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Title of Award: Influence of Pressure on Physical Property of Ammonia Borane and its Re-hydrogenation
PI: Jiuhua Chen
CoPI: Wendy Mao, Yusheng Zhao, Chichang Kao
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Accomplishments:

- *Pressure induced phase transition at room temperature*

A sequence of phase transitions in ammonia borane have been discovered and studied by using both *in situ* x-ray diffraction and Raman spectroscopy. Our earlier Raman measurements (Lin *et al.* 2008) confirmed a phase transition below 2 GPa observed previously and indicated two new transitions at 5 GPa and 12 GPa (Figure 1). Our sequential x-ray diffraction studies (Chen *et al.* 2010, Lin *et al.* 2012) demonstrated that the transitions at 5 GPa and 12 GPa are a $Cmc2_1$ to $Cmc2_1$ second-order phase transformation with a significant increase of bulk modulus from 12 GPa to 37 GPa (Figure 2) and a $Cmc2_1$ to $P2_1$ first order phase transformation (Figure 3) respectively.

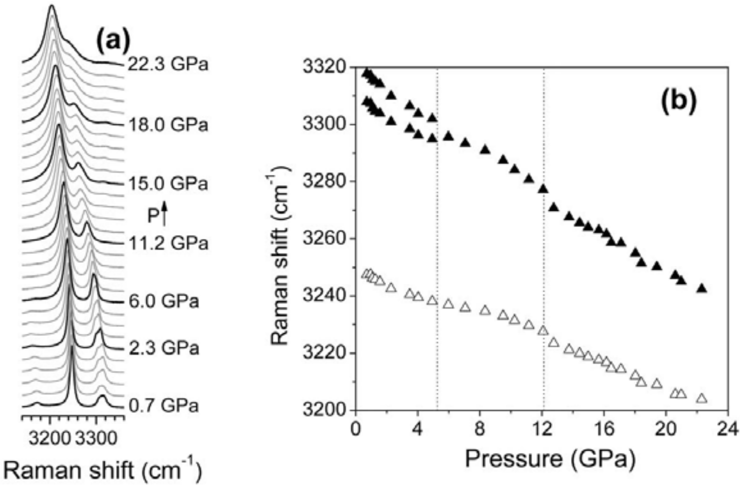

Figure 1. (a) Raman spectroscopy of ammonia borane at high pressures. (b) Corresponding Raman shift as a function of pressure. Significant feature changes at about 5 GPa and 12 GPa indicate possible phase transitions (Lin et al. 2008).

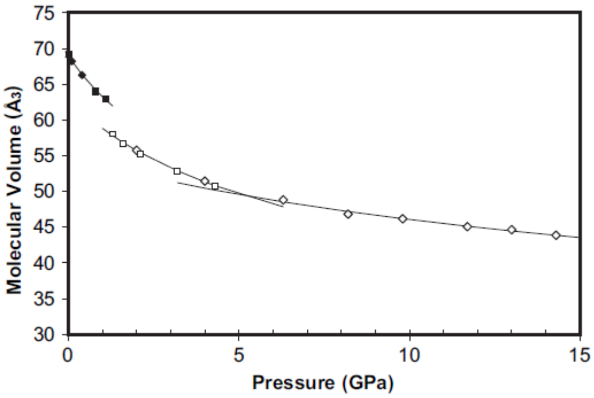

Figure 2. Volume per molecule of ammonia borane as a function of pressure. Solid and open symbols are the I4mm phase and the Cmc21 phase, respectively. Lines represent the fitting result to the third order Birch Murnaghan equation of state for the indicated pressure range. A compressibility change is observed at 5 GPa indicating a second order phase transformation (Chen et al. 2010).

