

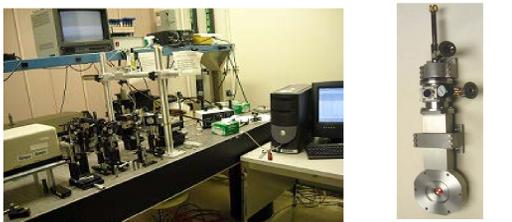
## Abstract

Behavior of Ammonia borane under high pressure up to 20 GPa and temperature from 80 – 350K has been studied using Raman spectroscopy/x-ray diffraction and a diamond anvil cell (DAC). Abundant phases are found in this molecular crystal at this pressure and temperature range. More changes in the feature of Raman spectroscopy are observed than the crystal structure changes identified by x-ray diffraction, indicating Raman spectroscopy may identify bonding changes in addition to crystal structural transitions. Based on Raman spectra of ammonia borane, four new phases are observed for the first time at high pressure and low temperature. Confining the sample into mesopores of nano-scaffold (SBA-15 with 1:1 ratio to sample) shifts the pressure induced phase transitions at ~0.9 GPa and ~10.2 GPa to ~0.5GPa and ~9.7GPa respectively, and the temperature induced transformation from 217K to 195K in ammonia borane. Raman spectroscopy study has also been conducted on lithium amidoborane at high pressures up to 19 GPa and room temperature. Two new high pressure phases are observed.

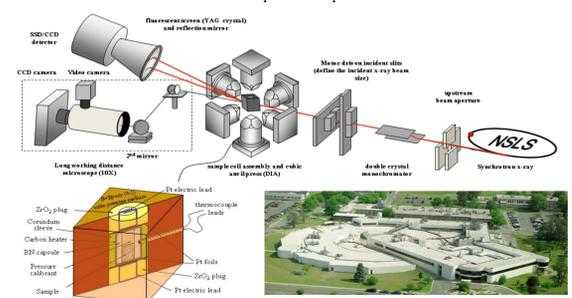
## Experimental Method



Diamond anvil cell (DAC) for high pressure generation

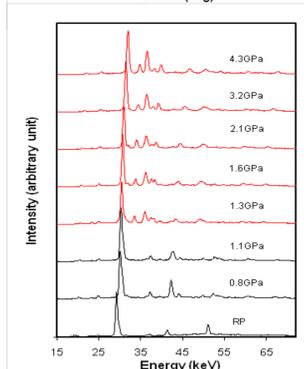
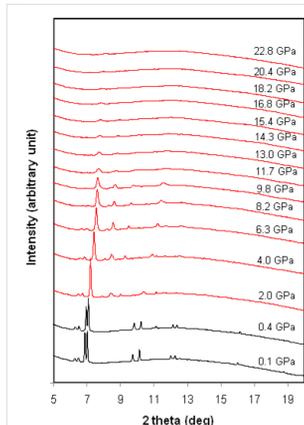


Raman spectroscopy system and Cryostat that houses the DAC for high pressure and low temperature experiments.

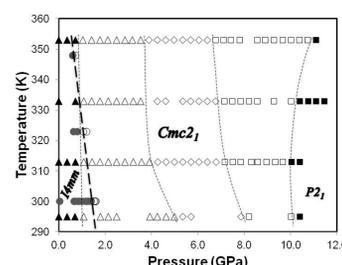


X-ray diffraction system at National Synchrotron Light Source of Brookhaven National Lab and high pressure cell assembly used in the multi anvil press.

## Results and discussions

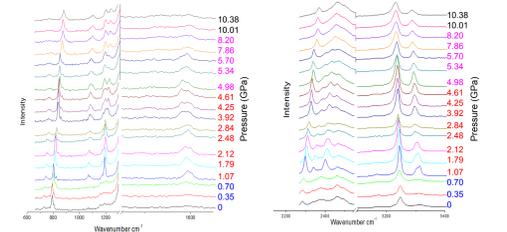


In situ x-ray diffraction patterns of ammonia borane in DAC (left) and MAP (right) at ambient temperature. Black and red colors represent the patterns from the *I4mm* phase and the *Cmc2<sub>1</sub>* phase, respectively.

