



Annealing effects on hydrogen ordering in KOD-doped ice observed using neutron diffraction

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ARTICLE INFO

Article history:

Received 16 December 2009

Accepted 4 February 2010

Available online 10 February 2010

Keywords:

Neutron diffraction

Water

Ice

Planet

ABSTRACT

We measured the neutron powder diffraction of 0.013 M KOD-doped D₂O ice to investigate the formation process of ice XI, a hydrogen-ordered phase of ice Ih. The doped ice Ih transformed to ice XI after annealing at 57 and subsequently at 68 K. The mass fraction of ice XI to that of the doped ice (*f*) was estimated using Rietveld analysis for each sample. The *f* value of the doped ice, which had once experienced being ice XI (*f* = 0.23), was larger than that of the doped ice, which had never experienced being ice XI (*f* = 0.14). Results indicate that small hydrogen-ordered domains remained in the ice Ih, which had once transformed to ice XI, and accelerated the phase transition from ice Ih to ice XI. Results further suggest that large amounts of ice on icy bodies in our solar system can transform to ice XI, which might be detectable using infrared telescopes or planetary exploration in the near future.

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1. Introduction

Ice has more than 15 crystalline phases. Ice Ih (“one h”), which is a crystalline phase of ice, exists at pressures less than 200 MPa. The structure of ice Ih is described as having oxygen atoms with a hexagonal arrangement (space group *P6₃/mmc*) and hydrogen atoms. The hydrogen atoms in ice Ih are disordered, having two equivalent crystallographic sites along the O–O bond. Bernal and Fowler [1] and Pauling [2] suggested this model, which was confirmed later by Peterson and Levy [3] from neutron diffraction measurements.

A crystal structure with an ordered arrangement of hydrogen is a thermodynamically stable structure at quite low temperatures. The hydrogen-ordered phase, designated as ice XI (“eleven”), is ferroelectric. Singer et al. [4] and Knight et al. [5] theoretically predicted that a transition from ice Ih to ice XI would occur at low temperatures. In practice, ice XI has been prepared for KOH-doped ices [6,7]. The KOH dopant acts as a catalyst for the phase transition from ice Ih to ice XI. The OH[−] ions, derived from KOH, substitute H₂O sites in the ice [8], and increase the mobility of the hydrogen atoms. The structure of deuterium-substituted ice XI doped with KOD was described in previous neutron studies [9,10].

Fukazawa et al. [11,12] proposed a hypothesis based on neutron diffraction studies of KOD-doped ice: ferroelectric ice XI exists in

cold space environments (e.g., Pluto, Kuiper Belt Objects, and interstellar molecular clouds). Electrostatic force attributable to the ferroelectricity might affect the agglomeration of ice particles in space [13,14]. Ice XI in space might therefore play an important role in planetary formation. Ice grains in space have been identified from infrared (IR) observations of interstellar molecular clouds and of gaseous clouds around low-temperature stars. Recently, infrared absorption spectra of laboratory-prepared ice XI were reported, and the astronomical search for ice XI will be available in future [15].

To elucidate properties of ice XI, nucleation and growth processes must also be studied. To estimate where and how much ice XI exists in space, we must investigate the ice XI formation process in detail. For this study, we prepared deuterium-substituted KOD-doped ice, and investigated how the temperature history affects ice XI formation.

2. Experiment

All neutron diffraction measurements were performed on 99.95% deuterium-substituted ice. First, we prepared KOD-doped powder ice by rapid solidification of misted 0.013 M KOD solutions at 77 K. The mist passed through an atomizer with 400 μm nozzle diameter into a cold stainless-steel vessel with a shallow pool of liquid nitrogen. By quickly freezing the solutions, a substantial amount of KOD is accommodated as an impurity in the ice lattice [16]. Evaporation of all the liquid nitrogen left powder ice on the bottom of the vessel. About 2 g of the powder ices was sealed in a vanadium can (10 mm diameter, 60 mm length) with helium gas.

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The sample was kept at $T_1 = 57$ K and annealed for $t_1 = 20$ h, where T_1 and t_1 , respectively, signify the first annealed temperature and time. The temperature was then raised to $T_2 = 68$ K and annealed for $t_2 = 98$ h to grow ice XI (Sample A), where T_2 and t_2 , respectively, represent the second annealed temperature and time. After annealing the sample, the neutron powder diffraction profile was measured at $T_3 = 68$ K. After the measurement, the sample temperature was raised to 100 K – above the transition temperature of 76 K – to back-transform the sample from ice XI to ice Ih (Sample B). We measured the neutron powder diffraction profile of the Sample B at $T_3 = 100$ K. Subsequently, the sample was cooled again and annealed at $T_1 = 57$ K for $t_1 = 20$ h and at $T_2 = 68$ K for $t_2 = 71$ h (Sample C), respectively, and the neutron powder diffraction profile was measured at $T_3 = 68$ K.

Neutron diffraction measurements were performed using the high-resolution powder diffractometer (HRPD) installed in the JRR-3 research reactor at the Japan Atomic Energy Agency, Ibaraki, Japan. All diffraction patterns were collected in the range of $2\theta = 2.50$ – 162.45° using a wavelength of 1.82035 Å, which was obtained from the 331 reflection of the Ge monochromator. These data were obtained using a step angle of 0.05° .

