The glass-to-liquid transition of the emulsified high-density amorphous ice made by pressure-induced amorphization

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Emulsified high-density amorphous ice, made by pressure-induced amorphization of emulsified ice Ih, was decompressed at about 160 K. The onset of an endothermic event was observed around 0.4 GPa during the decompression. This is consistent with existence of the glass transition to a liquid state, implying the close relationship between melting and amorphization. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1774151]

I. INTRODUCTION

Liquid water at low temperatures is a current topic of vigorous discussion. According to the second critical-point hypothesis,[1] liquid water separates into low- and high-density liquid phases in its supercooled region, and becomes the known low- and high-density amorphous ices[2] (LDA and HDA) at much lower temperatures. Direct experimental confirmation of the hypothesis by using bulk water is unfeasible because of crystallization of the liquid. Although the two amorphous solids seem to be the glassy states of the two liquids from their general structural resemblance,[3–6] there has remained some possibility that HDA may not relate to liquid.[7] This is because HDA is mechanically collapsed ice[8] made by pressure-induced amorphization of ice Ih, and because no glass-to-liquid transition has been observed in any pressure-amorphized material. Generally, a relaxed glassy solid absorbs heat when it becomes liquid. In this paper, I describe detection of the onset of an endothermic event in emulsified HDA, and it is suggested to be the glass transition to liquid water. Some implications are discussed.

II. EXPERIMENTS AND RESULTS

I used emulsified H_2O (1–10 μm in droplet size) in order to hinder nucleation of ice crystals.[9] About 1 cm^3 of the sample, emulsified by stirring together liquid H_2O (1 cm^3), methylcyclohexane (0.75 cm^3), methylcyclopentane (0.75 cm^3), and sorbitan tristerate (50 mg), was compressed in a piston-cylinder apparatus. Compressed to 1.4 GPa at 77 K, the emulsified ice Ih was transformed to emulsified HDA by pressure-induced amorphization around 1 GPa (Ref. 10). The HDA emulsion was then heated to 160 K at 1.05 GPa at 20 K/min. Showing monotonous change in temperature and volume, the emulsified HDA continuously changed into its annealed state. Note that we can make this annealed state by the pressure-induced amorphization of the emulsified ice Ih above ~140 K (Ref. 10). Then, I decompressed the emulsion sample at 0.2 GPa/min keeping the cylinder temperature to be ~160 K. During the decompression I measured the sample temperature to ±0.01 K of relative error with a thermocouple brought into the sample, and piston displacement to detect the change in sample volume as well.

As shown in Figs. 1(a) and 1(b), the sample temperature gradually started to decrease around the pressure indicated by the gray zone in Fig. 1(b) (the arrow *G*) while the sample volume gradually increased slightly more rapidly (not shown). Immediately after this decrease in temperature, the sample temperature suddenly increased as shown by the arrow *X* in Fig. 1(b), accompanied by a slight decrease in the sample volume (not shown). Even though the decrease in temperature at the gray zone was quantitatively small, I observed the decrease clearly and reproducibly. Additionally, I always observed the decrease in temperature of the annealed HDA emulsion on the 160 K decompression through different experimental procedures as well as in the differential thermal analysis in which the reference point was set in the high-pressure chamber. These observations demonstrated that the decrease in temperature was not artificial. In the experiments using only the emulsion matrix without H_2O, or in the experiments of emulsified high-pressure crystalline ice, the sample temperature changed smoothly all around this gray zone and showed neither noticeable temperature decrease nor increase [the broken lines in Fig. 1(b)]. It is difficult to think that the transition indicated by the arrow *X* has induced the preceding gradual temperature decrease, because the increase in temperature (the arrow *X*) had begun suddenly. It is also difficult to think that the decrease in temperature represents crystallization of the HDA since crystallization is generally accompanied with heat evolution. The samples before and after these temperature changes [*A* and *B* in Fig. 1(a)] were the annealed HDA and an ice III-like (or IX-like) solid, respectively, as identified by the x-ray measurement at 1 bar and 77 K of the recovered sample (Fig. 2). Accordingly, it seems natural to think that the decrease and the following increase in the sample temperature were, respectively, caused by some endothermic glass transition in the emulsified and annealed HDA and by the following exothermic crystallization.

