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This is an article published in **Journal of Chemical Physics**

Citation for the published paper:

Ove Andersson, Gyan P Johari

Time-dependent amorphization of ice at 0.8-0.9 GPa

Journal of Chemical Physics , 2004, Vol. 121, Issue 8: 3936 - 3938

[URL: <http://dx.doi.org/10.1063/1.1775792>]

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Citation: *J. Chem. Phys.* **121**, 3936 (2004); doi: 10.1063/1.1775792

View online: <http://dx.doi.org/10.1063/1.1775792>

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NOTES

Time-dependent amorphization of ice at 0.8–0.9 GPa

Ove Andersson

Department of Experimental Physics, Umea University, S-901 87, Umea, Sweden

G. P. Johari

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

(Received 5 March 2004; accepted 1 June 2004)

Thermal conductivity measurements show that ice continues to amorphize for several days when kept at a fixed pressure p in the 0.79–0.88 GPa range, and fixed temperature T in the 127–130 K range. Thermal conductivity κ decreases according to a stretched exponential in time, and its limiting long time value $\kappa(\infty)$ varies with p and T . At 0.8 GPa and 128 K, $\kappa(\infty)$ remains 2.5 times the value observed for high-density amorph. Consequences of these findings for our understanding of amorphization are discussed. © 2004 American Institute of Physics.
[DOI: 10.1063/1.1775792]

At high pressures and low temperatures, hexagonal and cubic ice densify to an amorphous solid known as the high-density amorph (HDA).^{1–6} During this pressure amorphization of ice at a fixed temperature T , volume decreases with increase in pressure p according to an inverted sigmoid-shape curve.^{1,2,4–6,7} Limiting high-frequency dielectric permittivity,² thermal conductivity,³ and ultrasonic velocity and attenuation⁸ of ice have been found to change with increase in p in a similar manner. When heated at $p > 0.8$ GPa, this HDA is said to transform apparently to a new form, very HDA (VHDA), when T reaches 160 K (Ref. 4), and when heated at 0.1 MPa, the structure of HDA is found to change gradually until features of low-density amorph are established.⁹ It is believed that HDA formed at different T may be structurally different.¹⁰ As part of our study of amorphization of ice, we have found that amorphization is also a time-dependent process. Here we report the kinetics of amorphization of ice Ih by measuring, as before,^{3,11} its thermal conductivity κ .

Ice Ih was formed by freezing water contained in an ~25 ml capacity can-shaped teflon vessel tightly fitted inside a 45 mm internal diameter piston-cylinder assembly used before.^{3,11} Water at 0.05 GPa pressure was frozen by cooling at 0.5 K/min by means of a built-in helium cryostat. The p and T of the sample were computer controlled during the course of the experiment. The cooling rate was 3–6 K/h and the heating rate 6–15 K/h, at T near 130 K. Pressurizing rate of ice was 0.05–0.1 GPa/h and depressurizing rate of the amorph was ~0.1 GPa/h, which are at least 1/10th of the rates used in earlier studies.^{1,2,4–6} Ice Ih amorphized slowly, and the amorph formed remained under pressure over a period of several days, i.e. much longer than 1 h or less used in

earlier studies.^{1,2,4–6} Their T , p , and κ were measured in real time. The onset pressure of ~0.8 GPa at 130 K observed here agreed with that observed in earlier studies at 130 K.^{3,6,8,11} Ice Ih was pressurized to $p > 0.78$ GPa, the control program was switched from the pressure-increase mode to the fixed-pressure mode, and the sample maintained at a fixed p . Samples were thus studied at different p and T and their κ was measured with time. The data are accurate to within ± 0.05 GPa for p (at 1 GPa and 100 K), ± 0.3 K for T , and $\pm 3\%$ for κ . The κ values are precise to within $\pm 0.3\%$.

In one experiment, p was kept constant at 0.8 GPa and 128 K for 30 h (106 ks) as its κ gradually decreased with time t as shown in Fig. 1(A). The measured $\kappa(t)$ was fitted to the equation, $\kappa(t) = [\kappa(0) - \kappa(\infty)] \exp[-(kt)^\beta] + \kappa(\infty)$, where the initial κ at 0.8 GPa and 128 K is $\kappa(0) = 3 \text{ W m}^{-1} \text{ K}^{-1}$, and the final value, $\kappa(\infty) = 1.8 \text{ W m}^{-1} \text{ K}^{-1}$. The rate constant $k = 1.1 \times 10^{-5} \text{ s}^{-1}$ and the distribution parameter is $\beta = 0.6$. Accordingly, it would take 120 h to reach a state whose κ value is within 5% of $\kappa(\infty) = 1.8 \text{ W m}^{-1} \text{ K}^{-1}$. The value of $\beta = 0.6$ indicates a distribution of rate constant. This means that k is either a function of t , as for diffusion-controlled reaction kinetics in highly viscous liquids and glasses,¹² or it varies from site to site in a microscopically heterogeneous sample.

