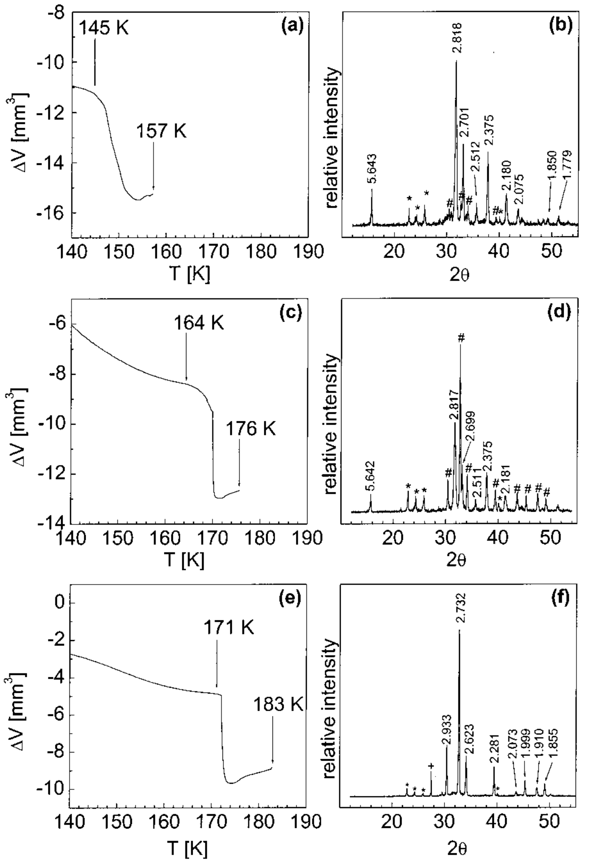

Figure 2. Formation of H_2O ice IV (H_2O ice XII) on isobaric heating of HDA at 0.81 GPa. (a) The ΔV versus T plot on isobaric heating of HDA at 0.81 GPa at a rate of 0.4 K min^{-1} up to 157 K and (b) the X-ray diffractogram of recovered ice IV containing a minor amount of ice XII (ice XII reflections are marked by a hashmark). (c) The ΔV versus T plot on isobaric heating of HDA at 0.81 GPa at 4.0 K min^{-1} up to 176 K and (d) the X-ray diffractogram of the recovered sample containing comparable amounts of ice IV and ice XII (marked by a hashmark). (e) The ΔV versus T plot on isobaric heating of HDA at 0.81 GPa at 15 K min^{-1} up to 183 K and (f) the X-ray diffractogram of recovered pure ice XII. An artifact in Figure 2f is marked by a cross, and reflections of ice Ih are marked by asterisks.

the precooled sample plate holder of the diffractometer. This is consistent with our observation that Raman spectra of recovered HDA, ice XII, or ice IV containing 5% D_2O did not contain the decoupled OD-stretching band of ice Ih. In these recovered samples ice Ih from incomplete conversion to HDA would have shown this decoupled band.

With increasing heating rate, an increasing amount of ice XII is formed. Figure 1e shows the pressure-displacement curve of D_2O HDA heated at 0.81 GPa at a rate of ≈11 K min^{-1}. The diffractogram of the recovered phase (cf. Figure 1f) contains mainly reflections of ice XII.[15,18,25] Two weak reflections of ice IV are marked by empty circles. The experiment on isobaric heating D_2O HDA at 0.81 GPa at a rate of 0.4 K min^{-1} (curves c and d) was repeated, but the sample was heated to 195 K instead of 162 K (curve g). The X-ray diffractogram of the recovered phase shows only the Bragg peaks of ice IV (curve h) and no indication for those of ice XII.

