Understanding Evolution of Icy Satellites through Cryogenic LM and Raman Studies

Mathieu Choukroun, Martin Barmatz and Julie Castillo-Rogez
Ice Physics Laboratory, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

INTRODUCTION

The team in the Ice Physics Laboratory at NASA's Jet Propulsion Laboratory in Pasadena has been developing cryogenic facilities to measure the thermophysical properties of icy compositions relevant to geophysical applications. The primary goal of this project is to better understand the thermal evolution and behavior of icy bodies in the solar system, and help explain phenomena such as cryovolcanism, plate tectonics, and tidal heating on these celestial bodies. We are trying to bring answers to questions such as: could there be liquid lakes and oceans beneath the icy satellites, as suggested by space missions like Galileo and Cassini-Huygens, and if so where does the thermal energy to sustain them come from?

The study of ices with different grain sizes and porosities and their mechanical properties, such as the elasticity moduli, viscosity, and anelasticity, as a function of loading frequency, is important for modeling tidal heating, i.e. the heating of the interior of one planetary body caused by stresses induced from the gravitational pull of another. This process is considered to be a significant source of energy in some of these objects, and could help preserve a deep ocean in Europa or promote intense cryovolcanic activity at the south pole of Enceladus. The first step toward understanding these mechanical properties requires the production of samples whose composition and structure are perfectly controlled.

This is the reason why a major task of the Ice Physics Laboratory is to create materials detected at the surface or suspected in the interior of icy satellites such as Saturn’s satellites Titan and Enceladus, and the Galilean satellite Europa, and then study their chemical, thermal, and mechanical properties. One of our early goals was to create and study water ice with a range of grain sizes and porosities, as well as clathrates.

Clathrate hydrates, which form under low temperature and high pressure conditions [e.g. 1], have a water ice skeleton that forms cages in which gas molecules can be trapped individually. As clathrates are expected to be present in outer planet satellites, such as Enceladus [2] and Titan [e.g. 3], understanding their mechanical behavior will help to better model the geological and geophysical evolution of these objects. Understanding the microstructure of clathrates and their stability as they warm up, and as the trapped gas starts dissociating from the water cages, is particularly important when trying to understand how methane can be released into the atmospheres of Titan [4] and Mars [5] and into the south polar region of Enceladus [6]. A next step is to characterize hydrated sulfates of magnesium and sodium and sulfuric acid, which are believed to be present in Europa’s icy shell [7, 8].

This article describes the methods that we have developed to produce controlled samples of clathrates and characterize their quality, which must meet certain standards in order to support our research-grade studies.

MATERIALS AND METHODS

Sample Preparation

The JPL group has developed facilities for making and characterizing different types of water ice and clathrates. First, ice was prepared in a cold room, at temperatures between -15 and -20°C. The ice was ground and then sieved and sorted to the range of desired grain sizes (100-150 µm, or 400-700 µm). From ice seeds into clathrate hydrates, the ice was then placed in a high-pressure low-temperature...

**Figure 1:**
The cryogenic light microscopy setup.
An ice sample, prepared at -30°C within the cryostage, was observed at 300x magnification under reflected illumination (image displayed on the computer screen).
vessel, kept at -10 to 0°C, and exposed to 160 bars of nitrogen gas (or other gas) for up to two weeks. CO₂ clathrates were synthesized along the liquid-vapor equilibrium, i.e. at CO₂ gas pressures of 30-35 bars, depending on temperature. Once synthesized, the samples were stored in a liquid nitrogen (LN₂) container. In order to prepare compact samples (i.e. with no porosity), the ice seeds or the clathrates were then compressed within a custom-made press placed on a 10-ton hydrostatic bench for several hours at a pressure of 1000 bar and at dry ice temperature.

**Light Microscopy**

For sample characterization, we used an Olympus BX51 polarization and phase contrast microscope with an Olympus SC-30 camera. Both transmitted and reflected light observations were possible with this setup. The samples were preserved in a LN₂-cooled Linkam LT350 cryostage, which allowed thermal regulation between -196 and 350°C.

Clathrate hydrates samples were deposited in the cryostage pre-cooled to -160°C, whereas ice, much more stable, is studied at -40 to -30°C. A few grains of clathrate hydrates or ice seeds were scratched off the sample, using a spatula pre-cooled with LN₂. The grains were then placed on a microscope slide inside the cryostage. For the solid ice samples, a thin flat, solid slice was cut and placed on the microscope slide. In the cold room, the samples were transferred directly to the cryostage to avoid melting or destabilization. The cryostage was then moved from the cold room to the microscope. The cryostage was kept under constant gaseous N₂ flow to avoid condensation inside and on top of the viewing window.

**RESULTS**

**Clathrate hydrates**

Figure 2 shows images of N₂ clathrates obtained with this experimental setup upon heating from -160 to -6°C (123 to 266K).

Although one would expect the dissociation of N₂ clathrates into ice and nitrogen to occur around -160 to -130°C at atmospheric pressure, the images indicate that the clathrates exhibited a strong metastability up to a temperature of about -15°C. Based on these preliminary images, it appears that at the lower temperature of -160°C, the clathrates were stable. At temperatures above -15°C, the clathrates started to dissociate massively, accompanied by outgassing. Further tests still need to be conducted to fully characterize the metastability of clathrates.

