

## Reversible Formation of Glassy Water in Slowly Cooling Diluted Drops

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This letter presents experimental results obtained with a differential scanning calorimeter (DSC), which indicate that glassy water can be produced reversibly within slowly cooling diluted  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  drops.

Glassy water or low-density amorphous ice (LDA) is a solid whose structure exhibits a disordered liquidlike arrangement.<sup>1</sup> From liquid state, LDA is produced by hyperquenching pure water drops<sup>2</sup> on a plate held at 77 K or by jet-freezing diluted aqueous drops<sup>3</sup> at a cooling rate of  $\sim 10^6$  K/s. There is no consensus whether highly viscous water (HVW), into which LDA “melts” after heating above glass transition at  $T_g \approx 136$  K,<sup>1</sup> is a new phase of water<sup>4,5</sup> or an extension<sup>1,6</sup> of normal water existing above homogeneous freezing temperature,  $T_h \approx 233$  K. This paper shows, to the best of our knowledge for the first time, that LDA is reversibly produced in diluted  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  drops subjected to a cooling rate  $\sim 10^8$ -fold smaller than that used before, a finding which is consistent with the hypothesized extension of normal liquid and glassy states of water.<sup>1,6,7</sup>

On heating, HVW crystallizes to cubic ice  $I_c$  at temperature  $T_c$  between 150 and 160 K.<sup>1,2</sup> The region between the  $T_h$  and  $T_c$ , which separates supercooled normal water from HVW, is a kind of “no man’s land”, as experiments on the liquid phase cannot be performed.<sup>1</sup> Some theories<sup>4,5</sup> preclude existence of normal liquid water below the  $T_h$ ; some<sup>1,6,7</sup> support hypothesized continuity of normal water and LDA; others<sup>8</sup> substantiate that, at  $T_g \approx 136$  K, there is only a “shadow” of the real glass transition which occurs at higher temperatures, and it cannot be probed directly. Lowering  $T_h$  into the “no man’s land” is possible by adding solutes to water.<sup>9</sup> If, after freezing, such solutions separate into pure ice and residual concentrated solution formed by expelling solute molecules from the ice lattice, then the low-temperature behavior of the solutions is similar to that of water.<sup>3</sup> Neither homogeneous freezing ( $T_h$ ) nor crystallization on warming ( $T_c$ ) was suppressed in order to reversibly produce LDA in *slowly* cooling/warming diluted drops.<sup>1</sup> If LDA were reversibly produced, HVW could be considered a thermodynamic continuation of normal water.<sup>5</sup> Experimental results presented below indicate that LDA is reversibly produced within diluted  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  drops.

We prepared diluted  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  drops of diameter  $\sim 0.5$ – $6$   $\mu\text{m}$  by emulsifying 5–31.5 wt %  $\text{H}_2\text{SO}_4$  solutions according to ref 9 and studied their freezing/melting behavior with a differential scanning calorimeter (DSC). The DSC allows detection of melting, freezing, and glass transitions occurring in a sample of the material which is subjected to linear temperature change at a predetermined scanning rate.<sup>9</sup> Emulsions

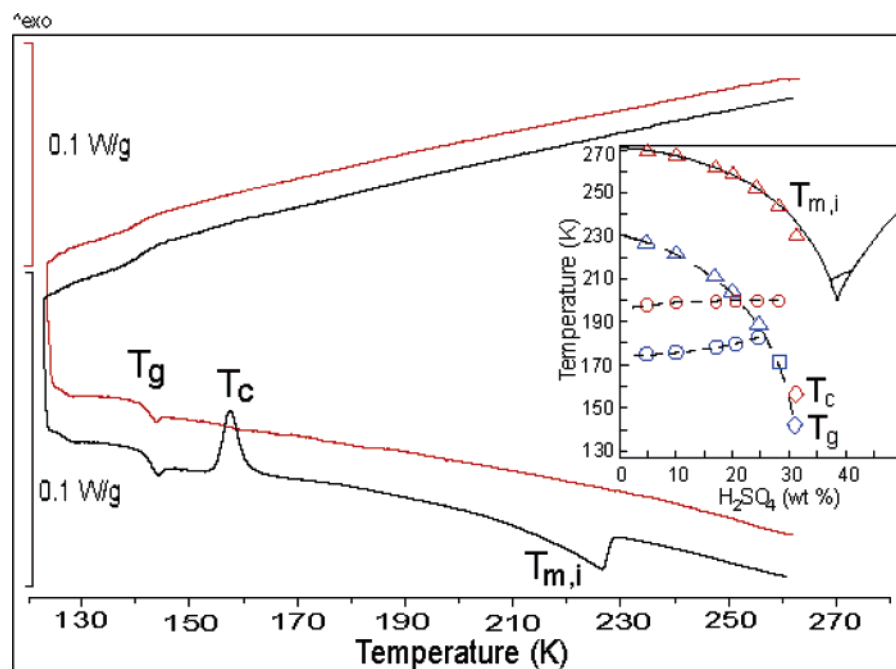
of weight  $\sim 20 \pm 5$  mg were studied at scanning rate of 3 K/min between 123 and 283 K. Repetitive scans were made to verify reproducibility of the results.