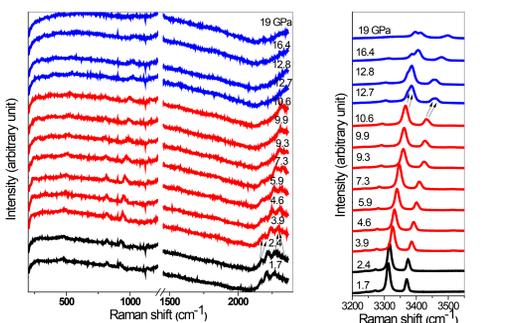


Above: Phase boundary of ammonia borane at high pressure and elevated temperature. Solid and open circles represent *I4mm* and *Cmc2<sub>1</sub>* phases respectively, determined by x-ray diffraction. Solid triangles and squares represent *I4mm* and *P2<sub>1</sub>* phases respectively, determined by Raman spectroscopy. Open symbols between *I4mm* and *P2<sub>1</sub>* phases represent *Cmc2<sub>1</sub>* phase.

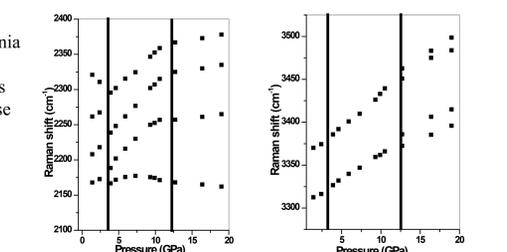
Left: Phase boundary of ammonia borane at high pressure and low temperature determined by Raman spectroscopy



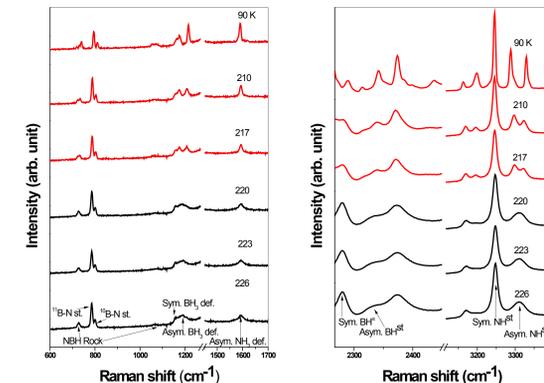
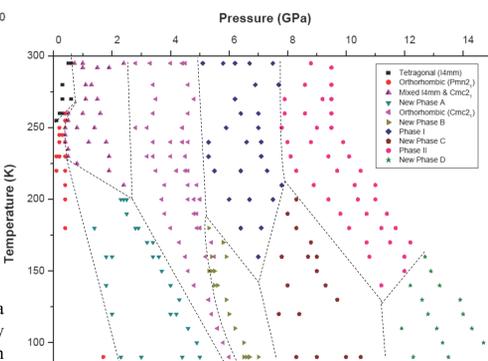
High Pressure Raman Spectra of Ammonia Borane. Numbers next to the spectra indicate the pressure (difference colors represent phase change, blue: *I4mm*, red and pink: *Cmc2<sub>1</sub>*, black: *P2<sub>1</sub>*, phase change between red and pink is a second order transition)



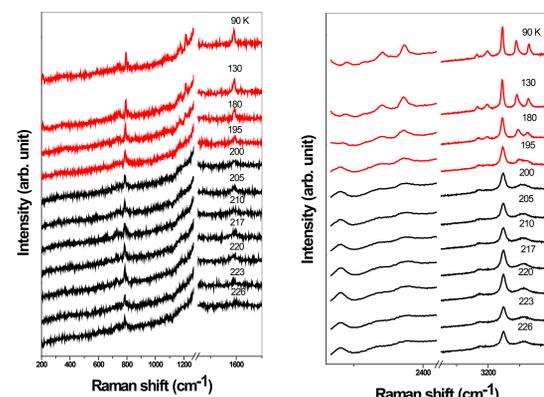
High Pressure Raman Spectra of lithium amidoborane. Numbers next to the spectra indicate the pressure in GPa. Two phase transitions are observed at about 3 GPa and 12 GPa respectively.



Pressure dependence of Raman peaks of lithium amidoborane. The first phase transition is observed about 3 GPa for peak splitting at 2175  $\text{cm}^{-1}$  and peak merging at 2300  $\text{cm}^{-1}$ . The second phase transition is observed at about 12GPa for peak splitting at 3375  $\text{cm}^{-1}$  and 3450  $\text{cm}^{-1}$ .

