Supporting Information

Slow Crystal Growth of Cubic Ice with Stacking Faults in a Glassy Dilute Glycerol Aqueous Solution

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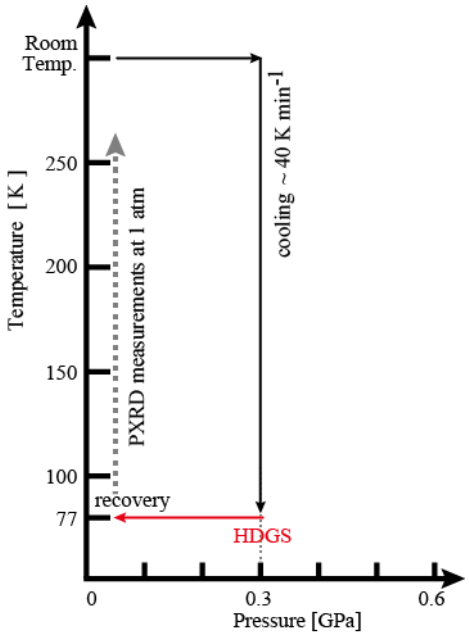

Figure S1: Temperature-pressure protocol for the preparation of high-density glassy glycerol aqueous solution using the pressure liquid cooling vitrification method.

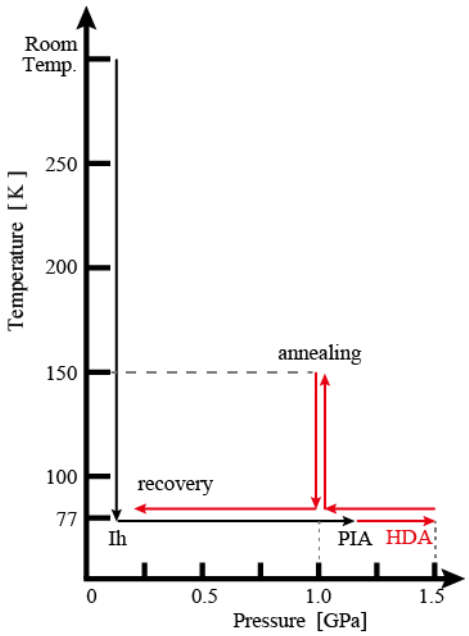

Figure S2: Temperature-pressure protocol for the preparation of high-density amorphous ice (HDA) of pure water. HDA was made by the pressure-induced amorphization (PIA) of ice Ih. In this study, the HDA was annealed at 1.0 GPa at 150 K for 10 minutes because of the relaxation of glassy structure.

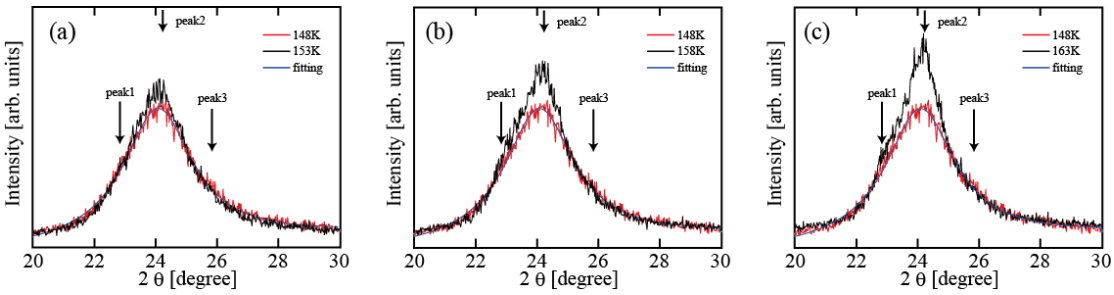

Figure S3: Enlarged PRXD patterns of GLaq solution in the region between 20˚ and 30 ˚. The PXRD pattern of 148 K (red) was compared with the PRXD patterns of (a) 153K, (b) 158K and (c) 163 K. The PXRD pattern of 148 K (red) is fitted by a single Lorenzian function (a blue curve) and it does not have peaks related to ice Isd (peak 1 and sharp peak 2). Peak 1 and peak 2 does not appear in the PXRD pattern of 153 K. These peaks start to appear in the PXRD pattern of 158 K, but peak 3 does not appear. The crystalline ice in the temperature range between 148 and 158 K is ice Ic with no or few stacking faults and the transformation to ice Isd starts to occur around 158 K.