Similar experiments on emulsified LiCl aqueous solutions suggested that the temperature decrease around the gray zone in Fig. 1(b) corresponds to the glass transition to a liquid state. I compressed and decompressed the emulsion of the glassy LiCl solutions at various temperatures. During the
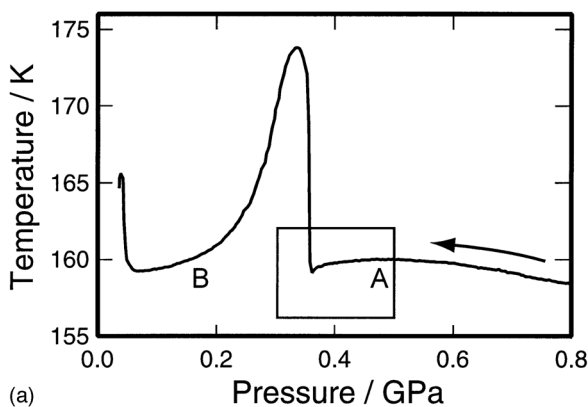
(a)
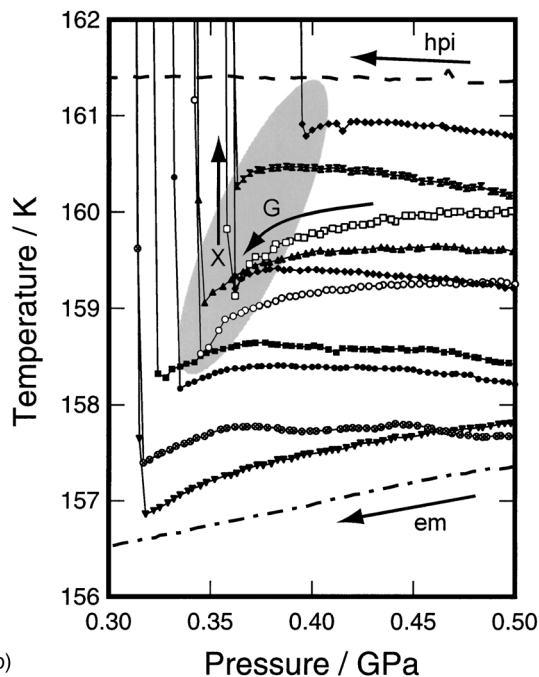
(b)

FIG. 1. The change in temperature of the emulsified HDA sample during decompression at ~160 K. (a) A typical example of the temperature change. In different experiments, the samples were recovered from A or B to 1 bar and 77 K for the x-ray diffraction measurement (Fig. 2). The increase in temperature at ~0.05 GPa is due to the ice III (IX)-to-ice Ic transition. Errors of absolute pressure and absolute temperature are ±0.01 GPa and ±1 K, respectively, and pressure is calibrated by using the triple points among ice phases at high temperatures. (b) A magnified figure of the region indicated by the rectangle in (a). Several examples of the temperature changes are shown. The temperature of the sample (for example, the open-square line) decreases along the arrow G around the gray zone, and increases along the arrow X. The broken lines indicate two examples of smooth temperature changes obtained in the experiments of an emulsified high-pressure ice (the arrow hpi) and the emulsion matrix (the arrow em).

decompression, I could easily detect the decrease in temperature of the emulsified solutions (Fig. 3). This decrease was also observed in bulk glassy LiCl solutions. The difference in pressure, or temperature, of the endothermic event between the emulsified and bulk solutions was small and about the experimental uncertainty (Fig. 3). The pressure and temperature of the endothermic event of these emulsified and bulk solutions agreed with those of the previously reported glass-to-liquid transition of the bulk LiCl solutions in the region of overlap [Fig. 4(a)]. These observations indicate that the decrease in temperature of the solutions corresponds to the
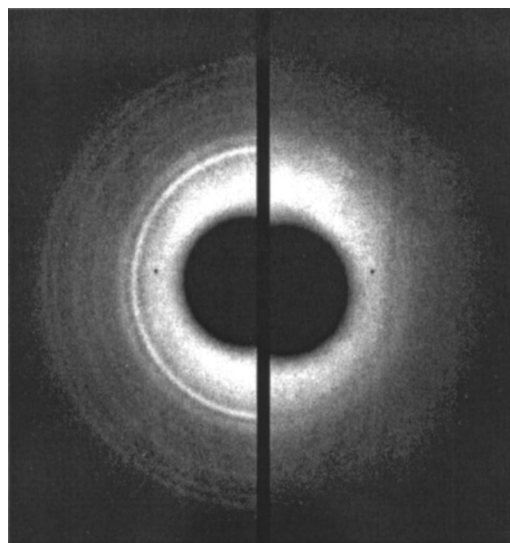