Similar dependence of the relative yields of ice IV and ice XII on heating rate was observed for H_2O HDA. On slow isobaric heating of H_2O HDA at 0.81 GPa at a rate of 0.4 K min^{-1} up to 157 K (Figure 2, curve a) and subsequent recovery of the phase at 77 K and 1 bar, mainly, ice IV is formed according to the diffractogram and only a minor amount of ice XII (Figure 2b, ice XII reflections marked by a hashmark). On increasing the heating rate to 4.0 K min^{-1} (Figure 2c), comparable amounts of ice IV and ice XII are contained in the recovered sample (Figure 2d, ice XII reflections marked by a hashmark). This is already observable in the ΔV versus T plot (Figure 2 c) where slow decrease of ΔV with increasing temperature is caused by formation of ice IV and subsequent rapid decrease to ice XII formation. On further increase of the heating rate up to 15 K min^{-1} (Figure 2e), the recovered sample consists of pure ice XII, without any ice IV (Figure 2f).

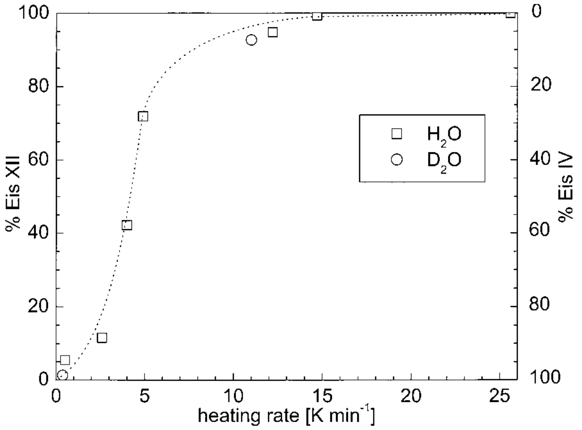

Figure 3. Percentage of ice IV yield (right) and of ice XII yield (left) plotted versus heating rate.

We have estimated the relative yields of ice IV and ice XII by integrating their Bragg peaks. This estimation seems reliable because the densities of ice IV and ice XII are very similar.[25] The small amount of ice Ih in the diffractogram is not included because ice Ih most likely contaminates the sample during the transfer. The estimation gives 93% ice XII and 7% ice IV for the diffractogram of Figure 1f, and for those of Figure 2, the yields of ice IV (ice XII) are 95% (5%) for Figure 2b, 58% (42%) for Figure 2d, and 0% (100%) for Figure 2f. These yields and additional ones from other experiments are included in Figure 3 where the dependence of the percentage of recovered ice IV (right ordinate) and of ice XII (left ordinate) on heating rate is plotted.

Whereas pure D_2O ice IV is obtained on heating at ≈0.4 K min^{-1}, H_2O ice IV made on heating at the same rate contains a minor amount of ice XII (cf. Figure 2b and Figure 3). Engelhardt and Whalley[4] had already remarked that the nucleation of ice IV from liquid water "appears to be more probable for D_2O than for H_2O", and similar behavior seems possible for ice IV from HDA. However, we expect that pure H_2O ice IV can also be made from HDA on decreasing the heating rate even further, below the ≈0.4 K min^{-1} rate used in this work. This is not possible at present with our pressure vessel.

Careful analysis of the crystallization kinetics of ice IV versus ice XII formation by the Johnson−Mehl−Avrami relation[26−29] requires isothermal studies which are at present not feasible. Because of that, we discuss in the following only in a qualitative manner which parameters control whether ice IV or ice XII forms on heating HDA. The ΔV versus temperature curves of Figures 1 and 2 show that formation of ice IV starts at a lower temperature than that of ice XII [cf. Figure 1 parts c and e (D_2O) and Figure 2 parts a and e (H_2O)] but that ice XII formation is much faster than that of ice IV once a certain temperature region has been reached (cf. Figure 1 parts c and e (D_2O) and Figure 2 parts c and e (H_2O)]. It is instructive to calculate from the heating rate and the temperature region of the phase transition the time it takes: this gives 1900 s for formation of D_2O ice IV according to Figure 1c and 17 s for the formation of D_2O

