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Research paper

Matrix sublimation method for the formation of high-density amorphous ice

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ABSTRACT

A novel method for the formation of amorphous ice involving matrix sublimation has been developed. A CO-rich CO:H_2O mixed ice was deposited at 8–10 K under ultra-high vacuum condition, which was then allowed to warm. After the sublimation of matrix CO at 35 K, amorphous ice remained. The amorphous ice formed exhibits a highly porous microscale texture; however, it also rather exhibits a density similar to that of high-density amorphous ice formed under high pressure. Furthermore, unlike conventional vapor-deposited amorphous ice, the amorphous ice is stable up to 140 K, where it transforms directly to cubic ice Ic.

1. Introduction

The importance of amorphous ice is widely recognized in the fields of physics, chemistry [1,2], and cryobiology [3], but is of particular interest in planetary science and astrophysics [4]. Various procedures for the preparation of amorphous ice have been developed in order to investigate the relationship between its structure and method of formation [2] (Fig. 1). Vapor deposition methods were often applied to prepare amorphous solid water (ASW) in a vacuum [5,6]. When water (H_2O) vapor is deposited onto a surface below 40 K, high-density ASW can be produced. In contrast, deposition at 40–70 K results in low-density ASW [6,7]. Unique property of ASW that is distinct from other amorphous ices is that ASW has larger surface area and higher porosity [8,9]. Rapid cooling of micron-sized water droplets or thin film can form amorphous ice referred to as hyperquenched glassy water (HGW) [10,11]. HGWs formed at ambient and high pressures are low- and high-density forms, respectively [12].

Disruption of ice crystals by compression or irradiation with high-energy particles is also known as formation method of amorphous ice [13–16]. High-density amorphous ice (HDA), which is distinct from the ASW and HGW formed at low pressures, could be formed by compression of ice crystals at high pressure [13,14]. HDA transforms low-density amorphous ice (LDA) by warming up at ambient pressure. Ice crystal in a vacuum can be amorphized by the irradiation with high-energy electron beam [15] or UV-rays at low temperature [16].

Since the structure of amorphous ice has been found to strongly depend on the method of its formation [2,17–19] and formation conditions [2,6,7,12], as described above, unknown amorphous ice structures may still be discovered through new formation methods. In this Letter, we report a new method for the formation of amorphous ice, matrix sublimation method. Remarkably, ice prepared by sublimation of a carbon monoxide (CO) matrix from a H_2O/CO mixture at around 35 K shows a highly porous texture different from that of ASW, and a density similar to that of HDA prepared under high pressure. This new method contributes to our understanding of the structure and physical properties of amorphous ice and to the development of new materials.

2. Experimental

Amorphous ice was prepared according to a newly developed matrix sublimation method, illustrated in Fig. 2. We observed this process *in situ* using the ultra-high vacuum (UHV) transmission electron microscope (TEM) and Fourier-transform infrared (FTIR) spectrometry.

A specially designed UHV TEM (JEOL JEM-2100V) for *in situ* observation of ice was developed following Kondo et al. [20]. Since the specimen was surrounded by a liquid nitrogen shroud, the pressure around the specimen was lower than the pressure of the specimen chamber (1×10^{-6} Pa). We used a liquid He cooling holder (Gatan ULTST) for specimen cooling, and a 5-nm-thick amorphous Si film (SiMPore Inc.) as a substrate for sample

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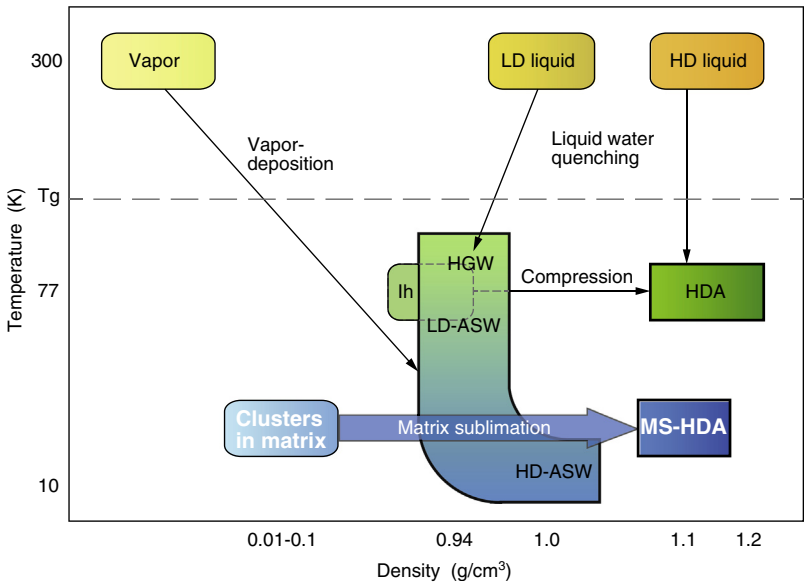

