A Sapphire Cell for High-pressure, Low-Temperature Neutron Scattering Experiments

by

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Abstract

A single-crystal sapphire cell for performing neutron scattering experiments on gas hydrates synthesized in situ was designed and fabricated to operate at pressures up to 350 bar and temperatures between 10K and 300K. The single-crystal cell is cut off-axis from the c-axis of sapphire to avoid Bragg diffraction in the scattering plane for the Debye Scherrer geometry. The cell is pressurized from a boosted pumping station via small-diameter stainless steel pipe. The cell is cylindrical with no external supports. The design of the cell allows the unobstructed detection of neutrons scattered from the sample. This requirement necessitated a departure from the predominant style of sapphire cells reported in the literature. Several iterations of design modifications and finite element modeling were performed prior to building the prototype. The cell was tested hydrostatically at room temperature. Preliminary inelastic neutron scattering data is reported to verify the performance of the cell.

Introduction

The study of the structure and stability of gas hydrates is motivated by the potential for gas hydrates to both supply energy and sequester carbon dioxide. Gas hydrates are not stable at ambient temperatures and pressure; therefore, special temperature-controlled pressure vessels are required for their study. Elastic and inelastic neutron scattering are useful in the study of gas hydrates because neutrons are capable of scattering off the light elements that dominate the hydrate structure. Furthermore, neutrons are weakly interacting and are able to pass through bulky pressure cell walls with little attenuation. This paper describes a new type of high-pressure sapphire cell for synthesizing gas hydrates *in situ* and performing neutron powder diffraction over a range of temperatures and gas pressures.

Sapphire is a desirable material for high-pressure applications because of its strength[1], chemical inertness[2], and transparency to visible light[3]. In addition, since it contains only aluminum and oxygen, sapphire possesses low incoherent neutron scattering and absorption crosssection and thus has a low contribution to the background[4]. Sapphire does contributes Bragg reflections to the measured pattern; however that effect can be minimized with proper engineering considerations.

Reports of sapphire cells being used for neutron-scattering studies are uncommon. The exception is small-angle neutron scattering (SANS), for which the use of sapphire windows in high-pressure cells is routine and includes examples at extremes of both pressure and temperature[5,6].

Design Considerations

Size and shape

The shape of the cell was chosen to be an unsupported cylinder as shown in Figure 1. Removing the full-length support bolts present in other designs allows unobstructed spectroscopic access to the cell. Flanges were added to the ends of the cylinder to provide a clamping surface for the sealing endcaps. Sealing endcaps were designed with a grooved ring and intruding boss in order to create a crushed seal using soft maleable metals [5,7] (Figure 2).

The overall size was chosen to maximize sample exposure to the neutron beam, yet allow the cell to be installed on a closed-cycle helium refrigerator. The external dimensions of the sapphire (without endcaps) as shown in Figure 1 are 100 mm long x 30 mm wide. With endcaps, the cell exterior dimensions are 126 mm long x 48 mm wide. The internal dimensions are 10 mm diameter x 100 mm long and the volume is 7.8 mL. The axis of the cell was chosen to be 5° off the c-axis of the sapphire single crystal from which it was cut. This orientation was selected to minimize reflections from the sapphire cell in the diffraction plane. To determine this orientation a Laue diffraction pattern was calculated from the crystal structure parameters of sapphire.

Maximum stress on a cylinder of sapphire

For a thick-walled cylinder subjected to an internal pressure and no external pressure, the maximum tangential stress, Φ_{max}, occurs on the inner surface of the cylinder and can be calculated as:

$$\Phi_{max} = \frac{a^2 P}{b^2 - a^2}\left(1 + \frac{b^2}{a^2}\right) \tag{1}$$

where a is the inner radius, b is the outer radius, and P is the internal pressure. The value of b was chosen such that Φ_{max} was much less than 50% of the yield strength of sapphire. Since the length of the cylinder is greater than the inner radius, length does not have influence on the calculation. For a = 0.5 cm, b = 0.9 cm and considering an internal pressure of 350 bar, Φ_{max} = 663 bar or 66.3 MPa. This value is –17% of the reported tensile strength of sapphire (400 MPa) as supplied by the manufacturer, Crystal Systems, Inc. [8].

Finite element modeling.

A finite-element stress analysis of the cylindrical sapphire cell was carried-out using the commercially-available software package ANSYS v.5.0. Because of axial and circumferential symmetry, only a 2-D analysis of one-half of the cell was performed using axisymmetric plane-2D elements. The boundary conditions consisted of uniform pressure on the inner walls of the cell to simulate internal pressurization, and fixed displacements on the ends to simulate the clamping constraints imposed by the metallic flanges.

