Ice crystal growth under the presence of krypton and methane at low temperature

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ABSTRACT

To investigate the influence of foreign gas inclusion on the crystallization of ice, we studied the low-temperature ($74 < T < 160$ K) vacuum deposition of water molecules mixed with Kr or CH_4 in a wide range of H_2O/gas mixing ratios ($0.004 < R < 4$) by means of in-situ X-ray diffraction. When H_2O vapor containing either Kr or CH_4 was condensed onto a cold substrate, ice Ih crystals were found to grow below 130 K in a film of amorphous solid water (ASW), whereas pure H_2O gas formed only ASW below 135 K. Small to moderate concentrations ($R > 0.2$) of Kr and CH_4 enhance the formation of ice Ih and increase the crystal size, while at high foreign gas contents ($R \leqslant 0.2$) that may develop Kr or CH_4 crystals below 92 K, the crystal size and relative amount of ice decrease strongly. The maximum ice Ih crystal size in the order of 200 nm was observed with either Kr or CH_4 at 92 K for R = 0.2. We propose that Kr and CH_4 induce the crystallization of ice by acting as a surfactant.

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1. Introduction

Water reveals a variety of phases depending on the temperature and pressure. It has been shown that amorphous solid water is formed by either rapidly cooling water at atmospheric pressure [1–4] or upon low-temperature deposition of water under vacuum. When water is cooled at a high cooling rate under atmospheric pressure, it forms metastable glassy water below 130 K and metastable ultraviscous water at $130 < T < 150$ K [3]. Between 220 and 273 K, which corresponds to the supercooled metastable state, water crystallizes rapidly. Above 273 K, water is liquid.

On the other hand, amorphous solid water was found to be formed upon vacuum deposition on a substrate below 160 K [5]. It is reported that the diffusivity of H_2O molecules in amorphous solid water is six orders of magnitude larger than in crystalline ice at 150 K but far smaller than 10^{-20} cm^2/s below 135 K [6,7]. While the amorphous solid water can be regarded as a "frozen" state below 135 K in the sense that crystallization is suppressed, it crystallizes above 135 K [8,9].

Amorphous solid water is frequently found in outer space, where the temperature is as low as 30 K [10,11]. A characteristic property of amorphous solid water is to trap many kinds of foreign gases [12,13]. On the other hand, crystalline ice is found in comets, icy satellites, interstellar matters, and in the Kuiper belt, which is a birthplace of comets although the temperature there is below the crystallization temperature [14–16].

In previous work, the condition for ice crystallization has been investigated and expressed in terms of the surface diffusion coefficient of H_2O molecules and the time required to cover the surface with adsorbed H_2O molecules [17]. In recent work, it is reported that the crystallization of ice occurs at a temperature of 12 K through H_2O/neon matrix sublimation upon annealing from 6 K, and the crystallization mechanism has been attributed to the increased mobility of H_2O molecules due to the sublimation of neon [18].

In this work, we used in-situ X-ray diffraction to investigate the effect of foreign gases on the ice crystal growth by co-depositing H_2O and Kr or CH_4 at certain low temperatures and thereby demonstrate that in presence of a foreign gas, ice Ih crystallizes at temperatures much lower than the crystallization temperature of pure H_2O.

2. Experimental

We have measured in-situ X-ray diffraction (XRD) patterns during ice growth at beamline BL09 of the synchrotron radiation (SR) facility SPring-8 in Japan. The SR photon energy was 9.4 keV with an energy width of 25 meV. The SR enters the sample preparation chamber through a beryllium window and then is scattered by the

sample deposited onto a beryllium substrate. Kr and CH_4 were used as foreign gases. The scattered X-rays were detected with avalanche photodiode detectors in air. The sample preparation chamber was mounted on a rotation stage, on which the sample can be rotated with an angular resolution of 1 mrad. To estimate the crystal grain size D, we applied the Scherrer formula described by the following equation [19] to the (002) peaks of Ih ice, Kr, and CH_4:

$$D = K\lambda/\beta \cos\theta_B. \tag{1}$$

Here K, λ, β, and θ_B are the Scherrer constant, the SR wavelength, the width of the diffraction peak, and the Bragg angle. For simplicity, we assumed that the value of K is unity. The Bragg diffraction peaks of Ih ice, solid Kr, and solid CH_4 are assigned by using the lattice constants of these solids [20–22].