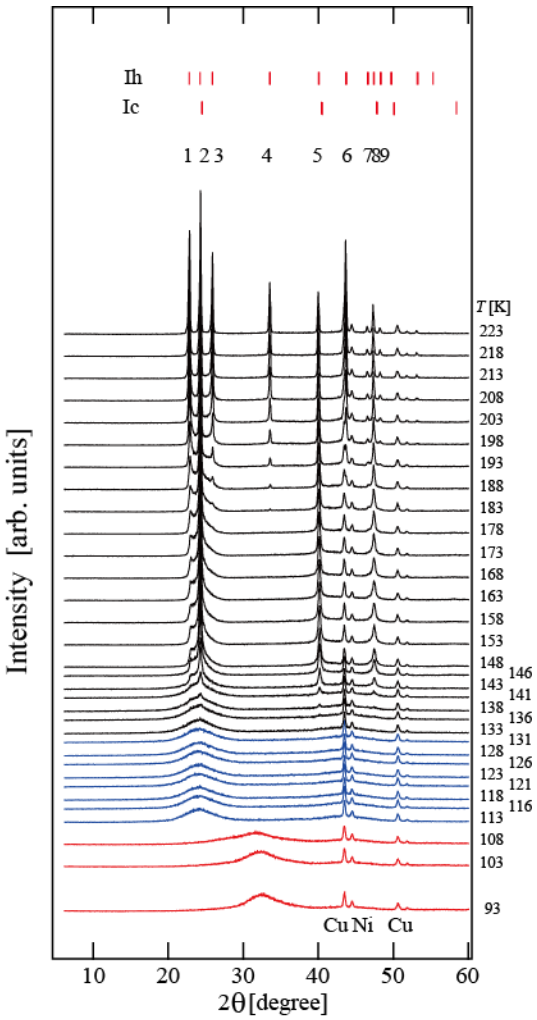

Figure S4: Change in PXRD patterns by the heating of pure HDA at 1 atm. HDA transforms into LDA between 108 and 113 K, and then LDA starts to crystallize at ~131 K. The crystallization of LDA seems to complete until 133 K. The PXRD patterns of HDA, LDA, and crystalline sample are colored red, blue, and black, respectively. The PXRD patterns are shifted vertically for the sake of clarity.

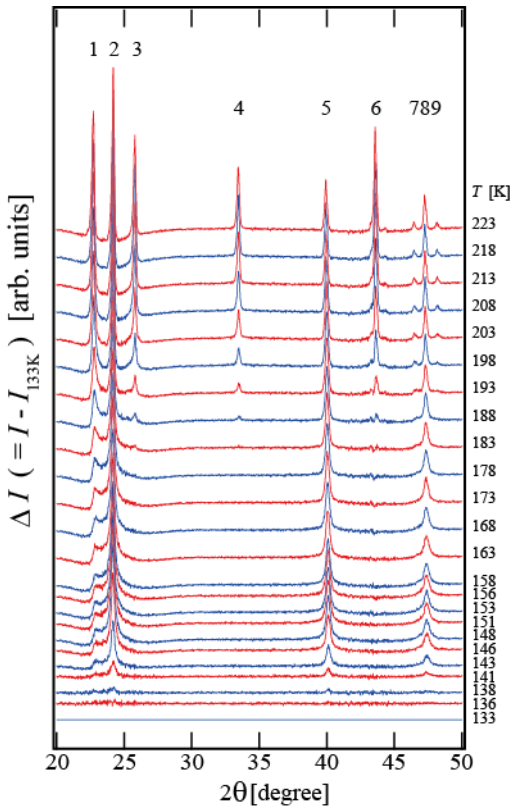

Figure S5: Residual intensity of PXRD patterns of pure water, ΔI (= I - I_{133K}). The PXRD patterns are shifted vertically for the sake of clarity.

