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LETTERS

Thick Glassy Water by Liquid Quenching on a Diamond Wafer

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By quenching water on a liquid nitrogen cooled diamond wafer, we have produced 0.7 mm thick glassy water disks about 1000 times thicker than previously produced by quenching liquid water. Our in situ measured cooling rates of 110−271 K/s are far lower than the 10^5-10^6 K/s previously thought necessary for formation of a glass from liquid water. Conversely, these are also the highest measured cooling rates that we are aware of for quenching this thickness of water. The glassy disks quenched on diamond are transparent, have a density of 1.04 g cm^{-3}, and exhibit a glass-transition temperature of 138 K and a crystallization temperature range of 150−190 K.

Introduction

Glassy water has been produced at 77 K by vapor deposition,[1,2] by rapid quenching of atomized liquid droplets,[3] and by applying high pressure to hexagonal or cubic ice.[4,5] Extraterrestrial water might exist as a glass. Amorphous solid water (ASW) formed from water vapor may be the form of water on planets and comets of which the atmospheric pressures and temperatures are too low for liquid water to be an equilibrium phase.[6,7] The high-density amorphous (HDA) water formed by applying 10 kbar to hexagonal ice at 77 K may be the form water takes on planets exhibiting low temperatures and hyperbaric pressures in the planetary crust.[6,7] For a glass to contain water-based living organisms, such a glass would have to be formed from liquid water. To form hyperquenched glassy water (HGW), Johari et al. quenched atomized liquid droplets, which were sheared down to submicron thick flakes, upon on a copper substrate at 77 K, resulting in an estimated 10^5 K/s cooling rate and the avoidance of ice.[3] We report here the formation of glassy water by quenching liquid water on a diamond wafer at 77 K at a thickness of 0.7 mm, about 1000 times thicker section of liquid quenched glassy water (QGW) than previously reported for HGW.[3] Our in situ measured cooling rates of 110−271 K/s are up to 1000 times slower than the previously estimated cooling rates thought necessary to produce glassy water from liquid water.

Experimental Section

The 0.7 mm thick transparent disk of QGW shown in Figure 1a was produced by dropping 0.057 cm^3 of pure water (high-quality, double-deionized reagent grade, <0.1 mho/cm conductivity) from a syringe onto a diamond wafer cooled in liquid nitrogen to 77 K. The 4.8 mm diameter drop was sheared down to a 0.7 mm disk by dropping it from 25 cm above the diamond wafer, which was held at 45° half-submerged in the liquid nitrogen. The evaporating nitrogen kept frost from condensing on the diamond. Quenching on the dry diamond surface allowed conductive cooling, whereas impact on the liquid nitrogen would result in much slower convective cooling through a layer of boiling nitrogen. This 0.25 mm thick diamond wafer was prepared by Norton Diamond Film of Saint-Gobain Industrial

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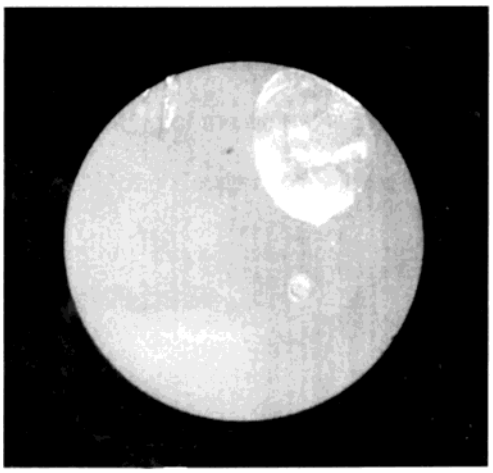
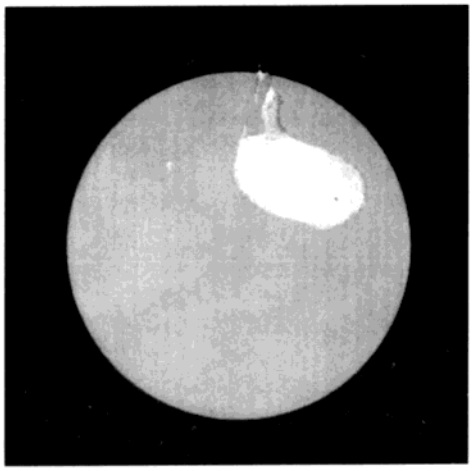