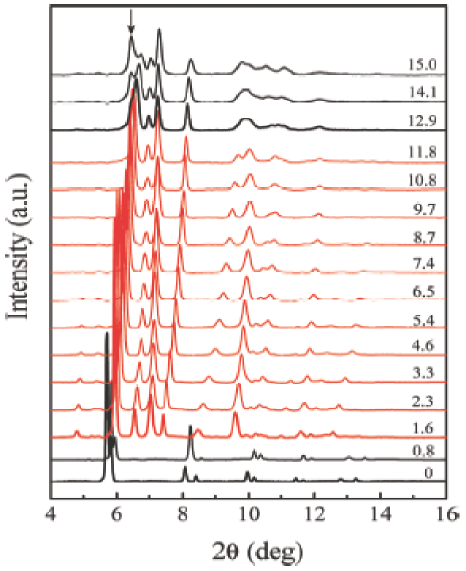

Figure 3. X-ray diffraction of ammonia borane at high pressures collected at Advanced Photon Source (Lin et al. 2012). The sequence of patterns shows the evolution of the XRD of ammonia borane as a function of pressure up to 15.0 GPa. First-order phase transitions were observed at 1.6 and 12.9 GPa, indicated by different colors of the diffraction patterns. The numbers on the right-hand side indicate pressure in GPa. The arrow shows the (101) reflection in the *P*2*₁* phase. Quality of diffraction patterns is improved significantly compared with previous work such that the crystal structure can be determined with assistance of theoretical simulation.

- *Phase relation at high P and low T*

In situ Raman spectra of ammonia borane have been collected at high pressure up to 14 GPa and temperature down to 80 K. Abundant Raman feature changes were observed in this pressure and temperature range. The phase boundary between the room temperature tetragonal (*I4mm*) phase and low temperature orthorhombic ($Pmn2_1$) phase is determined having a positive Clapeyron slope (dP/dT = 25.7 MPa/K), indicating that the transition is exothermic (Najiba *et al.* 2012). Figure 4 show the phase relation below room temperature. Four new phases are observed in the Raman scattering experiments (Najiba *et al.* 2013).

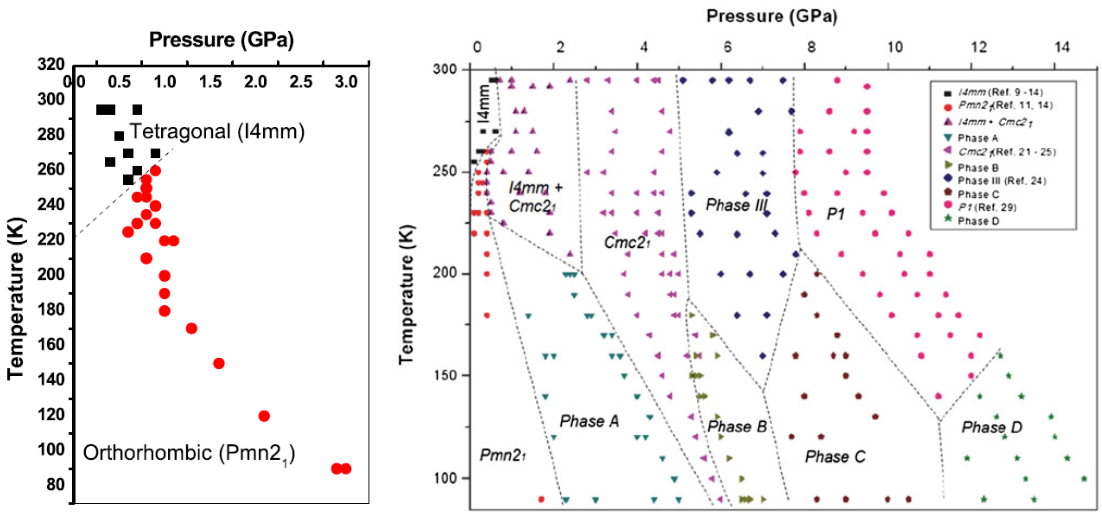

Figure 4. Phase boundary of ammonia borane at high pressure and low temperature determined by Raman spectroscopy (Najiba et al 2012, 2013)

