Porous Ice Phases with VI and Distorted VII Structures Constrained in Nanoporous Silica

Jinlong Zhu,*†‡ Zewei Quan,*§ Yu-Shen Lin,‖⊥ Ying-Bing Jiang,♯ Zhongwu Wang,♭ Jianzhong Zhang,‡ Changqing Jin,♭ Yusheng Zhao,¶ Zhenxian Liu,● C. Jeffrey Brinker,∥ and Hongwu Xu*§

†National Lab for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China
‡LANSCE and §EES Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States
∥Center for Micro-Engineered Materials, †Department of Internal Medicine, Division of Molecular Medicine, and ♯TEM Laboratory, The University of New Mexico, Albuquerque, New Mexico 87131, United States
♭Cornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, New York 14853, United States
¶HiPSEC, Department of Physics and Astronomy, The University of Nevada, Las Vegas, Nevada 89154, United States
●Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, United States

Supporting Information

ABSTRACT: High-pressure compression of water contained in nanoporous silica allowed fabrication of novel porous ice phases as a function of pressure. The starting liquid nanoporous H2O transformed to ice VI and VII at 1.7 and 2.5 GPa, respectively, which are 0.6 and 0.4 GPa higher than commonly accepted pressures for bulk H2O. The continuous increase of pressure drives the formation of a tetragonally distorted VII structure with the space group Pn3m, rather than a cubic Pn3m phase in bulk ice. The enhanced incompressibility of the tetragonal ice is related to the unique nanoporous configuration, and the distortion ratio c/a gradually increases with increasing pressure. The structural changes and enhanced thermodynamic stability may be interpreted by the two-dimensional distribution of silanol groups on the porous silica surfaces and the associated anisotropic interactions with H2O at the interfaces.

KEYWORDS: Nanoporous ice, high pressure, DAC, SAXS, WAXS

Water is the most abundant species on the surface of the Earth and is of vital importance to the terrestrial life. The interaction of water with biological matter can result in the formation of nanoscale water in biological systems. For example, a large fraction of cellular waters are commonly referred to as nanoscale waters, including semiclathrate water, layered water, and hydrogen-bonded chains, with lifetimes over tens of picoseconds in a series of biological processes such as protein folding, pressure-driven unfolding, and a series of procedures developing anisotropic stresses and constrained effect of water. Interfaces between amorphous silica and water generally exist in environmental, chemical, and biochemical systems. Technologically, micro- or even nanodevices are fabricated from amorphous silica, which often involves the surface contact with water for oxide coating. However, intense efforts have mostly been focused on the investigation of structural complexity of water in bulk forms over a wide range of pressure (P)/temperature (T) conditions. Consequently, more than 15 crystal structures have been revealed in H2O, which are related to either proton-order or disorder state. Although nanoscale H2O has been well recognized of importance in various environments or systems, very little is known about the structures of liquid/solid H2O confined at nanoscale due to the synthetic and technical difficulties. Currently, nanoscale manipulation of H2O can be reasonably achieved by trapping H2O in nanoporous networks (e.g., zeolites) or nanochannels (carbon nanotubes). Once water is trapped in these nanoscale spaces, a series of in situ characterizations can be performed to explore its interaction with surrounding medium at interfaces, such as the hydrophilic –OH group or the hydrophobic –CH3 group. Characterization of the associated structure and property changes allow us to understand possible influence and rearrangement of the hydrogen bonds of bulk H2O in various environments.

Nanoscale materials including nanotube, nanoslit, and nanoporous silica can be considered as ideal media to trap water or ice inside, thereby producing either one, two, or three-dimensional nanoscale forms of water or ices with various packing symmetries. Nanoporous silica possesses large surface areas and constitutes two-dimensional (2D) hexagonal arrays of hollow channels with tunable diameters.

Received: August 17, 2014
Revised: October 20, 2014
Published: October 22, 2014
typically in the range of 2–15 nm. Fabrication of high-quality nanoporous silica with control of the pore/channel size has enabled feasible manipulation of H$_2$O into embedded nanoscale channels, providing new opportunities to exploit the H$_2$O–H$_2$O or silica–OH group interactions and possible anisotropic ordering of H$_2$O molecules at the nanoscale. To understand the nanoscale confining effect of H$_2$O and construct nano-enabled phase diagram of H$_2$O, we used a pressure-processing approach to fabricate the nanoporous water and ices via use of a nanoporous silica template (amorphous SiO$_2$). Thus, by employing a diamond–anvil cell (DAC) coupled with newly developed synchrotron-based small-angle/ wide-angle X-ray scattering (SAXS/WAXS) techniques, we simultaneously monitored the evolution of the porous superlattice array and pressure-induced atomic-scale structural changes of porous ice.