(a)



(b)

Figure 1. Photos of water disks quenched on a 38 mm diameter diamond wafer at 77 K: (a) transparent quenched glassy water with some opaque crystalline ice on its bottom left. A 0.25 mm thick diamond wafer was partly submerged in liquid nitrogen and a 0.057 cm^3 water drop was deposited just above the liquid nitrogen level, forming a rapidly quenched 0.7 mm thick disk. Panel b shows all opaque crystalline ice formed by depositing a 0.057 cm^3 water drop on the diamond wafer at room temperature, then slowly cooling the diamond wafer and water disk with the liquid nitrogen vapor.

Corporation by plasma-assisted chemical vapor deposition on a substrate that was subsequently removed.[8] Copper−constantan (0.08 mm diameter) thermocouples placed 0.25 mm above the diamond surface measured cooling rates in the liquid water of up to 271 K/s in the 0.7 mm water disk at that depth. Shown for comparison in Figure 1b is a slowly cooled 0.057 cm^3 water drop, which was opaque. The QGW disk in Figure 1a was transparent over much of its area, but the regions near the bottom of the disk were opaque, indicating that some crystallization occurred during quenching. Most of the QGW disks appear to be fully transparent; this one was chosen to image the contrast between the transparent glassy portion and the polycrystalline opaque portion. Hallbrucker et al.[5] estimated about 5% as quenched crystallization in HGW flakes.

Results and Discussion

Figure 2 shows the in situ thermocouple cooling and reheating curves for a disk of water that formed QGW as it quenched on the diamond wafer at 77 K. The average cooling rate for curve 1 was 110 K/s during quenching of the liquid water from 300

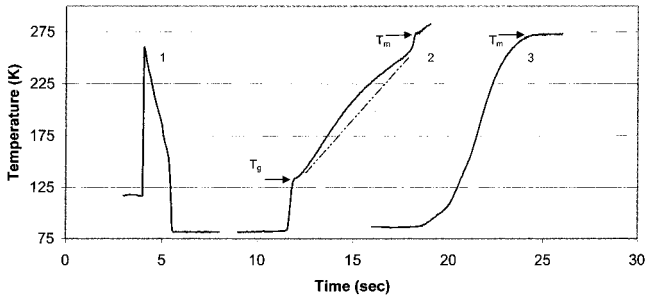


Figure 2. In situ thermocouple cooling and reheating curve for water quenched on a diamond wafer. A thermocouple was placed 0.25 mm above the diamond wafer surface prior to depositing the 0.057 cm^3 water drop on the diamond film at 77 K, which covered the thermocouple bead. The disk on the diamond wafer with the thermocouple still embedded was reheated by placing this assembly on a room-temperature copper block. Curves 1 and 2 show rapid quenching and reheating of the quenched glassy water disk on the diamond wafer. Curve 3 shows rapid reheating of a slowly cooled ice disk.

to 77 K. No detectable crystallization exotherms occurred, which would have been manifested as a decrease in the cooling rate. The average reheating rate, curve 2, from 80 to 135 K was 180 K/s. During reheating, a glass-transition endothermic slope change, labeled T_g, occurred at 135 K, after which the heating rate slowed to 28 K/s. At higher temperatures, 140−248 K, a slow exothermic crystallization of the QGW caused a slight increase in the heating rate, as highlighted by the dotted line below curve 2. A melting endotherm, labeled T_m, occurred at 273 K, the melting point of hexagonal ice. The endothermic glass-transition shift and the broad crystallization exotherm on curve 2 are both absent on curve 3, the reheating curve for a slowly cooled crystalline ice disk, which shows only the thermal arrest associated with the melting endotherm at T_m.

