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Temperature induced immiscibility in the NaCl–H_2O system at high pressure

Mark R. Frank[a,*], Henry P. Scott[b], Steven J. Maglio[a], Vitali B. Prakapenka[c], Guoyin Shen[d]

[a] *Department of Geology and Environmental Geosciences, Northern Illinois University, DeKalb, IL 60115, United States*
[b] *Department of Physics and Astronomy, Indiana University South Bend, South Bend, IN 46634, United States*
[c] *Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, United States*
[d] *HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439, United States*

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ABSTRACT

High-pressure polymorphs of H_2O are a major component in many outer planets, extra solar bodies, and icy satellites. This study sought to examine the influence of ionic impurities on the phase stability, thermal expansion, and melting curve of ice VII. Powder diffraction patterns of ice VII formed from pure H_2O and 5 wt.% NaCl aqueous solutions were taken at room temperature up to 11.1 ± 0.3 and 26.6 ± 0.4 GPa, respectively. Thermal expansions, α, of all ice VII samples were recorded and modeled up to the melting point of the samples. Ice VII formed from a NaCl-bearing aqueous solution at pressures greater than 2.2 GPa and less than 500 K can be indexed by ice VII only, whereas at temperatures greater than 500 K, diffraction lines indicative of halite (NaCl) are observed and become more intense with increasing temperature and only disappear at the melting point of the high-pressure ice. This phenomenon was observed in all NaCl-bearing ice samples that were heated to greater than 500 K. The melting curves of ice VII formed from pure H_2O and a 5 wt.% NaCl aqueous solution suggest that the presence of Na^+ and Cl^- in the ice VII structure results in a depression of the melting curve by approximately 40 K. The exsolution of halite from the NaCl-doped ice VII and the depression of the ice VII melting curve suggest that the presence of ionic impurities in ice VII *may* promote the formation of a self-segregating zone deep within ice-rich bodies. This zone could initiate the formation of solute-rich melt pockets that may ascend toward the surface and result in surface manifestations such as solute-bearing aqueous vents, unexplained domes/diapirism, and/or salt-rich regions.

1. Introduction

High-pressure phases of H_2O, specifically ice VI, VII and X, have been hypothesized to make up a significant portion of the interiors of select outer planets, extra solar bodies, the Galilean satellites, and Saturn's Titan (Consolmagno and Lewis, 1976; Anderson et al., 1996, 1997, 2001; Carlson et al., 1996; Kivelson et al., 1996; Schubert et al., 1996; Khurana et al., 1998; McCord et al., 1998; Brown and Calvin, 2000; Greeley et al., 2000a, 2000b; Zimmer et al., 2000; McCord et al., 2001; Schenk et al., 2001; Head et al., 2002). For example, Gliese 436 b (or GJ 436 b), discovered in 2004 (Butler et al., 2004), is a Neptune-sized body orbiting the star GJ 436. The planet's density falls between hydrogen-rich gas giants (like Jupiter) and the terrestrial planets. Its semi-major axis is less than 10% that of Mercury; thus, the surface of GJ 436 b is very hot with temperatures ranging from 650 K on the daylight side to as low as 475 K on a possibly tidal locked night side. Gillon et al. (2007) estimated the planet's diameter as $50.4 \pm 4.5 \times 10^3$ km and suggested that the vast majority of its interior is composed of solid H_2O phases stable at elevated temperatures (an alternative to this model is a terrestrial core surrounded by gas). The two most likely phases within the body are ice VII and ice X which, at room temperature, are stable from 2.2 to 62 GPa and at pressures greater than 62 GPa, respectively. Ice VII has a body-centered cubic structure with disordered hydrogen bonding through the water hexamers, whereas ice X has protons which are equidistant between the oxygen atoms (Pruzan et al., 1997; Goncharov et al., 1999; Loubeyre et al., 1999). The transition from ice VII to X is also marked by a slight decrease in the unit cell volume.

The emerging planetary importance of high-pressure H_2O polymorphs in the formation and distinctiveness of H_2O-rich bodies, such as GJ 436 b, require H_2O-rich systems be studied in detail at pressures and temperatures likely in planetary interiors. At present, few data exist on the effects of impurities on the bonding and unit cell parameters of solid H_2O at high pressure, much less at elevated temperatures. Yet, for differentiated ice-rich bodies, there has likely been substantial interaction between hot H_2O-rich fluids and their rock components (McCord et al., 2001; Shock and McKinnon,

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* Corresponding author. Tel.: +1 815 753 8395.
E-mail address: mfrank@niu.edu (M.R. Frank).

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1993; Ransford et al., 1981; Scott et al., 2002). This study examined an H_2O-rich portion of the NaCl–H_2O system at high pressure and high temperature to provide an improved first-order approximation of impurity-rich high-pressure H_2O phases to be used in the next generation of phase stability and density profile models of H_2O-rich bodies. The NaCl–H_2O system was chosen due to its relative simplicity, well documented behavior over a large range of pressure and temperature, applicability to other ionic impurities, and as an extension of the room temperature, high-pressure work of Frank et al. (2006). Although the direct applicability of this system to a specific planetary body is limited, this study will serve as a good first-order approximation on the impacts of impurities on the equation of state and melting curve of high-pressure phases of H_2O and can be used as analogues for more complicated planetary systems.