Clathrate hydrate samples were also characterized via in-situ Raman spectroscopy. A few CO₂ clathrate hydrate grains were transferred into the Linkam LTS 350 cryostage, pre-cooled to 120°C. Raman spectra were obtained with a Horiba Jobin-Yvon LabRam HR confocal Raman spectrometer, coupled to a 532 nm solid-state laser with an input power of 50 mW. The spectral resolution using a 600 grooves mm⁻¹ grating was 1.7 cm⁻¹. Optical fibers carried the laser beam onto the sample through the microscope objectives. The Raman signal was collected by the same fiber optics, and transferred to the spectrometer.

The spectra obtained (Figure 3) provided a clear identification of CO₂ clathrate hydrates: they showed the typical regions of the Raman signature of clathrate hydrates, and a consistent CO₂/ice intensity ratio throughout the sample. A slight shift of the CO₂ gas peaks of around -5 cm⁻¹ was characteristic of the clathrate hydrate structure.

**Water Ice**

The characterization of ice microstructure by light microscopy requires a very good understanding of the processes associated with samples synthesis, compaction, preparation for imaging, and preservation. This is particularly due to high sublimation rates of water ice at temperatures above -30°C, high sensitivity to local warming (melting), and frost deposition when in direct contact with the atmosphere at room temperature. All these processes affect the surface of the sample, and therefore need to be controlled in order to acquire good quality images.

Sublimation is an important process of sample preparation, because it does not affect the microstructure at the bulk sample scale much, and it actually helps enhance the microstructure characterization, because it first occurs at grain boundaries. Figure 4 illustrates this with...
an extreme case, where an ice sample, compacted from 350-425 µm ice seeds, was left at -12°C in the cold room for 18 h before observation. As in the case of the clathrate hydrates, the pure water ice samples were transferred directly in the cold room to the cryostage. The cryostage was regulated at -40°C for sample transfer and then imaging. Figure 4a shows an average grain size of 150 µm for this sample (the grains that appeared smaller than 100 µm corresponded to the cross-section of grains far from their elongation axis), i.e. a reduction in grain size by a factor of ~2-2.5 upon compaction. Figure 4b and 4c show how the grain surfaces were affected by sublimation: grooves formed, then became deeper and wider at the grain boundaries as sublimation proceeded; the grain surface, not affected much at the beginning of the sublimation, started displaying a network of small pits, 10-20 µm across, which became more and more apparent as the sample was being etched. Figure 4d shows a cryo scanning electron microscope (cryoSEM) image acquired with a FEI XL30 equipped with a Polaron liquid nitrogen-cooled stage on a different sample, which was cryo-etched at -70°C under high vacuum. The grain surface structures are very similar in Figure 4c and 4d, which indicates that most of the ‘sub-grain features’ observed in the cryoSEM were associated with sublimation. Therefore, combining the cryoSEM imagery with cryo light microscopy allowed us to identify the processes that affected the microstructure during sample preparation, and to decipher the original microstructure of the samples whose thermo-physical properties were measured.

Figure 5 shows images of pure, solid water ice samples obtained with the cryo-microscope setup after preservation of the sample for about three days at -30°C. Some sublimation occurred during that period, but it affected only the grain boundaries, which could then stand out. This situation offers optimal conditions for characterizing the microstructure. Figure 5a (crossed-polarized) shows the variability in crystalline orientation of ice grains within the samples. The enlarged view (5b) demonstrates that porosity was absent in the sample, and shows the relief of the grains. These images also indicate that the overall grain size decreased from 100-150 µm initial seeds (not shown) to 50-100 µm during the compaction process.

CONCLUSIONS
A careful assessment of the microstructure and composition of icy samples is a prerequisite to obtaining accurate measurement of their mechanical properties. A cryogenic light microscopy setup and a Raman spectrometer were used for these analyses. Procedures for the synthesis, compaction, and observation of the samples have been developed to characterize the samples accurately. Using these techniques, we could demonstrate our capability to constrain the sample grain size and microstructure. We have shown that the combination of cryogenic light microscopy with cryogenic scanning electron microprobe imaging provides a way to distinguish the processes that affect the microstructure of the samples. Also, cryo-LM offers some advantages over cryo-SEM, despite a smaller spatial resolution (~0.5 µm vs <100 nm): this technique is easy to use, convenient, since the setup can be located just beside the cold room and other cryogenic equipment, fast for image acquisition, and quite inexpensive.

The work being performed by JPL’s Ice Physics Laboratory has many implications for understanding solar system bodies on which ice is present. The physical processes are studied on a microscopic scale, but the results give insight into large-scale processes such as cryovolcanism, tidal dissipation and the thermal evolution of various planets and satellites, including icy regions on Earth, outer planet satellites, Mars, meteorite parent bodies, and the outer solar system. This research is critical to the interpretation of data from space missions like past Galileo (to Jupiter), current Cassini-Huygens (Saturn), Dawn (asteroid Ceres), or New Horizons (Pluto-Charon and Trans-Neptunian Objects), as well as to the definition of scientific instruments for future missions to icy bodies.

REFERENCES
©2011 John Wiley & Sons, Ltd