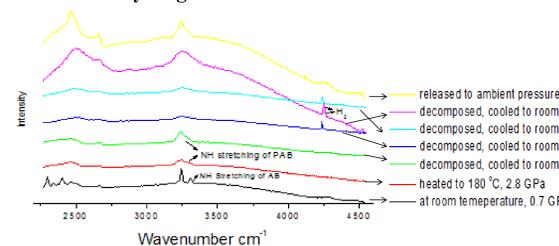


Raman spectra of ammonia borane as a function of temperature

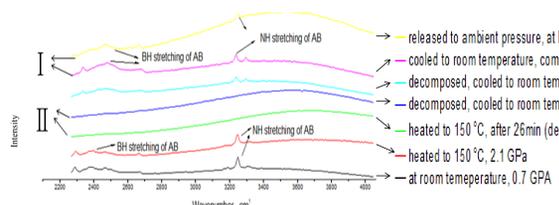


Raman spectra of ammonia borane confined in SBA15 nanoscaffold as a function of temperature

## Dehydrogenation and rehydrogenation of ammonia borane with and without nanoconfinement



Raman spectra of neat ammonia borane (2250 $\text{cm}^{-1}$  - 4750 $\text{cm}^{-1}$ ) during heating and subsequent compression



Raman spectra of ammonia borane confined in SBA15 (2250 $\text{cm}^{-1}$  - 4150 $\text{cm}^{-1}$ ) during heating and subsequent compression. NH stretching peaks of ammonia borane reappear during the subsequent compression (after dehydrogenation) to 6 GPa.

Confining ammonia borane in mesoporous confinement (i.e. SBA15 silica nanoscaffold) not only change its dehydrogenation temperature and kinetics but also influence its phase equilibrium. Comparative study using Raman spectroscopy was conducted to observed such influence on the temperature induced body centered tetragonal (*I4mm*) structure to low temperature orthorhombic (*Pmm2<sub>1</sub>*) structure. Nanoconfinement shifts the phase transition from 217 K to 195 K (see figures on the left).

A similar influence of the nanoconfinement on pressure induced phase transitions is also observed using Raman spectroscopy. The phase boundary between the phase and high pressure *Cmc2<sub>1</sub>* phase at ambient temperature is shifted from 0.9 GPa to 0.5 GPa; and that between the *Cmc2<sub>1</sub>* phase and higher pressure *P2<sub>1</sub>* phase is shifted from 10.2 GPa to 9.7 GPa.

More remarkably, confining ammonia borane makes it possible to reverse its thermolysis process by applying high pressure to the system. Figures below show the comparison of behaviors of neat and confined ammonia borane during heating and subsequent compression.

## Future Direction

- Expand the in situ high pressure study of the ammonia borane derivative, lithium amidoborane, from ambient temperature to both elevated temperature and low temperature.
- Study pressure influence on dehydrogenation and rehydrogenation of lithium amidoborane. Apply the same experimental protocol used in ammonia borane system to lithium amidoborane system to explore reversibility of its thermolysis process through pressure.
- Synthesize and characterize aluminum amidoborane.

### Publications:

Jiuhua Chen, Helene Couvy, Haozhe Liu, Vadym Drozd, Luke L. Daemen, Yusheng Zhao and Chi-Chang Kao, In situ x-ray study of ammonia borane at high pressures, International Journal of Hydrogen Energy, 35 (20), October 2010,11064-11070, doi:10.1016/j.ijhydene.2010.07.085.

Shah Najiba, Jiuhua Chen, Vadym Drozd, Andriy Durygin, Yongzhou Sun, Tetragonal to orthorhombic phase transition of ammonia borane at low temperature and high pressure, Journal of Applied Physics, 2012 in print.

Shah Najiba, Jiuhua Chen, Vadym Drozd, Andriy Durygin, Yongzhou Sun, Raman spectroscopy study of ammonia borane at low temperature and high pressure, in Energy Technology 2012: Carbon Dioxide Management and Other Technologies, Edited by Maria D. Salazar-Villalpando, Neale R Neelameggham, Donna Post Guillen, Soobhankar Pati, and Gregory K. Krumbick, TMS (The Minerals, Metals & Materials Society), 2012, pp 339-346

Ali Hadjikhani, J. Chen, S. Das, W. Choi, Raman spectroscopy of graphene and plasma treated graphene under high pressure, 2012 TMS Proceedings: Volume 2: Materials Properties, Characterization, and Modeling, TMS (The Minerals, Metals & Materials Society), 2012, pp 75-79

Yu Lin, Hongwei Ma, Charles Wesley Matthews, Brian Kolb, Stanislav Sinogeikin, Timo Thonhauser, and Wendy L. Mao, Experimental and Theoretical Studies on a High Pressure Monoclinic Phase of Ammonia Borane, Journal of Physical Chemistry C, 116, 2172–2178 (2012).

### Support and facility:

DE-FG02-07ER46461