FIG. 2. The x-ray diffraction pictures of the emulsified and annealed HDA (right) and the ice III-like (or IX-like) emulsion (left) taken at 1 bar and 77 K. The samples, respectively, recovered from A and B in Fig. 1, were placed in a special liquid-nitrogen glass-vacuum flask and exposed to Zr-filtered Mo characteristic x-rays as in our previous work (Ref. 10). A polaroid film is exposed to the x-rays diffracted from not only the water sample but also the liquid nitrogen, thin glass walls of the flask, and emulsion-matrix materials. Although it is difficult to draw a halo of the HDA or to determine an exact crystalline ice structure, it is possible to find whether ice crystals exist in the sample and to suppose the ice phase.

glass transition to liquid, and that the glass transition of emulsified solutions is approximately the same as that of bulk solutions. The glass transition temperature and pressure usually depend on the solute concentration. I experimentally studied the dependence of the LiCl concentration on the glass transition pressure of the emulsified solutions between 140 and 170 K and between 3.2 and 11.1 mol %. Emulsion of the homogeneous glassy solution could be easily made in this concentration range. Then, I estimated the pressure and
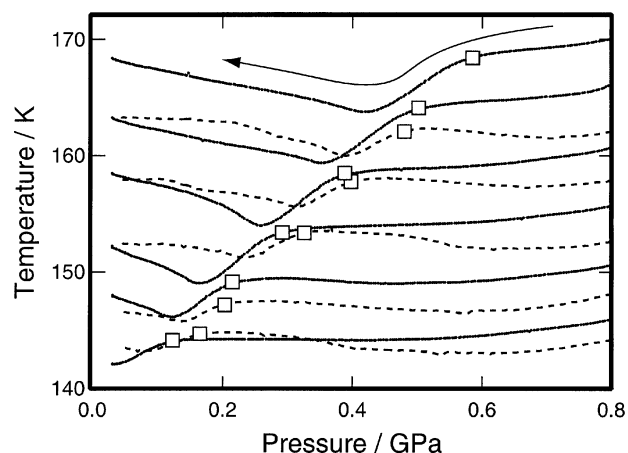

FIG. 3. The temperature change of the bulk (solid line) and emulsified (broken line) 11.1 mol % LiCl solution during decompression (arrow). Open square: the onset of the glass transition. When the emulsified liquid solution is, on the other hand, compressed, its temperature is always higher than the cylinder temperature until the liquid vitrifies by compression, showing that heat evolution lessen significantly above the glass transition pressure (not shown).
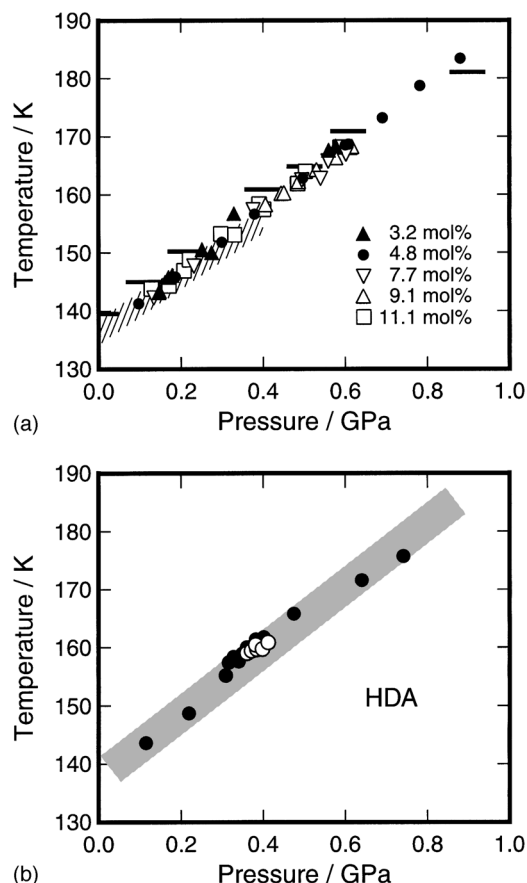
(a)

(b)