The samples were prepared by depositing gas mixtures onto a beryllium substrate through a gas doser. Ultra-pure H_2O was vacuum-degassed, and either Kr or CH_4 were mixed in at an arbitrary ratio using a mass flow controller. The mixing ratios (R) of H_2O to Kr or CH_4 were varied in the range from 0.05 to 4 and from 0.0125 to 1, respectively. The mixed gas was introduced into the preparation chamber through a doser and deposited in the surface-normal direction onto a beryllium substrate cooled at low temperature. The base pressure of the chamber was below 0.1 Pa. The preparation chamber was sealed off by closing the valve between the preparation chamber and the vacuum pumping system during sample preparation. The contamination caused by the residual gas was estimated to be less than 1 ppm, which is negligible for sample preparation. The substrate temperature during deposition of the H_2O/Kr and H_2O/CH_4 mixtures was kept constant and was varied between different experiments in the range from 84 to 160 K for the former and from 74 to 92 K for the latter, respectively. By vacuum pumping the liquid nitrogen reservoir connected to the sample holder, the sample was cooled down to 74 K. The mass flow of the mixed gases was in the range from 10^{-3} to 10^{-2} Pa m^3 s^{-1}, and the dosing time was 10^3 s. The deposited amount was equivalent to a film thickness of 5–50 μm.
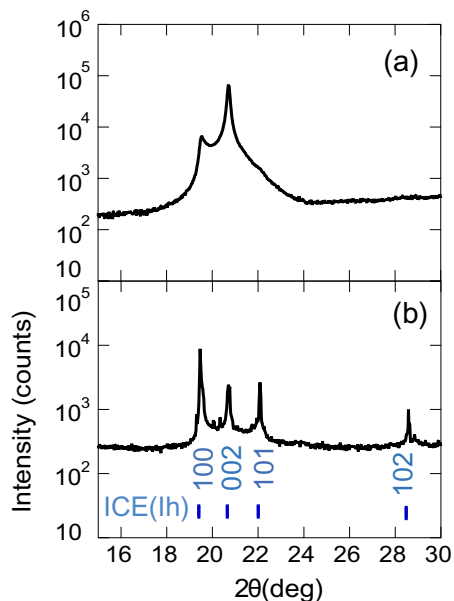
3. Results

Fig. 1 shows the XRD pattern after deposition of pure H_2O and of H_2O mixed with Kr at 160 K. Both data show XRD peaks of crystalline ice. The crystal grain sizes in Fig. 1(a) and (b) are estimated to be 63 and 126 nm, respectively. The crystal grain size estimated from Fig. 1(b) is larger than that derived from Fig. 1(a). The broad component in Fig. 1(a) corresponds to amorphous solid water. The reason for the weaker peak intensity in Fig. 1(b) compared to Fig. 1(a) is X-ray absorption by Kr atoms trapped in the solid water. In addition, the peak at $2\theta = 20.6°$ is stronger than the other peaks in Fig. 1(a).

There is a possibility that the (111) peak of ice Ic, which may be formed at low temperature [23], overlaps with the (002) peak of ice Ih. However, although the crystallizations of ice Ih and Ic are competing processes, ice Ih has a lower Gibbs free energy than Ic in the temperature range from 180 to 240 K [24]. Thus, provided that there is sufficient mobility of H_2O molecules in the presence of Kr at the temperatures in this work, we consider that ice Ih should crystallize prior to ice Ic. We will argue in the discussion section that the surface diffusivity of H_2O molecules is increased due to Kr at the surface and indeed sufficient to allow for ice crystallization under our experimental conditions. Therefore, we assign the XRD peak at $2\theta = 22.0°$ to (101) of ice Ih.

Fig. 2 shows three XRD patterns obtained after depositing H_2O/Kr mixtures with ratios of (a) 0.05, (b) 0.2, and (c) 1 at 83 K. Although pure water molecules form the amorphous solid phase at 83 K, crystalline ice is clearly observed in Fig. 2(b) and (c). In addition, in Fig. 2(a)–(c), the diffraction peak of solid Kr is seen.
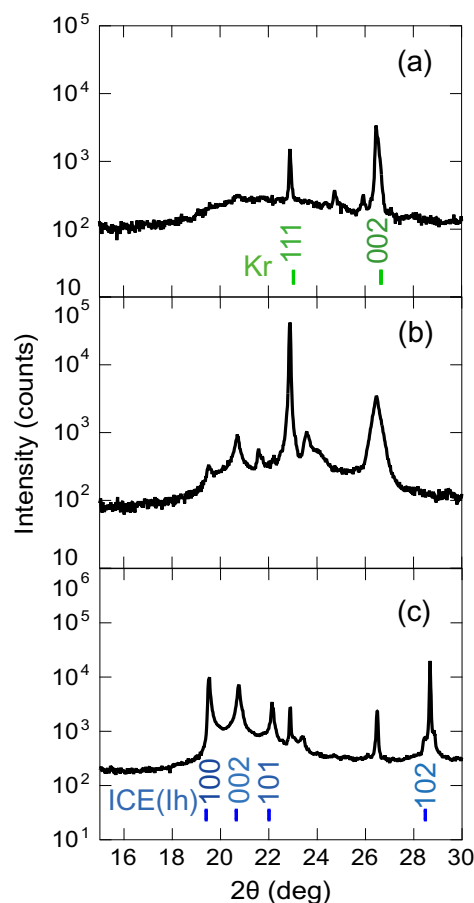

Fig. 1. XRD patterns for the growth at 160 K of (a) pure H_2O and (b) H_2O mixed with Kr for a mixing ratio (H_2O/Kr) of 1.

Fig. 2. XRD patterns for the growth at 83 K for several mixing ratios R of H_2O to Kr. The values of R are (a) 0.05, (b) 0.2 and (c) 1, respectively.