



# Formation of clathrate hydrates under crystallization of gas-saturated amorphous ice



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## ABSTRACT

Layers of methane-saturated amorphous ice were obtained by deposition of molecular beams of water and gas on a substrate cooled with liquid nitrogen. Their heating is accompanied by glass transition (softening) and subsequent spontaneous crystallization. The avalanche-type initiation of crystallization centers captures the gas molecules and does not lead to their displacement by the motion of the crystallization front. Under crystallization of amorphous water–gas condensates in conditions of deep metastability the formation of gas hydrates takes place. Glass-transition and crystallization temperatures of the condensates were determined by changes in their dielectric properties under heating. The method of differential thermal analysis has been used to investigate the kinetics of crystallization of amorphous water layers. Properties that characterize the water crystallization kinetics have been determined on the basis of the obtained data on the dependence of the crystallization temperature on the heating rate.

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## 1. Introduction

The interest in gas hydrates is caused by the existence of enormous reserves of hydrocarbon raw materials (mainly methane) on the Earth in the gas-hydrate form and the prospects of its use as a fuel source, the possibility of gas storage and transportation in a gas-hydrate state, the effect of natural gas hydrates on the climate of our planet [1,2]. An important place in the solution of applied problems connected with gas hydrates is occupied by the efforts aimed at the prevention and elimination of anthropogenic hydrate formation in gas-producing and gas-pumping equipment [2]. For the disposal of greenhouse gases it is suggested that they should be transferred into the gas-hydrate state and buried at the bottom of the world ocean [3–5]. It is clear that without a profound knowledge of the properties of gas hydrates and the stability boundaries, the kinetics of their formation and decomposition it is impossible to solve the whole complex of problems connected with both the use of the energy resource of natural gas hydrates and the possibility of their use as peculiar containers for gas storage and transportation and the effect of gas hydrates on the climate of the Earth.

A lot of experimental and theoretical works are devoted to the investigation of properties of gas hydrates and the conditions of their formation and decomposition [6–11]. Among them an important place is occupied by investigations of the kinetics of nucleation and growth of hydrates [6,7]. Topical are developments of

new methods of obtaining gas hydrates and intensifying the hydration process. The present-day methods are connected with the use of high pressures and low temperatures in conditions close to equilibrium. For instance, the pressure that corresponds to the conditions of formation of methane hydrate at temperatures close to 0 °C is equal to tens of bars. In this case the formation of hydrates requires a long and intense stirring of the water–gas mixture. Such conditions are used in most of the well-known and patented methods of obtaining gas hydrates. To intensify the hydrate-formation process, various means were suggested, among which there are the fine-grained sputtering of water–gas mixtures in the gas atmosphere [12,13], the action of shock waves on a gas-saturated water medium [14], vibrational [15] and ultrasonic [16] action.

The aim of the present paper is to investigate the formation of gas hydrates at a considerable deviation from equilibrium conditions in low-temperature layers of gas-saturated amorphous ice. Amorphous solid (vitreous) layers of low-molecular substances may be obtained by deposition of molecular beams on a cooled surface. At low temperatures the stability of such condensates, which are highly supercooled frozen liquids, is ensured by the high viscosity and the small value of the rate of nucleation of the crystal phase. The condensation of molecular beams on a copper substrate cooled with liquid nitrogen can be used to obtain amorphous water layers [17,18] and aqueous solutions of organic liquids [19,20]. The heating of the condensates obtained is accompanied by their glass transition (softening) and subsequent spontaneous crystallization. The crystallization of water–gas amorphous condensates results in the formation of gas hydrates [21–27]. A clathrate structure in crystallized samples of gas-saturated supercooled water was

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observed with the use of classical Fourier-transform infrared spectroscopy both for samples obtained by low-temperature deposition of molecular beams of a water–gas mixture [25] and for samples of nanodisperse aerosols [26,27]. In conditions of deep metastability the avalanche-type initiation of crystallization centers captures gas molecules, therefore they are not displaced by the motion of the crystallization front. The formation of a hydrate is favored by the weak chemical affinity of a hydrate-forming substance and also the dimensions and shapes of its molecules corresponding to the geometry of cavities of the forming clathrate framework. Among such substances are the components of natural gas. Experiments on low-temperature condensates of water–methane and water–propane mixtures have shown the possibility of obtaining massive samples of crystalline hydrates with a high content of gas [23,24].

The task of the investigation is an experimental study of stability and phase state of amorphous water–methane condensates in the temperature interval 70–200 K, determination of glass transition and crystallization temperatures of the condensates at a fixed heating rate and study of the influence of gas composition in condensates on the transition temperatures. To solve the task use is made of a quick-response method based on the exploration of dielectric properties of a sample on its heating, and differential thermal analysis, which make it possible to obtain data on the phase state of the condensates and transitions in them on heating. The mechanism of crystallization of the low temperature amorphous condensates is investigated on samples of pure water.