FIG. 4. Comparisons of the glass transitions of the emulsified HDA and the emulsified LiCl solutions. (a) The glass transition temperature T_g of the LiCl solutions under pressure. The markers indicate the onset pressure of the temperature decrease during decompression. These data are obtained from the emulsified homogeneous glassy LiCl solutions with substantially no ice crystals. For example, the emulsified 3.2 mol % LiCl liquid solution seemingly completely vitrifies by cooling at 20 K/min at ~0.25 GPa. The dilute solutions, whose concentration is lower than ~3.2 mol %, crystallize during cooling in the present study, as detected by a distinct exothermic behavior at the crystallization. When the phase-separated emulsified solution, composed of the ice Ih crystals and thick glassy solution, was compressed beyond the amorphization pressure at 77 K and this solution with the produced HDA component was decompressed around 160 K, its temperature also began to decrease at ~0.4 GPa because of the suggested glass transition of the HDA component in the emulsion. Horizontal bar: the onset of the endothermic event during heating of bulk 11.1 mol % glassy solution at different pressures. The open-square points mark the glass transitions of both emulsified and bulk solution of Fig. 3. Hatched area: the region of the previously reported glass transitions for bulk 4.8, 7.7, and 11.1 mol % LiCl solutions (drawn from the data of Ref. 16). The presently obtained glass transition temperatures of the emulsified and bulk LiCl solutions (the markers and the horizontal bars) reasonably agree with the previous results (the hatched area). (b) The endothermic event (open circle) and exothermic crystallization (filled circle) observed during decompression of the emulsified HDA at different temperatures. The wide gray line indicates the estimated location of the glass transition for the emulsified pure water.

temperature of the glass-to-liquid transition of emulsified pure water by extrapolating the LiCl concentration to zero, and compared the onset pressure of the endothermic event of the emulsified HDA with the estimated glass-to-liquid transition pressure for pure water. As shown in Fig. 4(a), the glass transition pressure (temperature) of the solutions appeared nearly constant in the examined concentration range; the glass transition pressure (temperature) might increase
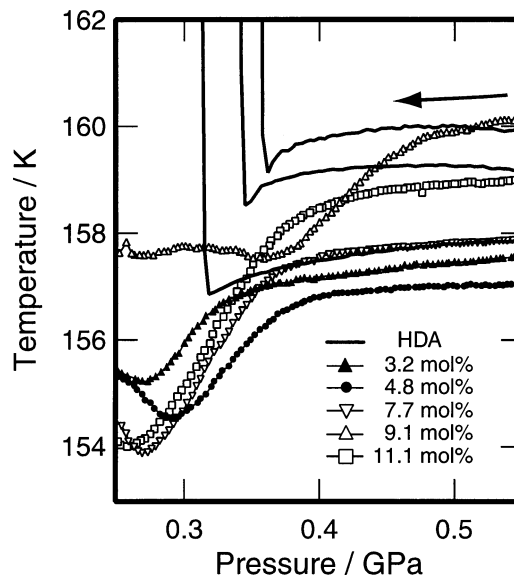

FIG. 5. The comparison of the temperature changes during decompression (arrow) of the emulsified HDA (solid lines) and the emulsified (3.2, 4.8, 7.7, 9.1 mol %) and bulk (11.1 mol %) LiCl solutions (lines with markers) around their glass transition pressures. The continuous temperature decrease of the solid line around 157–158 K is that of the low-temperature scan in Fig. 1(b).

(decrease) as the LiCl concentration decreases from 11.1 mol %, and might change to decrease (increase) below ~9 mol %, but the deviation, if any, is small. As shown in Fig. 4(b), the endothermic event of the emulsified HDA started about the estimated glass-to-liquid transition pressure of the emulsified pure water. Additionally, the temperature decrease of the HDA near the endothermic event during decompression, including the continuous temperature decrease for the lower temperature scan in Fig. 1(b) as well, resembled the initial temperature change of the glass-to-liquid transition of the solutions (Fig. 5). Therefore, the observed endothermic event of the emulsified HDA appears to correspond to the glass-to-liquid transition of the emulsified pure water, suggesting that the emulsified HDA undergoes the glass transition to a liquid state. The estimated change in H_2O volume during the crystallization to ice III along the arrow X in Fig. 1(b) (~2% at 0.4 GPa, 160 K) was roughly the same as the known volume change of the liquid-to-ice III freezing (2.3% at 0.35 GPa, 256 K), consistent with this interpretation.

When the LiCl concentration of the solution was lower than ~10 mol %, the emulsified solution crystallized during decompression at a pressure lower than its glass transition pressure. This crystallization pressure tended to shift to higher values as concentration decreased and as temperature increased. Regarding the emulsified HDA, although it crystallized easily, its crystallization pressure was consistent with this tendency. When the emulsified HDA was decompressed at a temperature higher than ~161 K, it crystallized before the endothermic event was observed. At about 158–161 K, the HDA crystallized around 0.35–0.4 GPa immediately after the endothermic event had begun. This pressure region is roughly close to 0.2–0.3 GPa where the emulsified supercooled water is known to be relatively stable against crystallization.[9] Below ~158 K, crystallization seemed to

occur at a pressure higher than the pressure of the clear temperature decrease. It is noteworthy that the observed crystallization of the emulsified HDA occurred about the pressure and temperature of the estimated glass-to-liquid transition for the emulsified pure water [Fig. 4(b)]. On the other hand, pure bulk HDA seemed to crystallize on decompression at a pressure always higher than the estimated glass-to-liquid transition pressure (not shown).