3. Results

Fig. 1 portrays the neutron diffraction pattern of 0.013 M KOD-doped ice annealed at 57 K for 20 h and 68 K for 98 h (Sample A). After the measurement, the ice temperature was raised to 100 K and the sample transformed from ice XI to ice Ih (Sample B). Fig. 2 shows the neutron diffraction pattern of Sample B. Fig. 3 presents the neutron diffraction patterns of the ice further annealed at 57 K for 20 h and 68 K for 71 h (Sample C). The diffraction profiles of Sample A and C were measured at 68 K, and that of Sample B was measured at 100 K. The dots mark the measured intensities. The solid line shows the calculated diffraction pattern using the best-fit parameters from Rietveld analysis. The peak positions calculated from the structure of ice XI with the hydrogen-ordered arrangement ($Cmc2_1$) are shown by black ticks below the diffraction patterns in Figs. 1 and 3. The peak positions calculated from the structure of ice Ih with the hydrogen-disordered arrangement ($P6_3/mmc$) are shown by gray ticks. The bottom curves are the deviations between the measured and calculated intensities. The positions of all observed peaks for the doped ice are consistent with either the gray or black tick marks.

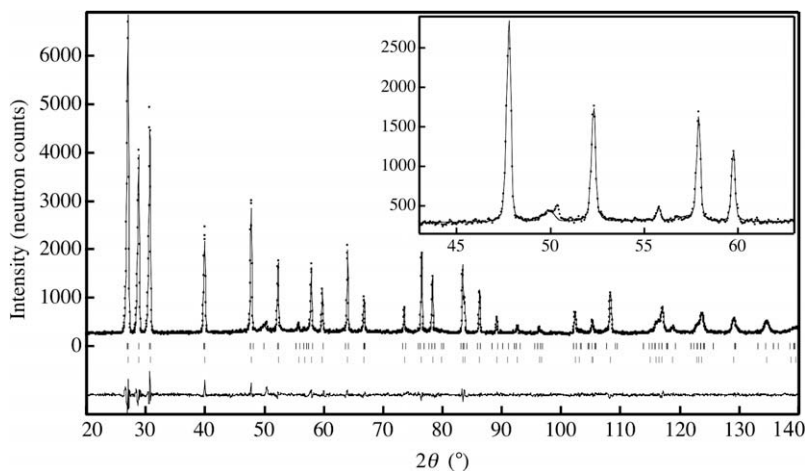


Fig. 1. Neutron powder diffraction profile of 0.013 M KOD-doped ice annealed at 57 K for 20 h and subsequently at 68 K for 98 h (Sample A). The measurement was performed at 68 K. The dots mark the measured intensities; the solid line is the calculated diffraction pattern using the best-fit parameters from Rietveld analysis. The peak positions simulated from the structure of ice XI are shown as black ticks below the diffraction pattern. The peak positions of ice Ih are shown as gray ticks. The bottom curves below the ticks are the deviations between the measured and calculated intensities. The insets show enlarged patterns in the range of $2\theta = 43$ – 63° . The 131 Bragg peak was observed at $2\theta = 49.95^\circ$.

The profiles in Figs. 1 and 3 have a 131 Bragg peak at $2\theta = 49.95^\circ$ that results from the structure of ice XI [9,10,17], although the profile in Fig. 2 exhibits no Bragg peak corresponding to the 131 peak. All profiles have a small peak at $2\theta = 50.3^\circ$. This peak was derived from diffraction of the vanadium sample can. Results show that Samples A and C contain ice XI, and that Sample B consists of pure ice Ih. Furthermore, the peak intensity of the 131 Bragg peak in Fig. 3 was apparently higher than that shown in Fig. 1.

4. Discussion

The neutron diffraction profiles of Samples A and C, the 0.013 M KOD-doped ice annealed at $T_1 = 57$ and $T_2 = 68$ K: both revealed the 131 Bragg peak at $2\theta = 49.95^\circ$. The results show that 0.013 M KOD-doped ice Ih transformed to ice XI after being annealed at 57 and 68 K. The peak intensity of the 131 Bragg peak for Sample C, which transformed to ice XI for the second time, was apparently larger than that for Sample A, which had never been ice XI before being annealed. The results suggest that the phase transition from ice Ih to ice XI occurs in Sample C to a notably larger degree than in Sample A.

The mass fraction of ice XI to that of the doped ice (f) was estimated using Rietveld analysis [18] of the diffraction profiles using a software, RIETAN 2000 [19]. A two-phase model, which includes ice Ih and XI, was applied; f values were obtained for each sample. The structural parameters of Sample C are presented in Table 1. These values are consistent with the conventional structural parameters of oxygen and deuterium atoms in ice XI or Ih. The lattice parameters of ice XI were $a = 4.472(1)$, $b = 7.846(2)$, $c = 7.303(2)$ Å, and those of ice Ih were $a = 4.5108(2)$, $b = 4.5108(2)$, and $c = 7.3131(2)$ Å. Fig. 4 presents the structure of ice XI described by the obtained structural parameters. The gray and black circles respectively represent oxygen and hydrogen atoms. The R_{wp} (R -factor based on the weighted profile) was 6.19%, R_e (an expected value of R_{wp}) was 5.25%, and S ($=R_{wp}/R_e$) was 1.18%. The values of R_{wp} and S , which well reflect the progress of the refinement [19,20], are sufficiently small. Therefore, the profile refinements using the two-phase model were successful, and the obtained parameters are reliable.

The obtained f values are presented in Table 2. The f value of Sample A, which had never been ice XI, was 0.14. In contrast, the f value of Sample C, which was obtained by annealing the ice sample that had once transformed to ice XI, was 0.23. The f value of

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