- *Phase relation at high P and elevated T*

In situ Raman spectra of ammonia borane have been collected at high pressure and elevated temperature to determine the phase boundary between the low pressure I4mm phase and high pressure Cmc2$_1$ phase. The phase transition shows somewhat hysteresis during compression and decompression. The transition hysteresis becomes less at higher temperature. Figure 5 shows the experimental data for the P-T phase relation above room temperature (Sun *et al.* 2014). The positive Clapeyron slope indicates that the pressure-induced phase transition from I4mm to Cmc2$_1$ is exothermic. One of the barriers for rehydrogenation of ammonia borane after the first two step decompositions is the high exothermic enthalpies during the decompositions. The current study indicates that the orthorhombic phase of ammonia borane has lower enthalpy than that of tetragonal phase. If we assume decomposition from the orthorhombic phase yields the same products as that from the tetragonal phase, the decomposition of the orthorhombic phase will be less exothermic. Therefore rehydrogenation from the decomposed product into the orthorhombic phase at high pressure may become easier. However, it is difficult to quantify the enthalpy of the high pressure transition to give a quantitative estimation of how much easier such a rehydrogenation is.

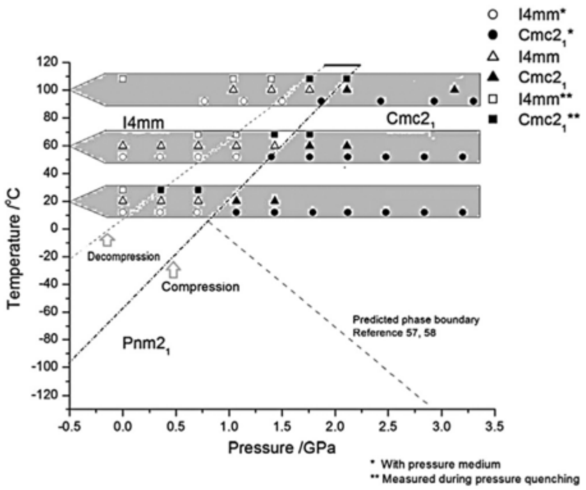

Figure 5. Phase boundary between I4mm and Cmc2$_1$ phases of ammonia borane at high pressure and elevated temperature (Sun et al. 2014). Open and solid symbols represent *I4mm* and *Cmc2$_1$* phases respectively. All the data within a horizontal shaded area are taken at the same temperature labeled on the left, but plotted separately for easy recognition.

- *Phase relation assembly in P-T space*

A P-T phase diagram of ammonia borane is summarized as shown in Figure 6 (Chen *et al.* 2014) .

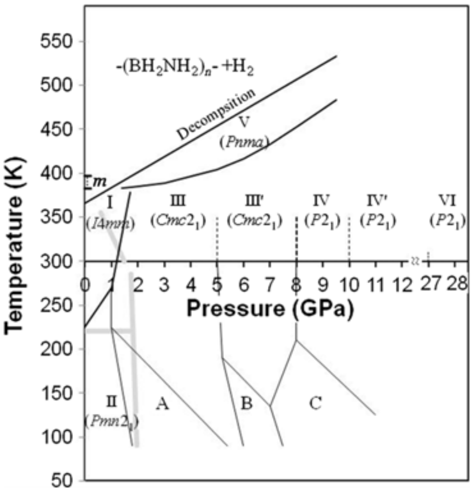

Figure 6 (right). Summarized P–T phase diagram of ammonia borane. I–VI indicated six distinct crystal structures. Phases III and III', IV and IV' were iso-structure phases, respectively. Broken lines indicated the boundaries estimated or extrapolated from room temperature and low temperature data. Gray lines represented the published data that were not adopted in this phase diagram. m indicated the temperature range of melting when fast heating rates were applied.

- *Influence of nanoconfinement on phase stability*

Influence of confining ammonia borane in mesoporous confinement (i.e. SBA15 silica nanoscaffold) on behavior of ammonia borane has also been studied. Not only does the nanoconfinement change the dehydrogenation temperature and kinetics of ammonia borance but also it influences phase equilibrium. Comparative study using Raman spectroscopy indicates that the temperature induced body-centered-tetragonal (*I4mm*) structure to orthorhombic ($Pmn2_1$) structure transition is suppressed from 217 K to 195 K when the sample is confined in SBA15 (Figure 7). Compared to the result with MCM-41, this result demonstrates a size effect on the influence of nanoconfinement. When the pore size is reduced from 7-9 nm to 3-4 nm, the tetragonal to orthorhombic structural transition is totally suppressed in the temperature down to 80 K. A similar influence of the nanoconfiement on pressure induced phase transitions is also observed using Raman spectroscopy. The phase boundary between the *I4mm* phase and high pressure $Cmc2_1$ phase at ambient temperature shifts from 0.9 GPa to 0.5 GPa; and that between the $Cmc2_1$ phase and higher pressure $P2_1$ phase shifts from 10.2 GPa to 9.7 GPa.