Figure 3a shows the mesh of the model along with the boundary conditions. Figure 3b shows the resulting distribution of tangential (hoop) stresses along with the deformed shape (exaggerated, not to scale). The maximum tensile tangential stresses occur on the inner surface of the cell, and the magnitude of these stresses decreases radially with the square of the radial position.

Fabrication

A cylinder was cut from a sapphire boule grown by the Czochralski method (Crystal Systems, Inc.) and machined to the final shape (INSACO). The cylinder axis was cut 5° off from the e-axis of the boule. Real-time Laue patterns verified that the sapphire reflections are directed out of the diffraction plane, and were also used to determine the optimum orientation of the cell within the diffractometer. The aluminum endcaps were fabricated at ORNL. The endcaps seal the sapphire using crushed indium metal. The top endcap is studded for mounting on a displex cold finger. The bottom endcap is identical, but with a tap and 1/16 compression fitting to allow pressure control and gas introduction. The current iteration only allows for the introduction of gasses through the bottom. Future iterations will include a second gas tap in the top endcap for pressure bleeding.

Performance

The cell was hydrostatically tested to 380 bar, at which pressure the crushed indium seals fail consistently. Although 350 bar is sufficient for most gas-hydrate studies, higher pressures can be attained using a stiffer crushed seal such as gold, lead or soft copper[3].

Elastic and inelastic neutron scattering was performed on the empty cell. No elastic reflections from the sapphire were observed. The contribution from the sapphire to the inelastic neutron scattering spectrum (Figure 4) was two orders of magnitude lower than in the presence of ground, loosely packed, hydrogenous THF hydrate (15 K).

Conclusion

A single-crystal sapphire cell has been constructed for in-situ neutron diffraction studies of gas hydrates. The elastic background contribution from the cell is negligible. The inelastic background contribution from the cell is two orders of magnitude lower than a typical fully hydrogenous hydrate sample. Although constructed to measure structural and dynaniical properties of gas hydrates using elastic and inelastic neutron scattering, the cell is part of the Oak Ridge National Laboratory's High Flux Isotope Reactor user facility and is available for general use in neutron scattering experiments not involving gas hydrates.

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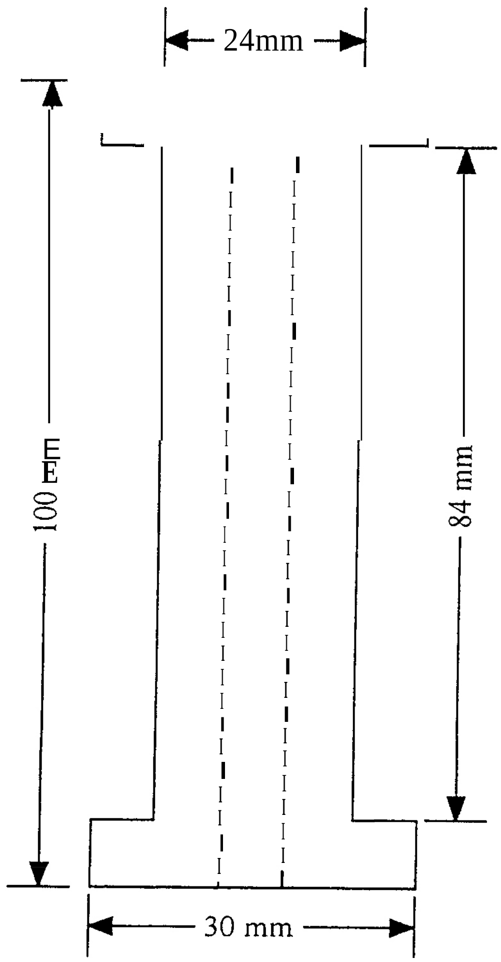

Figure 1: Schematic diagram of sapphire cell. The cell is a hollow cylinder with flanges on each end as support surfaces for sealing endcaps. No bolts run along the outside of the cell. No other external supports are needed.