III. DISCUSSION

I note that, as temperature decreases, the slope of the experimentally determined metastable melting curve of the emulsified ice Ih becomes practically parallel to the temperature axis around 160 K in the pressure-temperature phase diagram,[10] indicating little or no difference in entropy between the ice and liquid phases and the presence of glass transition near 160 K. Indeed, the crossover from melting to amorphization occurred around ~0.5 GPa and 160±5 K (Ref. 10). This crossover point is about the pressure and temperature of the presently estimated glass-to-liquid transition for emulsified pure water [Fig. 4(b)], and it is, therefore, reasonable to think that, when compressed, the emulsified ice Ih melts to ergodic (supercooled) high-density liquid above the glass transition temperature T_g and it amorphizes, or collapses, to a kinetically frozen state under the nonergodic condition below T_g (Ref. 10).

In the present study, the endothermic event was observed in the emulsified and annealed HDA around 0.4 GPa and 160 K, and this location is near the melting-amorphization crossover point and is the pressure and temperature of the expected glass-to-liquid transition for the emulsified pure water indicated by the experiments of the LiCl solutions. Because of this mutual agreement, it is suggested (not directly proven) that the endothermic event in the emulsified HDA is the glass transition to liquid. Although characterization of the liquid and confirmation of reversibility of the glass transition would be desirable, they have not yet been obtained due to experimental difficulty. The onset of fluid molecular motion in the emulsified HDA may trigger the crystallization. As the metallic glass made by mechanical alloying changes into the liquid state via the glass transition,[11] the mechanically collapsed ice is suggested to become liquid via the glass transition when it is emulsified and annealed and its crystallization is suppressed. That is, the pressure-induced amorphization of the emulsified ice Ih is suggested to be "cold melting" to the emulsified HDA that becomes liquid continuously.

The endothermic events in the HDA and in the LiCl solution could be detected in the present experiments by the simple temperature measurement under pressure. This suggests that the change in their heat capacity C_P at these events is adequately large, which contrasts with the extremely small change in C_P at the "shadow" T_g of pure bulk LDA near 136 K at atmospheric pressure.[12] Besides this similarity of the relatively large change in C_P between the HDA and the solution, the good correspondence of the crystallization temperature of the emulsified HDA, as well as its suggested T_g, with the estimated T_g of the emulsified pure water, or the T_g of the emulsified and bulk LiCl solutions, was observed in the wide pressure-temperature range [Figs. 4(a) and 4(b)]. If the crystallization of the emulsified HDA is assumed to occur near its glass transition, this apparent correspondence between HDA, pure water, and LiCl solution implies that the emulsified HDA is the emulsified pure water, or the solvent water of the LiCl solutions, and that the T_g of the emulsified HDA at atmospheric pressure is 135–140 K if the HDA does not transform [Fig. 4(b)]. Because this temperature is the expected $T_g (\sim 138 \text{ K})$ for pure water indicated by extrapolation of T_g of various high-concentration electrolyte solutions at atmospheric pressure,[13] and because the volume change at T_g of these solutions is continuous, it is also supposed that the emulsified HDA is the solvent water of the high-concentration electrolyte solutions.

The emulsified H_2O, possibly contaminated by some unknown composition, may differ from the pure bulk H_2O. However, there exists the indication that the emulsification affects the glass transition little. Regarding melting and amorphization of ice, which are likely related to the glass transition, there is a close similarity of the transition pressure between the emulsified and bulk H_2O (Ref. 10). The almost identical glass transition behavior between the emulsified and bulk LiCl solutions was also observed (Fig. 3). These facts suggest a possibility that the glass transition of bulk HDA exists near the pressure and temperature of the glass transition of the emulsified HDA, or near those of the estimated glass transition for the emulsified pure water [Fig. 4(b)], although the glass transition of the bulk HDA would be difficult to observe because of the crystallization. This possibility also implies that HDA is the solvent water of the electrolyte solutions as the emulsified HDA is supposed to be.

Since HDA-like ice exists in low-temperature biological tissues,[14,15] the present result has implications in the study of cryopreservation.

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