

Phase transition of KOH-doped amorphous ice

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In interstellar molecular clouds, dust grains from a silicate mineral surrounded by amorphous ice exist [1]. The elements such as H, O, C, and N are adsorbed on the dust grains and form various molecules such as H₂O, CO₂, NH₃, CH₄, H₂CO, and CH₃OH. The molecules undergo chemical evolutions to organic molecules through various reaction processes. A photochemical reaction caused by ultraviolet (UV) irradiation is one of the dominant reaction processes [2]. Since amorphous ice is a reaction field in interstellar molecular clouds, it is important to understand the mechanism of structural change of amorphous ice due to the UV irradiation. Recently, Tachibana et al. [3] found that the viscosity of the UV-irradiated amorphous ice decreases at around 50 K.

The OH⁻ defects formed by UV irradiation are expected as a cause of the decrease in viscosity. To investigate the effect of OH⁻ on the structural changes during heating, the infrared (IR) spectra of KOH-doped amorphous ice were analyzed. KOH, has an effect to introduce the OH⁻ defect on ice and to promote the rotational motion of water molecules in ice [4].

Amorphous ice was prepared with vapor deposition of a solution of KOH on a substrate of oxygen-free copper at a temperature of 43.5 K. The concentrations of KOH were 0.0049–0.1 M. The total pressure in the vacuum chamber was kept at about 5.0×10^{-5} Pa during the deposition. After the deposition of amorphous ice, the substrate was heated to 176 K at a rate of 1–4 K/min. The IR spectra were measured using Shimadzu IRPrestage-21 at every 15 seconds during the deposition, and measured at 2 K intervals during the heating.

The structural transitions during the heating in the temperature range of 43.5–176 K are classified into the following four processes (i) transition from high density amorphous (HDA) ice to an intermediate structure at around 60 K, (ii) transition from the intermediate structure to low density amorphous (LDA) ice at around 100–120 K via the glass transition, (iii) crystallization to cubic ice (Ic) at around 145 K, and (iv) phase transition from Ic to hexagonal ice (Ih) at around 175 K. These transition temperature can be analyzed from the variation in a changing rate of wave number of the O–H stretching mode in IR spectrum with heating. The result shows that the transition temperatures of the transition (ii) depends on KOH concentration. The doped KOH has effect to promote the rotational motion of H₂O, because the decomposed OH⁻ from KOH is introduced in the hydrogen-bonding network and acts as a defect. This indicates that the rotational motion is a dominant mechanism for the transition (ii). Furthermore, it was found that the transition temperature of the transition (iii) depends on the wave number of the O–H stretching mode at the deposited temperature (i.e., 43.5 K), whereas no dependence was observed for the transition (i). This suggests that the surface structure is a dominant factor for the crystallization, and a rearrangement of water molecules due to the translational motion of oxygen is a cause for the formation of the intermediate structure.

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