The results show that amorphization at a fixed p and T leads to a state of $\kappa(\infty) = 1.8 \text{ W m}^{-1} \text{ K}^{-1}$, which is 2.5 times of $\kappa(=0.7 \text{ W m}^{-1} \text{ K}^{-1})$ found for HDA formed at 1.15 GPa and 130 K,³ and κ in Fig. 1(A) would therefore not decrease further by $1.5 \text{ W m}^{-1} \text{ K}^{-1}$ to reach $0.7 \text{ W m}^{-1} \text{ K}^{-1}$. This is a crucial finding as it shows that the state known as HDA is not obtainable by keeping the sample at 0.8 GPa and 128 K.

FIG. 1. (A) Thermal conductivity of partially amorphized state at 0.8 GPa and 128 K. The line is calculated from stretched exponential relation given here. (B) Thermal conductivity of several samples plotted against time.

For a further investigation of amorphization kinetics, κ of several samples was determined at different p and T . However, unexpected failures of the measurement system restricted the data collection to a period of 4–6 ks. The measured κ values are plotted against t in Fig. 1(B). It is seen that the plots have different initial slopes and tend to reach different limiting values depending on the p and T conditions. Since the properties of a nonergodic state depend upon the p - T path used to reach that state, it is expected that amorphization even at closely similar p - T conditions would not lead to a state of identical κ , or $(d\kappa/dt)_{p,T}$, values. Samples that had been amorphized to a greater extent by keeping at a higher pressure, and had a lower $\kappa(0)$ value, showed a higher initial slope in their κ - t plot than samples that had been amorphized to a lesser extent and had a higher $\kappa(0)$ value. The lowest slope in Fig. 1(B) is for the $\kappa(t)$ plot for the lowest p of 0.79 GPa.

Most significantly, the curve for samples at all p and T conditions in Fig. 1(B) tends to $\kappa(\infty)$ values that are two to three times higher than the value of κ of $0.7 \text{ W m}^{-1} \text{ K}^{-1}$ found for the amorph produced by pressurizing the ice Ih at 130 K to 1.15 GPa.

Our study does not reveal the amorphization mechanism but it indicates two possibilities: (i) Ice Ih at T near 130 K transforms to a certain amorphous structure immediately after a certain p has been reached and thereafter the structure

gradually changes; at $p > 1.1$ GPa the apparent HDA at this T forms in a few minutes. (ii) Only a fraction of ice Ih at a certain T and p transforms to the state known as HDA, i.e., the sample remains structurally heterogeneous. Accordingly, at almost complete amorphization, a large population of randomly distributed amorphous regions in ice Ih would become connected to each other, and thereafter a small increase in p would cause an avalanche-like growth of the amorph until no ice Ih is left. Thus the shape of the inverted sigmoid-shape plot of κ against p at a fixed T would abruptly change to a vertical line at a pressure where this avalanche-like growth would occur. This may be observed by either increasing p very slowly or keeping p fixed for a long time to achieve a high extent of amorphization. Real time, neutron, or x-ray diffraction of a sample at p within the amorphization range may help resolve relative merits of these two mechanisms.

In a separate experiment, an amorph ($\kappa = 0.7 \text{ W m}^{-1} \text{ K}^{-1}$) was made by pressurizing ice Ih at 130 K from 0.1 to 1.15 GPa during a 13 h period. It was then depressurized to 1.0 GPa and cooled to 115 K, and finally heated at 1.0 GPa to 160 K at 0.3 K/min. Between 130 and 160 K, its κ at 1.0 GPa increased by $\sim 3\%$. Since both densification and heating are known to raise κ of an amorph, this small increase indicates that its structure did not significantly change on heating. This means that an amorph close to that of VHDA had already formed at 1.15 GPa and 130 K. We note in Fig. 1B of Ref. 4 that the volume of HDA decreased by about half relative to the net decrease on its conversion to VHDA when T reached ~ 130 K. Also, in our slow compression experiments, some ice Ih may have conceivably transformed to HDA before its p reached 0.80 GPa, but there is little evidence for its occurrence in our study.

Since there is no unique HDA or VHDA, we do not precisely know which amongst the many HDA's have been studied by neutron and x-ray diffraction at 0.1 MPa, and whether or not further structural changes had occurred in the process of their recovery for *ex situ* diffraction studies. (Even the density of HDA is found to be as high as $\sim 1.30 \text{ g/ml}$ at 77 K and 0.1 MPa⁷) Nevertheless, *ex situ* studies by Guthrie *et al.*⁹ have shown that when HDA at 0.1 MPa is slowly heated and/or annealed at $90 \text{ K} < T < 110 \text{ K}$, one H_2O molecule is slowly forced out of its structure's first coordination shell, until the basic features of the low-density amorph have been established. Here it seems that the opposite occurs, i.e., in the amorph's structure formed initially at $p > 0.8$ GPa, one H_2O molecule enters the first coordination shell in a t -, T -, and p -dependent manner. The amorphization kinetics, therefore, reflects the kinetics of this process.

To conclude, ice Ih continues to amorphize at a fixed p and T over a period of days and that the broad amorphization range and variation in the properties of the amorphs produced at different T and p are partly due to the slow kinetics of amorphization.¹³ In the amorphization range, the product obtained at a fixed p and T does not tend towards the HDA formed at 77 K at $p \geq 1.2$ GPa. A state very close to that of VHDA can be produced also by pressure amorphizing ice Ih at 130 K and 1.15 GPa.

This study was supported by the Swedish Research Council. G.P.J. is grateful to Natural Sciences and Engineering Research Council of Canada for general support of his research.

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