The nanoporous silica samples of varied pore sizes (1, 2.5, 2.8, and 6 nm pore diameters, Figure 1 and Figure S1) used in this study were synthesized according to previously developed approaches. The option of these four particular pore sizes is based on their close relation to the observed nanoscale waters. For instance, diffusion of water within ~1 nm at hydrophilic lipid vesicle surfaces is much slower than the translational diffusion of bulk water; the distance between four-helix bundles is estimated on an order of 2–3 nm, and inside semicladrate water is formed. At hydrophilic or highly charged surfaces, water molecules can aggregate and thus form a weak hydrogen-bonded zone with a thickness of ~6 nm, in which both cations and anions display selection rules due to biological processes. Using a symmetric DAC, a mixture of nanoporous silica and H$_2$O was loaded into a preindented (~60 μm in thickness) T301 steel gasket chamber with 200 μm in diameter. A small ruby chip was placed on the top of the samples as a pressure marker. Upon the increase of pressure, synchrotron-based SAXS and WAXS images were simultaneously collected from the same volume of the samples at the B1 beamline of CHESS. The incident X-rays collimated at $\lambda = 0.485946$ Å was used to illuminate the samples; the X-ray scattering signals were recorded by a large area MAR345 detector. Neutron diffraction under pressure was performed by using a 500-ton, toroidal anvil press (TAP-98) at the beamline of high-pressure-preferred orientation (HIPPO), Los Alamos Neutron Science Center (LANSCE). The time-of-flight neutron data of the powder samples were collected by three detector banks at a fixed Bragg angle of $2\theta = \pm 90^\circ$. Transmission electron microscopy (TEM) was used to characterize the pore size and structure of the starting and recovered nanoporous silica samples. Infrared (IR) spectroscopic experiments on nanoporous silica were performed at the U2A beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The IR spectra were collected in a transmission mode by a Bruker FTIR spectrometer using a nitrogen-cooled midband MCT (MCT-A) detector. The recorded frequencies are in the range of 600–8000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

IR spectra of nanoporous silica samples with different pore sizes indicate that the silanol (Si–OH) species generally exist on the surfaces of the nanoporous silica (Figure S2). Considering the large surface areas of nanoporous silica and therefore the large amount of hydrated bonds formed between the surface Si–OH groups and absorbed water, it is reasonable to obtain the phase diagram and nucleation pressures of H$_2$O in nanoporous system that are distinct from those in bulk H$_2$O. The nanoporous ice VI nucleates in porous silica at the pressure of ~1.7 GPa (Figure 2), significantly higher than 1.05 GPa observed in bulk ice. Further increase of pressure does not transform ice VI to cubic ice VII observed in bulk at 2.1 GPa, but, instead, to a distorted “pseudocubic” structure at a higher pressure of 2.5 GPa (Figure 2). Using Le Bail refinement approach, this “pseudocubic” ice VII was found to adopt a tetragonal structure with the space group $I4$. Consistent increases of transition pressures in ice VI and VII indicate that the two ice phases do not crystallize from H$_2$O confined in nanopores but instead from H$_2$O adsorbed on the surfaces of nanoporous silica (right inset of Figure 3a). Otherwise, the diffraction peaks of ice formed in different size pores should display different magnitudes of peak broadening, which were not observed in our wide angle diffraction patterns (Figure 2). The nanoporous ice VI displays a strong preferred orientation compared to bulk ice (Figure S3), implying that anisotropic interactions occur at the interfaces between surface Si–OH species and absorbed H$_2$O. Thus, the increase of transition pressure can be used to estimate the strength of the hydrogen interactions, allowing for qualitatively understanding of the influence of nanoscale water in biologically related systems. As shown in Figure 3a, the crystalization of ice VI displays a directional H···H$_2$O alignment. The first layer of H$_2$O molecules bonded with the −OH groups on nanoporous silica surfaces has a 2D configuration. Therefore, such a boundary layer prevents realignment of H$_2$O molecules once while the crystallization of ice VI occurs. The quasi-liquid layer of water or the ice-binding surface induces a strong stress which results in ~0.6 GPa enhancement of the ice nucleation pressure. This enhanced strength through contribution of nano water in biological systems is estimated on an order of 0.1 GPa, large enough to fold/unfold soft materials like protein. This further implies that the binding between H$_2$O and hydrophilic surface −OH groups becomes stronger. Accordingly, the enhanced activation barrier prevents effective diffusion of water on the surface, leading the ion diffusion rate 5 times slower than that in bulk water.
Fitting the volume–pressure data of porous ice VI yielded a bulk modulus of 14.6(15) GPa ($K' = 4$), similar to that in bulk ice VI. On the other hand, the bulk modulus of the tetragonally distorted VII ice is determined to be 24.7 (9) GPa, which is higher than all the reported bulk moduli of ice VII ranging from 12.5 (3) to 24.0 (9) GPa. In order to rule out the claim possibly made by accident or by a series of random works, this study employed four samples with different pore sizes to make investigations systematically and comparably. The bulk moduli of different sized samples are quite consistent, rather than a random distribution, implying a universal size-tuned increase of the bulk modulus. This elevated bulk modulus is most likely related to the H$_2$O/Si–OH interactions that control the formation of this nanoporous ice phase.