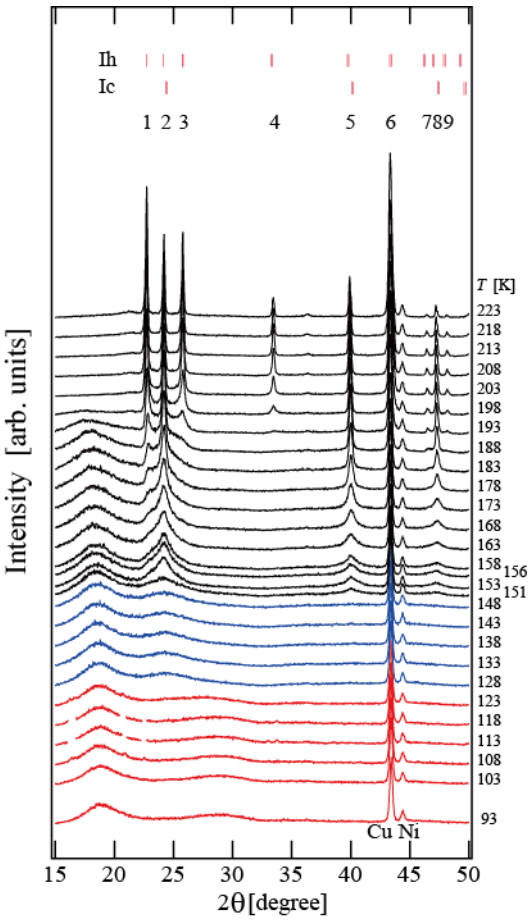

Figure S6: Changes of PXRD patterns by the heating of the emulsified GLaq solution when x = 0.03. The PXRD patterns were recorded between 15˚ and 50˚. A broad peak appearing between 15˚ and 22˚ is contributed from the emulsion matrix. The HDGD transforms into LDGS between 123 and 128 K, and then LDGS starts to crystallize around 151 K. The crystallization seems to complete until 153 K. The PXRD patterns of HDGS, LDGS, and crystalline sample are colored red, blue, and black, respectively. The PXRD patterns are shifted vertically for the sake of clarity.

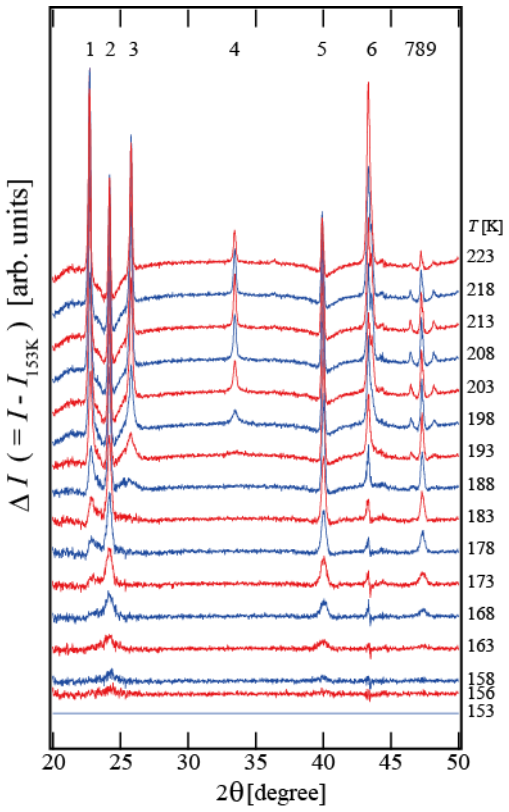

Figure S7: Residual intensity of PXRD patterns of the emulsified GLaq solution (x = 0.03), ΔI (= I - I_{153K}). The PXRD patterns are shifted vertically for the sake of clarity.

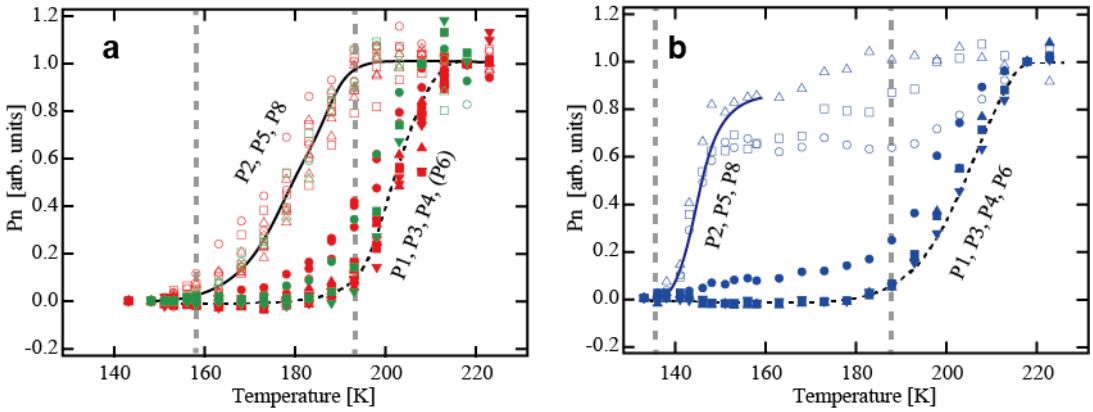

Figure S8: Temperature dependence of P_n. (a) Temperature dependences of P_n for glassy GLaq solutions when x = 0.07 (red) and 0.03 (green). The P_1, P_2, P_3, P_4 P_5, P_6, and P_8 are represented by ●, ○, ■, ▼, △, ▲, and □, respectively. The P_7 for sample when x = 0.07 and the P_6 and P_7 for sample when x = 0.03 are omitted because of the large errors. The vertical gray dashed lines stand for the onset temperatures of crystal growth to ice Isd (158 K) and the Isd-to-Ih transformation (193 K). (b) Temperature dependences of $P_{n=1-8}$ for pure water. The P_1, P_2, P_3, P_4 P_5, P_6, and P_8 are represented by ●, ○, ■, ▼, △, ▲, and □, respectively. The vertical gray dashed lines stand for the onset temperatures of crystal growth to ice Isd (136 K) and the Isd-to-Ih transformation (188 K). Black curves in panels a and c are drawn to guide of the eye.