The in situ thermocouple heating curves of Figure 2 were corroborated by differential scanning calorimetry (DSC) performed on a disk of QGW formed on the diamond wafer at 77 K and then removed from the diamond and inserted directly onto the DSC stage, which was precooled to 77 K. For comparison, ice formed by slow cooling a water disk to 77 K on the diamond film was also heated in the DSC. Figure 3 shows the two DSC scans resulting from heating the QGW and the ice disks at 30 K/min. The transformations of the various forms of amorphous ice through metastable intermediate phases and back to the equilibrium hexagonal ice have been summarized by Petrenko and Whitworth.[9] For the rapidly quenched disk, exotherms at 111 and 121 K in Figure 3, labeled as T_1 and T_2, are near the exothermic transition from high-density amorphous (HDA) water to low-density amorphous (LDA) water at 120 K reported by Whalley et al.[10] These two peaks are absent on the ice thermogram. Upon further heating of the QGW, an endothermic slope change characteristic of a glass transition occurred at 138 K, as indicated by T_g, close to the 135 K T_g reported for LDA formed from both vapor-deposited ASW and liquid-quenched HGW.[5] Again this feature is missing on the ice thermogram. A diffuse exotherm, occurring for the QGW over the range of 150−190 K, indicated by T_3, may be the result of crystallization of the QGW to cubic ice. Our results differ from Hallbrucker et al.[5] in that they reported a sharper crystallization DSC exotherm at 150 K for ASW and HGW. The ice exhibits no exothermic behavior in this range. Another broad exotherm, labeled T_4, occurred at 223 K for the QGW but was absent for the ice. Johari et al.[11,12] observed a similar DSC exotherm for HDA; presumably this is the transformation of cubic ice to hexagonal ice. We observed a melting endotherm for both disks at 273 K, as did Johari et al.[12] The endotherm at T_5 and the

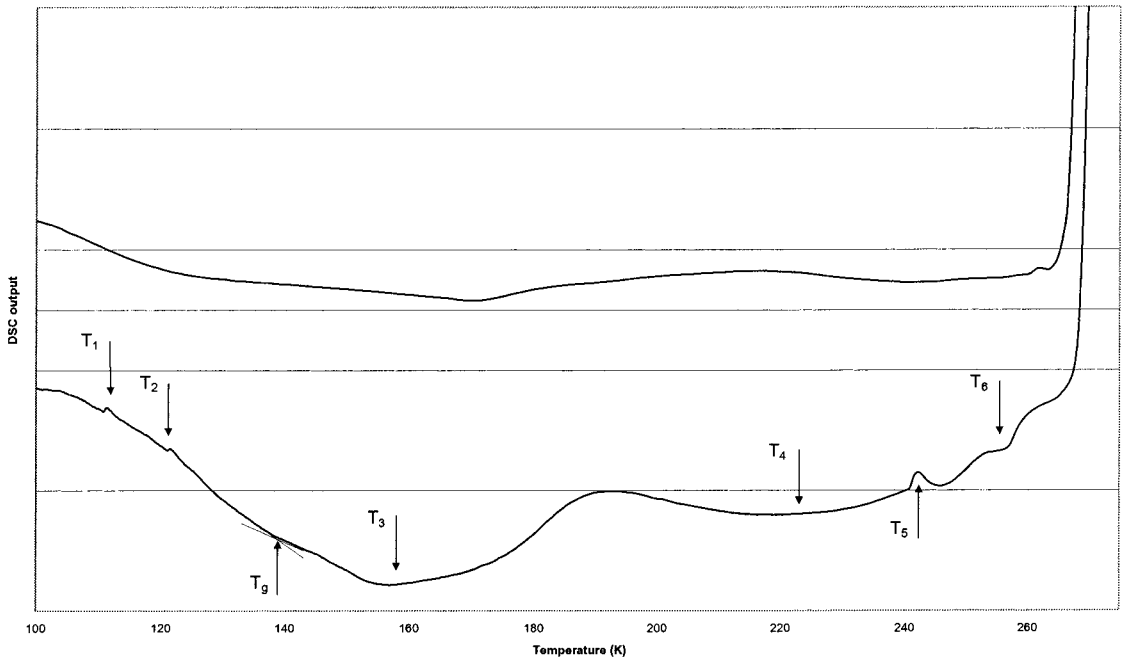


Figure 3. DSC scans of quenched glassy water (bottom) and slowly cooled ice (top) taken during heating at 30 K min^{-1}. Both curves are for pieces removed from a 0.057 cm^3 disk cooled to 77 K on the diamond wafer.