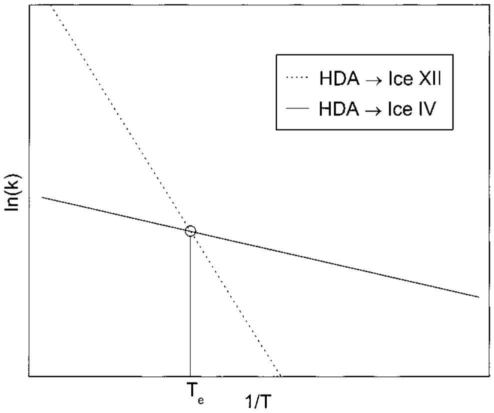

Figure 4. Schematic picture visualizing the requirement of different temperature dependence of rate constants for the HDA → ice IV transition (solid line) and the HDA → ice XII transition (broken). T_e is the temperature where the two rate constants have the same value.

ice XII in Figure 1e. Thus, at *low* temperatures, the rate constant for formation of ice IV ($k_{\mathrm{HDA\rightarrow ice\ IV}}$) must be much higher than that of ice XII ($k_{\mathrm{HDA\rightarrow ice\ XII}}$), whereas at *high* temperatures the opposite holds. This requires that $k_{\mathrm{HDA\rightarrow ice\ XII}}$ increases much more with temperature than $k_{\mathrm{HDA\rightarrow ice\ IV}}$ and that the activation energy for HDA → ice XII formation is much higher than that for HDA → ice IV formation.

This is visualized in Figure 4 in a schematic manner for Arrhenius behavior. Below a certain temperature, T_e, $k_{\mathrm{HDA\rightarrow ice\ IV}}$ is much larger than $k_{\mathrm{HDA\rightarrow ice\ XII}}$, and consequently, nearly pure ice IV is formed. Above T_e, the opposite holds, and nearly pure ice XII can be formed. This schematic picture also requires that so-called pure ice IV (ice XII) must contain a minor amount of ice XII (ice IV), and by "pure" we mean that the minor crystalline phase is not detectable in our X-ray diffractograms. T_e is the temperature where $k_{\mathrm{HDA\rightarrow ice\ IV}} = k_{\mathrm{HDA\rightarrow ice\ XII}}$ and, thus, where equal amounts of ice IV and ice XII are formed on isothermal reaction. It can be determined by heating HDA very rapidly to a given temperature, holding it at this temperature until complete conversion is achieved, cooling the sample to 77 K, and determining the relative yields of recovered ice IV and ice XII by diffraction. This is at present not possible.

We have further considered whether in addition some metastable ice IV transforms into metastable ice XII; that is, whether ice IV is more metastable in this p,T region than ice XII. Such an ice IV → ice XII transition would be barely recognizable in the ΔV versus T plots because their densities are nearly identical.[25] We surmize that ice IV → ice XII transition can be ruled out on the basis of ΔV versus T plots of Figure 1: pure ice IV was formed on slow heating at 0.4 K min^{-1} either to 162 K (Figure 1c) or to 195 K (Figure 1g). Thus, the additional slow heating of ice IV from 162 to 195 K does not lead to formation of ice XII from ice IV. This further proves that formation of ice XII on fast heating occurs from HDA, and not from ice IV, because ice XII formation had finished at ≈172 K (Figure 1e). The absence of an ice IV → ice XII transition could be for kinetic reasons, and an ice IV → ice XII transition is still possible at higher temperatures. However, in our experiment, the temperature range for that is very small because transition to stable ice VI sets in.[22]

We finally discuss implications for the polymorphism of silica which is important in geophysics, materials science, and fundamental physics.[30] Pressure-induced amorphization of crystalline silica occurs at 25−35 GPa and 300 K.[31] Although this amorphization is in a different $p-T$ domain than that of ice I at ≈1.0 GPa and 77 K, it demonstrates the remarkable similarity in physical properties of these tetrahedrally bonded compounds.[31,32] Teter et al.[13] point out that "it is still unclear what phases of silica are stable at high pressure, what types of metastable phases are possible, and what structural similarities may exist among them". It is conceivable that the effect of heating rate at a given pressure on the type of metastable phase formed as outlined in this study for HDA is also important for crystallization of pressure-amorphized silica and that its study clarifies contradictory experimental results.

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