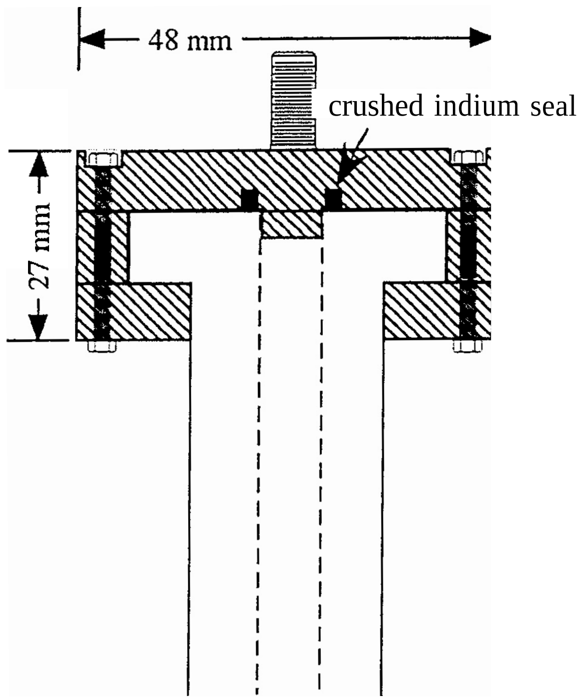

Figure 2: Aluminum endcap with intruding boss and crushed indium seal. Top endcap shown is studded for mount on closed-cycle helium refrigerator cold finger.

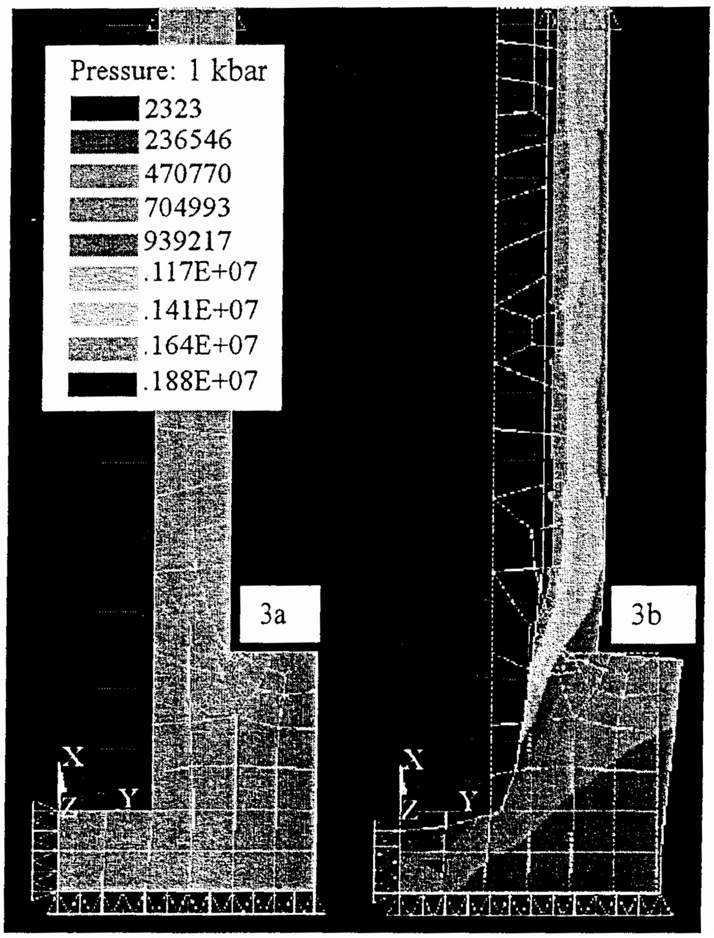

Figure 3a&b: Results of Finite Element Modeling of a cylinder of sapphire with the dimensions shown in Figure 1. Figure 3b shows cell under kbar pressure with exaggerated deformation. Legend denotes millibars.

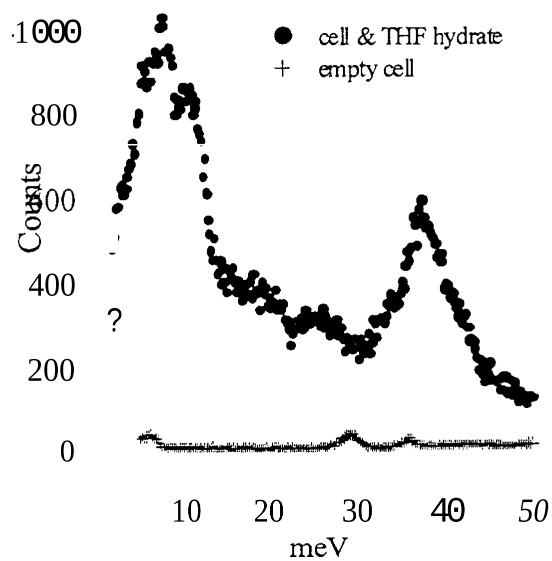

Figure 4: Inelastic neutron scattering of empty cell and cell with THF hydrate at 15 K. Contribution of cell is 2 orders of magnitude lower than loosely packed-sample.