Bulk ice VII has been extensively studied and considered as a proton disordered cubic structure with the space group $Pn\bar{3}m$,

In summary, we have successfully synthesized nanoporous ice phases that nucleate at higher pressures and/or in different structures. In particular, the tetragonally distorted ice VII phase possesses a new structure that has not been observed in bulk ice. In situ high-pressure SAXS and WAXS studies indicate that
Figure 3. (a) Volumetric changes (Le Bail method) of ice VI and distorted ice VII constrained in porous silica as a function of pressure at room temperature. Insets show the structures of ice VI (left), tetragonal distorted (I4mm) ice VII (middle), and the bonding interaction at the interface of porous silica and H2O; the red balls represent oxygen, yellow represent silicon, light gray represent hydrogen of water, and the blue balls represent the hydrogen of the Si–OH group on silica surface. (b) The dependence of c/a ratio of distorted ice VII on pressure. The data fittings by equation of state at room temperature give the bulk modulus and cell parameters: ice VI, \( K_0 = 14.6(15) \) GPa and \( V_0 = 234(5) \) Å³; distorted ice VII, \( K_0 = 24.7(9) \) GPa, \( V_0 = 40.7(5) \) Å³. \( K_0' = 4 \) was fixed for both ice VI and VII due to lack of enough data points and a narrow pressure range; upper left inset plots the (110/101) peaks of distorted ice VII at 14.1 GPa.

these ice phases crystallize from H2O on hydrophilic porous silica surfaces. The hydrogen binding interactions between H2O molecules and surface-absorbed Si–OH groups are likely responsible for the higher transition pressures and crystallization of the new distorted ice VII.

**ASSOCIATED CONTENT**

Supporting Information
Details of sample synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Authors**
*Jinlong Zhu: jzlzhu04@iphysics.ac.cn.
*Hongwu Xu: hxxu@lanl.gov.
*Zewei Quan: zquan@lanl.gov.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We acknowledge the support from NSF & MOST of China through research projects at Institute of Physics, Chinese Academy of Sciences. This work is also supported by the laboratory-directed research and development (LDRD) program of Los Alamos National Laboratory, which is operated by Los Alamos National Security LLC under DOE Contract No. DE-AC52-06NA25396. The neutron experiment has benefited from the use of the Lujan Neutron Scattering Center at Los Alamos Neutron Science Center, which is funded by the U.S. Department of Energy’s Office of Basic Energy Sciences. CHESS is supported by the NSF award DMR-0936384. U2A is supported by COMPRES under NSF Cooperative Agreement EAR 11-57758 and DOE-NNSSA (DE-FC-52-08NA28554, CDAC). Use of the NSLS was supported by the U.S. Department of Energy’s Office of Basic Energy Sciences. C.J.B. acknowledges support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Y.-S.L. acknowledges support from the Air Force Office of Scientific Research under grant #FA9550-14-1-0066 and the U.S. Department of Energy, Office of Science, Catalysis Science program under grant DE-FG02-02ER15368.

**REFERENCES**