Fig. 1. Temperature-density diagram schematic of the formation of amorphous ices. The starting materials are shown in rounded rectangles, formation routes as arrows with names of methods, and products in rectangles. T_g is the glass transition temperature. HD-ASW, high-density amorphous solid water; LD-ASW, low-density amorphous solid water; HGW, hyperquenched glassy water; HDA, high-density amorphous ice; HD, high density; LD, low density; MS-HDA, matrix-sublimated high-density amorphous ice; Ih, hexagonal ice.

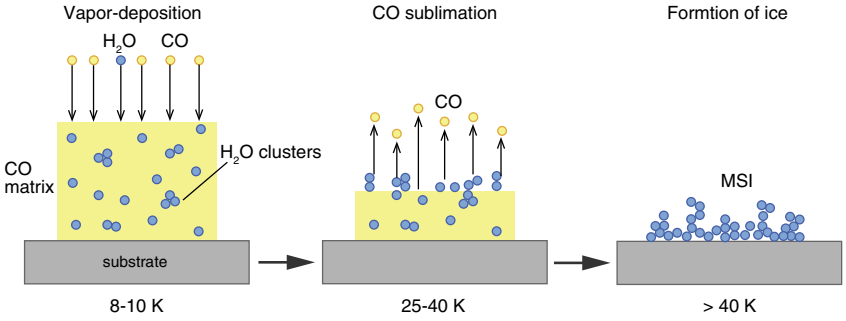

Fig. 2. Matrix sublimation method. Deposition of CO:H_2O on an 8–10 K substrate in an ultra-high vacuum chamber. After deposition, the substrate is warmed at a constant rate. Sublimation of matrix CO at 25–40 K. Formation of MSI at $T > 40$ K.

deposition. Of the three ports directed at the specimen surface, the one with an incident angle of 55° was used for a Ti gas inlet tube (inner diameter = 0.4 mm).

CO was used as the matrix because it is an astrophysically important molecule, active for IR spectroscopy, and could be evacuated by ion pumps equipped with a TEM. Mixtures of CO and H_2O at ratios of 50:1 and 10:1 were deposited on the Si thin film at about 8 K. We did not record TEM images during deposition to avoid damage from the electron beam. After deposition, the sample substrate was warmed at a rate of approximately 2.0 K/min, controlled manually. TEM images could not be recorded during the sublimation of CO because the pressure was higher than 10^{-4} Pa. The thickness of the ice samples remaining after CO sublimation was several tens of nanometres. To avoid electron-beam damage to the sample, a low-dose imaging technique was applied in which the accelerating voltage was 80 kV, the electron beam current was less than 0.1 pA/cm^2 and low magnification images were recorded using a CCD camera (Gatan ES500W). Furthermore, subsequent observations were taken from different positions of the sample. The edge of a single crystalline Si grid was used for the calibration of length in the analysis of the electron diffraction patterns.

For FTIR spectroscopy, we used a laboratory setup for surface reactions in interstellar environments (LASSIE) apparatus, as described previously [21]. The samples were prepared using a background deposition method on an Al substrate cooled to 10 K by He refrigeration. After deposition, the sample substrate was warmed at a rate of 2.0 K/min. IR spectra of samples were obtained and monitored by reflection–absorption spectroscopy. Typical column density of the samples after CO sublimation was 1.5×10^{16} molecules/cm^2.

3. Results and discussion

As shown in Fig. 3a, the CO:H_2O ice deposited at 8 K is a mixture of crystalline α-CO and a small amount of amorphous CO. Water molecules are embedded in the CO matrix as clusters (see Supplementary Fig. 1 and Supplementary Table 1. [22–24]). After the sublimation of CO at 25–40 K, we observed highly porous ice, as shown in Figs. 3b and 4; we term this the matrix-sublimated ice (MSI). The MSI shows wide textural variety at the micro- and submicroscale, with the ice exhibiting mainly concrete-like (Fig. 4a) or granite-like (Fig. 4c) textures, along with some minor occurrences of feather-like (Fig. 4b) or seaweed-like (Fig. 4d) textures. Conversely, these types of structures (micro- and submicroscale highly porous structures) are not observed in pure H_2O vapor-deposited