TABLE 1: Density Measurements at 77 K for Amorphous Pure Water in Various Conditions

thermal history	appearance	measured density, g cm^{-3}	comparable water phase from the references	density from the cited reference, g cm^{-3}
quenched on diamond at 77 K	transparent	1.04 ± 0.01	high-density amorphous[6]	1.17
			amorphous solid water[5]	0.94
slowly cooled on diamond	opaque	0.922	hexagonal[6]	0.933
quenched on diamond, held at 143 K		0.935	low-density amorphous[6]	0.94
quenched on diamond, held at 255 K	opaque	0.924	cubic[6]	0.931
quenched on diamond, held at 90 K		floated in liquid oxygen (1.14 g cm^{-3}) at 90 K		

exotherm at T_6 are unexplained, but these features also appear on the DSC scans of HDA and cubic ice reported by Johari et al.[12] The only source of cubic ice other than vapor deposition is transformation from one of the forms of amorphous water; this appears to be the case with QGW also.

We measured the density of various forms of water by weighing as quenched disks in liquid nitrogen and in the nitrogen vapor over the liquid, Table 1. As a calibration, we measured the density of a larger disk of slowly cooled hexagonal ice, of which the density at 77 K was 0.922 g cm^{-3}, close to the accepted value of the density of hexagonal ice at 77 K of 0.933 g cm^{-3}. Other quenched disks were weighed in liquid nitrogen and then immediately submerged in a liquid−solid pentane slush for 1 min at 143 K, a temperature well-above the transition temperature of HDA to LDA of 120 K and below the crystallization temperature of 150 K reported by Mishima et al.[6] The density was then measured again in liquid nitrogen. Densities of other QGW disks were measured after equilibrating in a freezer for 25 min at 255 K, well-above the LDA crystallization temperature. The density of the QGW was 1.04 ± 0.01 g cm^{-3}, an average of five disks. The disks of as-quenched QGW floated in liquid oxygen, the density of which at 90 K is 1.14 g cm^{-3}; the HDA with a density of 1.17 g cm^{-3} would sink in liquid oxygen. After exposure to 143 K in the pentane slush, the QGW density dropped to 0.935 g cm^{-3} , close to that measured for LDA of 0.94 g cm^{-3}. Vapor-deposited amorphous solid water (ASW) has a measured density of 0.94 g cm^{-3}. After exposure to 255 K, the QGW disk density dropped still further to 0.924 g cm^{-3}, close to our measured density for slowly cooled crystalline ice at 77 K of 0.922 g cm^{-3}. The reported density of metastable cubic ice of 0.931 g cm^{-3} is very close to that of hexagonal ice. At 255 K, the cubic ice had probably already transformed to the equilibrium hexagonal ice. The as-quenched QGW density of 1.04 g cm^{-3} is well-below that reported by Whalley et al.[10] for HDA of 1.17 g cm^{-3}, but our quenched glassy water was never exposed to the 10 kbar pressure, which produced HDA. It appears that the density of HGW, the other glassy water produced by quenching liquid water,[3] has never been measured as quenched, possibly due to the small HGW flake size. A 1.5 mm thick film of HGW composed of an aggregate of the submicron flakes was produced after 10 h of deposition of the droplets[3]. However, the aggregate film's density would likely be lower than the true HGW density. Our observed transitions of the QGW to LDA and then to crystalline ice as measured by DSC and density agree with similar transitions reported for vapor-deposited ASW, liquid-quenched HGW, and pressure-formed HDA.[9]

Conclusion

The high thermal conductivity of our CVD diamond wafer was measured to be 14 W/(cm K) by Norton Diamond Film, which compares well to previously reported values of 17 W/(cm K).[13] The use of this new material as a conductive heat-transfer medium allowed cooling rates never before achieved in quenching thick layers of liquid water and revealed that the cooling rate necessary to avoid the crystallization of water is far lower than previously expected. The concomitant thicker section and

larger volume of glassy water open the door for applications of glassy water not possible with the previous glass-forming processes. Rall and Fahy[14] utilized rapid quenching of a liquid to form a glass and successfully cryopreserved mouse embryos perfused with a glycerol solution. The properties of glassy water and biological materials suspended in it could also be important for extraterrestrial studies, where water may be present as a glass in comets[7] and in the planets.[6] Terrestrial microorganisms suspended in the Arctic and Antarctic tundra containing supercooled water have been shown to be viable after millions of years.[15] Perhaps, a glassy-water phase in an extraterrestrial tundra might hold living organisms billions of years old.

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