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A comparative study of the porosity and crystallization kinetics of compact and porous water ice.

Belén Maté*, Yamilet Rodríguez-Lazcano, and Victor J. Herrero
Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121-123, 28006, Madrid, Spain. E-mail: belen.mate@csic.es

Abstract

An investigation of porosity and isothermal crystallization kinetics of amorphous ice produced either by background water vapour deposition (ASW) or by hyperquenching of liquid droplets (HGW) is presented. ASW samples are found to be ~ 7 times more porous than their HGW counterparts, but little difference is found in the 150 K crystallization of the two types of samples due probably to pore collapse in ASW with growing temperature. Both the HGW and ASW data support the possible existence of a previously suggested different amorphous ice phase for ices generated at very low temperature (14 K).

1. Introduction

From an astrophysical point of view the study of amorphous solid water has great interest since it is generally assumed that most of the water in the universe is locked in the form of amorphous ice on dust grains in dense interstellar clouds, and on cold bodies in planetary systems. Astronomical ices, usually observed through their mid-IR spectra [1], are always dominated by water and can adopt compact or porous morphologies. In this work we present a comparative IR study of these two ice types.

2. Experimental part

The experiments were conducted in a high vacuum chamber, a detailed description of our experimental setup was given in refs [2, 3]. The amorphous ice samples were grown on a cold Si substrate using two different techniques: (a) by background vapor deposition (amorphous solid water, ASW), and (b) by injecting a directed flow of liquid water droplets perpendicular to the substrate (hyperquenched glassy water, HGW). Infrared transmission spectra (IR) were taken with FTIR spectrometer.

2. Results and discussion

Figure 1 shows infrared absorption spectra in the region of the OH stretching band of the two forms of amorphous ice. At 14 K two kind of dangling-bond (DB) bands are present, evidenced by a doublet at 3720 cm^{-1} and 3696 cm^{-1}, that correspond respectively to doubly- and triply- coordinated surface water molecules. These bands are related to the surface area and thus to the porosity of the sample [4]. The DB band area in the spectrum of the ASW film grown at 14 K represents 0.04% of the OH-stretching band total intensity. When the ASW is deposited at 40 K the DB/ OH-stretching band intensity ratio decreases by a factor ~1.5, representing only 0.026% of the OH stretching total intensity. This behaviour indicates that the ice grown at 40 K is less porous. For HGW generated at 14 K or 40 K the DB band (grey trace) is about seven times smaller than its ASW counterpart, which illustrates the appreciably lower surface (i.e higher compactness) of the HGW sample.

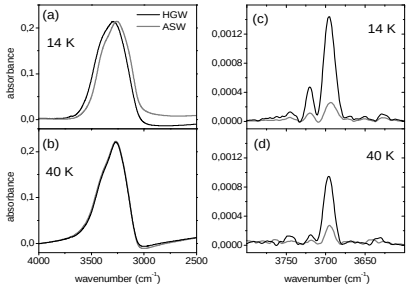

Figure 1: IR spectra of the OH stretching region of ASW (black) and HGW (grey) ices. Panels (c) and (d): an enlargement of the DB spectral region.

Adsorption isotherms of CH_4 on amorphous ASW and HGW ices are presented in Figure 2. Samples of the two types of ice with a similar number of water

molecules were prepared by comparing the OH-stretching band intensity in their infrared spectra. The specific surface areas extracted from the fits of the data of Figure 2 to the BET model are 280 ± 30 m^2/g for ASW and 40 ± 12 m^2/g for HGW, concluding that HGW ices are more compact than ASW ices.

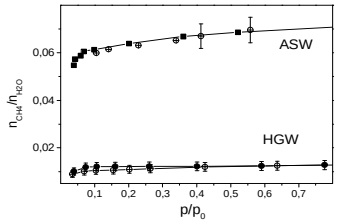

Figure 2: CH_4 uptake molecular ratio versus methane pressure, normalized by the saturation pressure, for ice films grown at 40 K by ASW or HGW.

The transformation at 150 K from an amorphous to a crystalline cubic phase was monitored as a function of time by following the evolution of the OD stretching band [5] in H_2O ice doped with 4% HOD. The time evolution of the fraction of ice crystallized at 150 K is represented versus the logarithm of time in Figure 3, for both ASW and HGW ices grown at 14, 40 and 90 K. Although in all cases the ice evolution finished after 50 min, ices grown at 14 K display a different behaviour, with a slower growth of the fraction of crystallized ice since the first minutes which supports the existence of a previously reported high density amorphous ice structure [6]

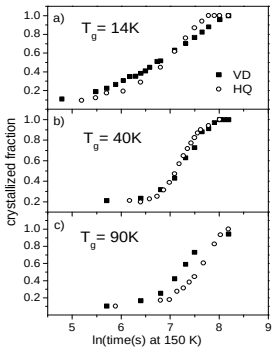

Figure 3: Fraction of water ice crystallized at 150 K versus the logarithm of time at 150 K.

3. Summary and Conclusions

Both ASW and HGW are good candidates for laboratory analogues of astronomical ices under different circumstances. ASW deposits are much more porous, with surface areas seven times larger than their HGW counterparts. The compaction caused by the heating of the ASW sample before crystallization erases a possible influence of its larger initial porosity. Even if the morphologies of HGW and annealed ASW are not identical, the possible differences are not manifest in the crystallization kinetics. Both the HGW and ASW results point to the possible existence of a different amorphous ice phase when the samples are generated at 14 K.

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