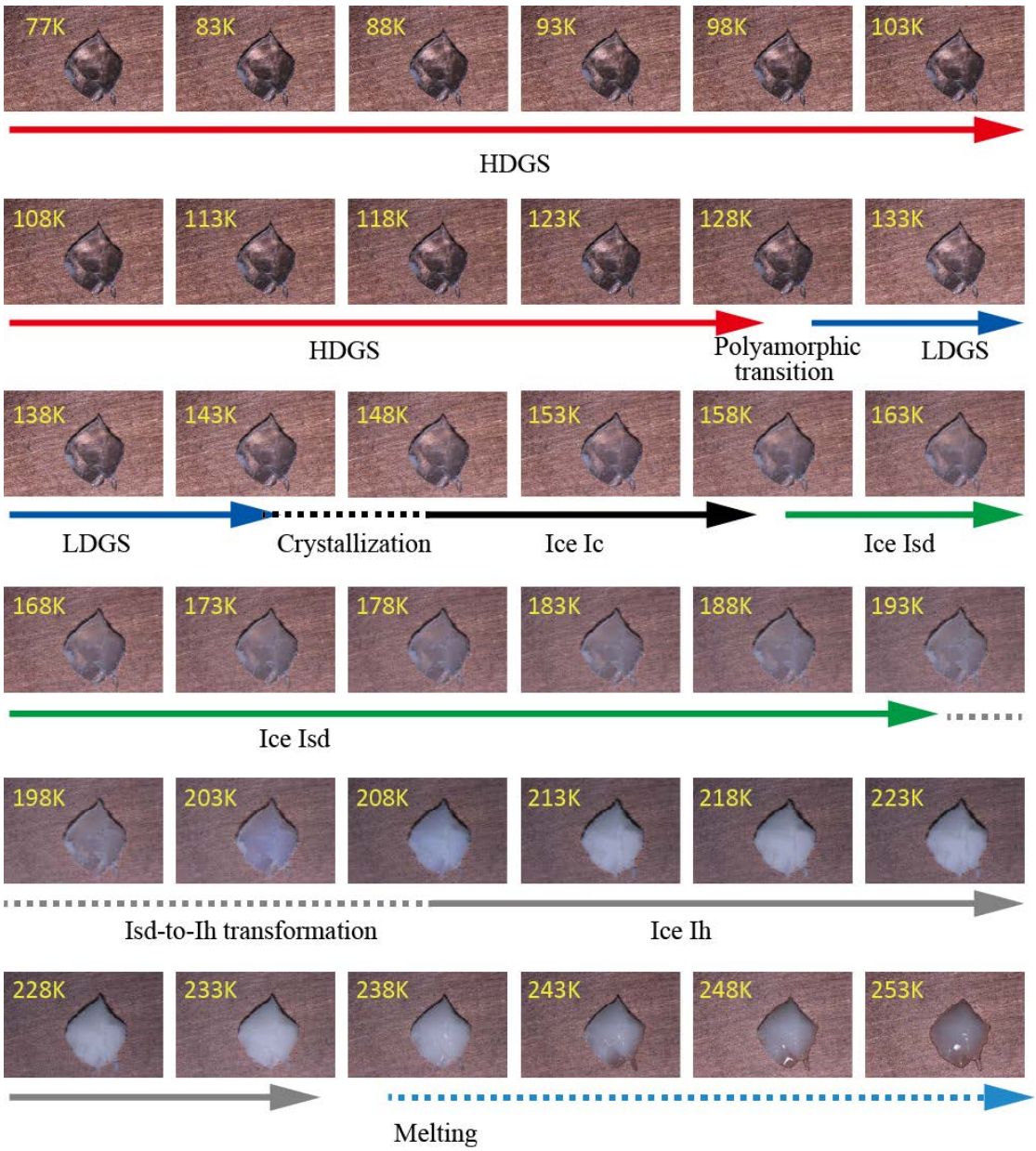

Figure S9: Change in appearance of HDGS (x = 0.07) by heating from 77 to 253 K at ambient pressure. The appearance was observed using a stereoscopic microscope. The heating rate is about 4 K/min. The size of sample is 1-2 mm. The background of sample is a Cu plate.

Text S1: In situ observation of glassy GLaq solution (x = 0.07) during heating at ambient pressure (Explanation of Movie S1). The high-density glassy GLaq solution (HDGS) of x = 0.07 was made using PLCV method and then recovered at 77 K and at ambient pressure. A small block of HDGS was placed on a Cu plate at 77 K and then heated from 77 to 233 K with the heating rate of ~4 K/min. The block size is 1-2 mm. The appearance of sample was observed using a stereoscopic microscope. The observations in Movie S1 and Figure S8 were performed separately under the same condition. The Movie S1 playback speed is 64 times faster.