## 2. Experiment

Amorphous condensates of water and a water–methane mixture were obtained in a vacuum cryostat by the deposition of molecular beams on a copper substrate cooled with liquid nitrogen. The evacuation of nitrogen vapors from the cryostat made it possible to lower the substrate temperature to 65 K. A vacuum no worse than  $10^{-5}$  mm Hg was maintained in the cryostat chamber. The deposition rate was  $\sim 200$   $\mu\text{m}/\text{h}$ . The molecular beams of the components entered the sputtering zone through separate vapor lines. The conditions of deposition of two-component condensates at fixed water and gas flow rates allowed obtaining samples of constant composition and ensured the removal of the condensation heat. The thickness of water–gas condensates was 500–600  $\mu\text{m}$ . In experiments use was made of double-distilled water. The purity of methane was 99.99 volume percent. The sample temperature was measured by a copper–constantan thermocouple, which made it possible to observe the temperature regime of condensation. The error of temperature measurements did not exceed  $\pm 0.5$  K.

For observing the sample use was made of a capacitive sensor, which was fixed on the substrate and made it possible to determine glass-transition and crystallization temperatures from changes in the dielectric properties of the sample under heating. The method of investigation of low-temperature amorphous condensates based on the measurement of dielectric properties under heating was used successfully in studying the glass transition of water and aqueous solutions of organic liquids. A detailed description of the measuring technique and the sensor design is given in Ref. [20]. The sensor was a film capacitor made by the method of thermal sputtering. The capacitor plates were thin strips (100  $\mu\text{m}$  thick, 50  $\mu\text{m}$  high) coated on a dielectric plate with a surface of  $20 \times 20$  mm and a thickness of 0.2 mm. In experiments we observed changes in the sensor capacitance and the dielectric loss tangent  $\text{tg}\delta$  of a sample deposited on the capacitor surface. Measurement was carried out in conditions of continuous heating at a constant rate and an electric-field frequency of 10 kHz. The temperature at the sensor surface during the deposition of the sample did not exceed 70 K, with its value on the copper substrate equal to

65 K. The transformations in the sample were judged from changes in the dielectric properties under changes in the temperature. The gas release during the heating of a condensate was registered by an ionization pressure detector. The thermal effects connected with the transformations were registered by a differential thermocouple. The accuracy of determination of glass-transition  $T_g$  and crystallization  $T_c$  temperatures was  $\pm 1$  K.

The composition of a two-component condensate was determined after its removal from the vacuum chamber. For this purpose the sample was located in a U-shaped measuring glass with pentane, one of the bends of which was sealed off and filled with liquid. When the sample was heated and melted, the gas released gathered in the sealed bend of the measuring glass. The gas volume was determined by the rise in the pentane level in the open, higher bend. After determining the volumes of gas and water in the sample, its composition was evaluated. The error of determination of the methane concentration in a water–gas condensate did not exceed 3%.

The method of differential thermal analysis was used for an experimental investigation of the crystallization kinetics of amorphous water condensates. The method sensibility was 0.05 K. The samples under investigation prepared at the temperature of liquid nitrogen had a thickness of 100–200  $\mu\text{m}$  and a diameter of 5 mm. The deposition rate was 100–500  $\mu\text{m}/\text{h}$ . Experiments were carried out in conditions of continuous heating at a constant rate  $\dot{T}$  in the range from 0.03 to 1 K/s. When the sample crystallized, one could observe an abrupt heat release, which was registered by the differential thermocouple. The reproducibility of the crystallization signal in temperature was  $\pm 0.5$  K.

## 3. Results

Fig. 1 shows changes in the dielectric properties of a water condensate under its heating. The behavior of the dielectric loss tangent  $\text{tg}\delta$  of the sample is shown in Fig. 1a. Fig. 1b presents temperature dependence of the difference of the sensor capacitances with a deposited sample and without it. The heating rate is 0.05 K/s. At temperatures above 135 K one can observe a noticeable increase in capacitance of the sensor and  $\text{tg}\delta$  connected with the structural relaxation in the glass transition region. The sharp decrease in the capacitance of the sensor and  $\text{tg}\delta$  at a temperature of 162 K is caused by the crystallization of the sample. The increase in the dielectric properties following the crystallization is characteristic of crystal ice. The sample heating above 200 K resulted in its evaporation in the vacuum chamber. The condensate crystallization

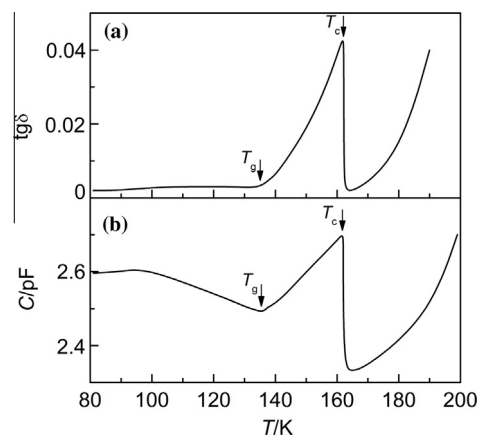


Fig. 1. Temperature dependence of dielectric properties of water condensates: (a) behavior of the sample dielectric loss tangent; (b) difference of capacitances of the sensor with a deposited sample and without it.

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