2. Experimental and analytical methods

Presently, few data exist on the effects of impurities on H_2O at high pressure. Frank et al. (2006) presented a systematic study detailing the influence of charged species, Na^+ and Cl^-, on the unit cell and OH bond length of ice VII. Based on the combination of the Raman and X-ray diffraction data, they hypothesized that the incorporation of those ions into ice VII resulted in a partial ordering of the protons by interionic attractions (Na^+ with O and Cl^- with H), which resulted in a transition to an ice X-like structure, where the protons are equidistant between the oxygen atoms (Frank et al., 2006). However, their work was restricted to room temperature and, hence, did not cover a large enough *PT* range for confident application to planetary systems. We hypothesize that the incorporation of Na^+ and Cl^- into ice VII will have only a minimal impact or slightly decrease the thermal expansion of ice VII, possibly through increased interionic attractions, but will decrease the melting temperature by increasing the Gibbs free energy of mixing. This study sought to test these hypotheses by examining the influence of Na^+ and Cl^- on the thermal expansion of ice VII and its melting curve. Ionic impurities that are more likely to be present in these planetary bodies, such as $MgSO_4{\cdot}nH_2O$ and NH_3, will be examined in future studies.

2.1. Experimental design

All experiments in this study were conducted by using externally heated Hydrothermal Diamond Anvil Cells, HDAC, designed by William A. Bassett (Bassett et al., 1993). The diamond anvils had 350 μm culets, were approximately 2 mm in length from the table to the culet, and were mounted on tungsten carbide seats using Resbond 940 brand cement. The gasket material was rhenium with an original thickness of 400 μm that was pre-indented to 40–60 μm. Sample chambers of 150 μm diameters were drilled in the compressed regions by using an EDM so that the holes acted as sample chambers bound on the sides by the gaskets and between the diamond anvils. Five weight percent, 1.60 mol%, NaCl aqueous solutions were prepared by dissolving crystalline NaCl (assay, anhydrous basis ≥99.0%) in deionized H_2O (>16.7 MΩ). The aqueous solutions were loaded into the sample chamber along with approximately ten 5–10 μm flakes of gold, used as a pressure indicator (Alfa Aesar® stock # 42154, lot # B13L23), and compressed, at room temperature, to seal the contents in the sample chamber. Each heating cycle utilized a separate sample loading and no runs were preheated.

Heating was achieved by passing current through chromel wires wrapped around the tungsten carbide seats of each diamond. High temperatures were obtained by using three variable transformers. A main 20 A maximum transformer controlled two 10 A maximum transformers that were connected separately to each heater of the HDAC. Temperatures were monitored with type-K thermocouples placed directly against the surface of each diamond. Temperatures were kept within 5 K of the set temperature during data collection. Argon–hydrogen (1% hydrogen) gas was allowed to flow over the diamonds and the heaters to prevent corrosion during high-temperature operation.

2.2. Analytical methods: X-ray diffraction

All experiments were conducted at the GSECARS 13-BM-D beamline at the Advanced Photon Source, Argonne National Laboratory. An angle dispersive X-ray diffraction technique using monochromatic X-ray radiation, 0.3344 Å, and a MAR345 online imaging system were used to analyze the powder X-ray diffraction lines of the sample as a function of pressure and temperature. The X-ray beam was 14 and 7 μm in the horizontal and vertical directions, respectively, and was rastered across the sample chamber to search for all phases present in the chamber and to minimize the effects of ice grain coarsening. Data were analyzed using the FIT2D software package (Hammersley, 1997). FIT2D software and a known calibrant, CeO_2, were utilized to calibrate the sample to detector distance, coordinates of the directed beam on the detector, and the angle and tilt of the detector. There was little to no overlap of the main diffraction lines for ice VII, halite and gold over the majority of the pressure and temperature range of this study. The unit cell parameter of gold, determined from the diffraction lines, was used in conjunction with the previously established Anderson et al. (1989) *PVT* equation of state (*EoS*) to estimate the experimental pressure. Although there are more recent *EoS* for gold (Fei et al., 2004, 2007; Shim et al., 2002), we chose to use Anderson et al. (1989) to maintain an internal consistency with previous studies on pure ice VII at high temperature (Fei et al., 1993; Frank et al., 2004) and the room temperature work on NaCl-doped ice VII (Frank et al., 2006). Variations in the gold unit cell volume calculated from the {1 1 1}, {2 0 0}, {2 2 0}, {3 1 1}, and {2 2 2} diffraction lines were monitored and used to assess deviatoric stresses in the non-hydrostatic diamond anvil cell (Meng et al., 1993). The uncertainty in the unit cell parameter for gold, and thus the calculated pressure, was propagated through the pressure calculation to provide a minimum pressure uncertainty.

3. Results

Frank et al. (2006) hypothesized that impurities can affect the properties of high-pressure H_2O polymorphs in H_2O-rich bodies and icy satellites. They examined the phase relations, OH stretching frequencies and unit cell parameters of ice VII samples doped with Na^+ and Cl^- by using a diamond anvil cell (DAC) with Raman spectroscopy and synchrotron X-ray diffraction. This study extended the work of Frank et al. (2006) to include the effects of Na^+ and Cl^- on the thermal expansivity and melting curve of ice VII at conditions of planetary interiors. Diffraction data were collected up to 800 K and 32 GPa and compared to the 298 K data from Frank et al. (2006) and the numerous studies on ice VII formed from pure H_2O (Hemley et al., 1987; Fei et al., 1993; Datchi et al., 2000; Wolanin et al., 1997; Lin et al., 2004; Dubrovinskaia and Dubrovinsky, 2003; Frank et al., 2004). Our highest-pressure experiments are limited to less than 450 K because the gasket failed during heating from 450 to 500 K.

3.1. X-ray diffraction

Powder diffraction patterns of gold (the pressure standard) and ice VII formed from pure H_2O (Fig. 1) and 5 wt.% NaCl aqueous