In Figure 1, an insert shows that, during the cooling/warming cycle, two freezing and two melting events occur in emulsions of composition  $< 26$  wt %  $\text{H}_2\text{SO}_4$ , indicating that two solids are formed on cooling. Freezing out of ice leaves behind a residual solution that freezes at colder temperatures (blue circles). In emulsion of 28 wt %  $\text{H}_2\text{SO}_4$ , the two freezing events overlap, but the two melting peaks remain separated. We conclude that the warmer solid is ice, because the warmer melting temperatures exactly match equilibrium ice melting points in a  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  phase diagram. The colder melting points at  $\sim 200$  K is eutectic melting of ice + SAT (sulfuric acid tetrahydrate,  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ).

Figure 1 shows that cooling pure emulsion of 31.5 wt %  $\text{H}_2\text{SO}_4$  (black curve) gives only the glass transition at  $T_g \approx 142$  K. On warming, after the glass transition, there is crystallization at  $T_c \approx 156$  K and a prolonged melting process with a peak at  $T_{m,i} \approx 228$  K. Phase separation occurring in the emulsions of  $< 26$  wt %  $\text{H}_2\text{SO}_4$  (see insert), and the fact that the temperatures  $T_g$ ,  $T_c$ , and  $T_{m,i}$  are close to those of the glass transition of water, crystallization of HVW, and melting ice in equilibrium, respectively, indicate that it is the water component, not the solution itself, that undergoes the glass transition. Using the DSC data from Figure 1, the jump of heat capacity calculated for water mass is  $\Delta C_p \approx 37$  J K<sup>-1</sup> mol<sup>-1</sup>, which is similar to  $\Delta C_p \approx 35$  J K<sup>-1</sup> mol<sup>-1</sup> determined for vapor-deposited LDA.<sup>10</sup> Addition of a small amount ( $< 1$  wt %) of aggregated fumed silica ( $\text{SiO}_2$ ) particles (11 nm) to bulk 31.5 wt %  $\text{H}_2\text{SO}_4$  solution and subsequent emulsification eliminates the crystallization at  $T_c$ , making formation of LDA totally reversible (red curves). Note that there is no transition from cubic to hexagonal ice,  $I_c \rightarrow I_h$ , which was observed around 210 K during warming of rapidly quenched aqueous drops.<sup>11</sup>

We explain reversible formation of LDA in the emulsion of 31.5 wt %  $\text{H}_2\text{SO}_4$  as follows. In the drops, the molecular ratio  $\text{H}_2\text{SO}_4/\text{H}_2\text{O} \approx 1:12$ . One-third of the  $\text{H}_2\text{O}$  molecules are strongly bonded to acid molecules to form a SAT molecular complex. The remaining  $2/3$   $\text{H}_2\text{O}$  form size-distributed pure water regions (domains) in which water hydrogen bonding is not strongly perturbed by  $\text{H}_2\text{SO}_4$ . The average diameter of the water domains is  $\sim 1.5$  nm. As the temperature decreases, the ice-like structure of water (all four hydrogen bonds are saturated) increases, and

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**Figure 1.** Cooling (upper) and warming (lower) calorimetric curves obtained from emulsions of 31.5 wt %  $\text{H}_2\text{SO}_4$ . Black curves are from the pure emulsion and red ones from emulsion seeded with  $\text{SiO}_2$  nanoparticles. The glass transition at  $T_g$  is manifested by a jump in the heat capacity,  $\Delta C_p$ . The exothermal peak at  $T_c$  is due to the heat of fusion evolved during crystallization of HVW on warming. The endothermic peak at  $T_{m,i}$  is caused by the heat of fusion consumed when ice melts. On the left side, black and red scaled bars are heat flows for each pair of the curves. In the insert, blue triangles and circles depict freezing temperatures of ice and residual solution, respectively. The blue square is a temperature where the two freezing events overlap. Melting points of the residual solution are shown by the red circles. Ice melting temperatures (red triangles) are superimposed on equilibrium phase diagram of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system (solid line).

at a temperature near  $T_g$ , minuscule ice embryos can form.<sup>12</sup> But even if a critical ice embryo forms in some domain, the drops do not freeze out to ice because of increasing viscosity. It is known that the viscosity of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  strongly increases with decreasing temperature. The increasing viscosity prevents diffusion of  $\text{H}_2\text{O}$  to the critical ice embryo, thus interrupting the incipient crystallization process. As a result, the glass transition occurs at  $T_g$ . On warming, after the glass transition, viscosity decreases, and the interrupted crystallization recommences resulting in freezing drops. In Figure 1, this is manifested by the crystallization peak  $T_c$ . In the seeded drops, fumed silica can suppress the crystallization on warming in two ways. (i) The very large surface area of silica ( $\sim 255 \text{ m}^2 \text{ g}^{-1}$ )<sup>13</sup> may reduce the size of water domains that will make formation of ice embryos less probable. The formation of ice embryos is a statistical process whose probability decreases with volume.<sup>12</sup> (ii) An electric field originated by the OH groups on the  $\text{SiO}_2$  surface<sup>13</sup> may perturb water hydrogen bonding that in turn prevents the formation of ice-like structure of water and hence reduces the probability of formation of ice embryos.

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