Preparation of ice Ic without stacking-disorder by emptying hydrogen hydrate

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Ice Ic is a cubic modification of ice with ABCABC… stacking sequence, whereas ordinary ice Ih has a hexagonal structure with ABAB…sequence. "Ice Ic (cubic ice)" was first identified in 1943 by König [1] using electron diffraction, and after that, many experimental pathways to obtaine "ice Ic" have been reported up to date [2]. Recent comprehensive researches [2-5] for ice Ic revieled that all of previously reported "ice Ic" have stacking-disorder more or less, and no one actually found the pure ice Ic without stacking-disoder. However, recent discoveries on ice XVI [6] and XVII [7] give us a hint to obtaine the pure ice Ic. Ice XVI and XVII are formed by degassing neon or hydrogen from their gas hydrates under vacuum at low temperatures. Such small guest molecules can be moved in the gas hydrates without breaking the host framework, and then, the remained frameworks can be regarded as pure ice phases. In fact, a host framework of a high-pressure form of hydrogen hydrate (called C_2) is iso-structural with the ideal ice Ic, and we recently managed to degass hydrogen from C_2, that is to say, the pure ice Ic without stacking-disorder, so that without double-quotation, was obtained. Here we report the procedure to prepare the ice Ic without stacking-disorder and its structure refinement by using powder neutron diffraction.

Deuterated water (D_2O) and magnesium deuteride (MgD_2) as an internal deuterium source were loaded in TiZr encapsulating gaskets, sandwiched by tungsten carbide anvils, and set on a temperature-pressure variable cell (the Mito system). Neutron diffraction experiments were performed at the PLANET beamline, MLF, J-PARC.

The sample was first heated up to 413 K and kept for 1 hour in order to decompose MgD_2 and release D_2 in the sample room (see inset in Fig. 1). The sample was once cooled down to 300 K and compressed up to around 3 GPa, yielding deuterated C_2. The sample was cooled down to 100 K and decompressed at the temperature. The C_2 structure remained at least to 0.5 GPa under decompression at 100 K, but surprisingly, the Bragg peaks of C_2 was mostly disappeared at 0.2 GPa. This phenomenum is totally unexpedted, because the host strucuture of gas hydrates keep its framework in the previous cases in ice XVI and XVII. The sample was further decompressed to 0 GPa, and evacuated using a tarbo molecular pump. The diffraction pattern corresponding to ice Ic appeared at this stage, but the peak was still broad at this stage, showing the small particle size. The broad peaks sharpenes with increasing temperature. A diffraction pattern at 130 K is analysed by the Rietveld methods using the structure model of ice Ic without taking stacking-disoder into account, and the result shows a good agreement as shown in Fig. 1. The peak profile of ice Ic shows still slightly broader considering the instrument peak resolution, which could be due to the small particle size of ice Ic. The characteristic feature of peak profiles in the stacking-disordered ice, which is typically shown around the strongest peak of ice Ic ($d \sim 3.67$ Å), is not found in the obtained profile. The obtained ice Ic shows remarkable stability, which remains up to at least 240 K without notable change of the peak profiles, and ice Ih starts to appear at 250 K. The temperature of 240 K is corresponding to the upper limit of reported metastable region of "ice Ic" [2]. In the case of stacking-disordered ice, however, the cubic stacking sequence starts to change to hexagonal one at much lower temperature, and the phase transition to ice Ih is mostly completed at 240 K. This notable stability of pure ice Ic would be derived from the lack of stacking-disorder, because the stacking-disordered ice may have more number of dislocations to promote the phase transition to ice Ih [8].
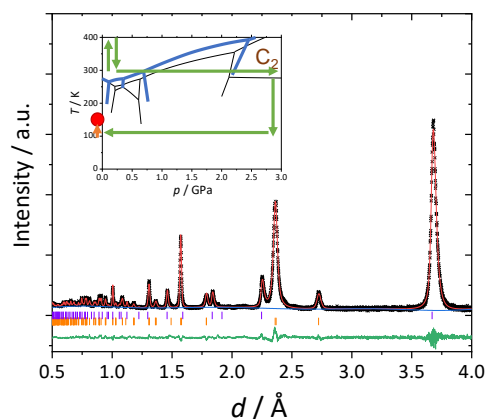

Figure 1. Neutron diffraction pattern of ice Ic at 130 K obtained by degassing deuterium from deuterated C_2, through the *p-T* path shown in inset. Upper and lower tick marks show peak positions for ice Ic and Mg(OD)$_2$, respectively.

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