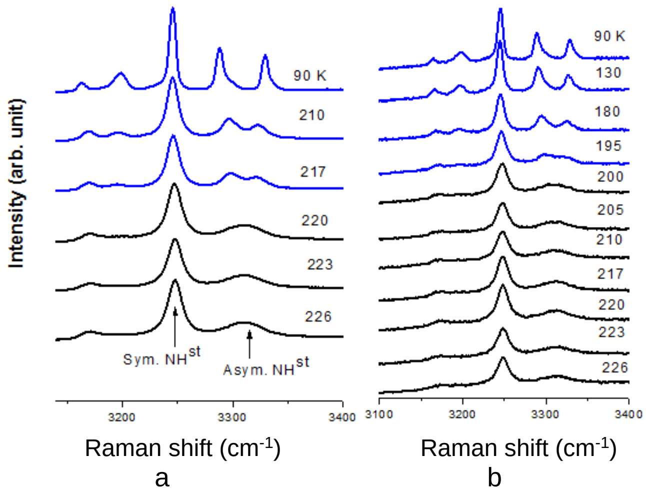

Figure 7. Selected Raman spectra of ammonia borane at different temperature in the spectral region of 3100 cm^{-1}-3400 cm^{-1}: (a) neat ammonia borane, (b) nanoconfined ammonia borane in SBA-15. Different colors indicate the phase transition from I4mm (black) to $Pmn2_1$ (blue). The sample temperature is indicated in each spectrum.

- *Rehydrogenation*

Remarkably, confining ammonia borane makes it possible to reverse its thermolysis process by applying high pressure to the system. While the bulk ammonia borane does not show clear evidence of reversal of the decomposition reaction at pressure up to 17 GPa, the sample confined in SBA15 indicate a rehydrogenation of the decomposed products when the system pressure is increased to about 6 GPa. The result is more promising for the case of lithium amidoborane (to be published). The bulk lithium amidoborane shows such a rehydrogenation at about 7 GPa even without the nanoconfinement.

- *Phase relation of lithium amidoborane*

In situ Raman spectroscopy study on lithium amidoborane has been conducted at room temperature and high pressure up to 19 GPa. The result indicates that the sample experiences two phase transition in this pressure range (Figure 8). The first transition is observed about 3 GPa for peak splitting at 2175 cm^{-1} and peak merging at 2300 cm^{-1}, and the second phase transition is observed at about 12GPa for peak splitting at 3375 cm^{-1} and 3450 cm^{-1} (Figure 9).

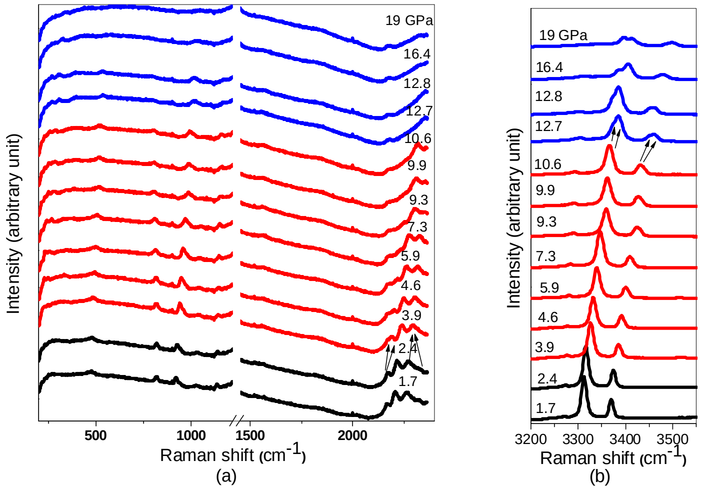

Figure 8. High Pressure Raman Spectra of lithium amidoborane. Numbers next to the spectra indicate the pressure in GPa.

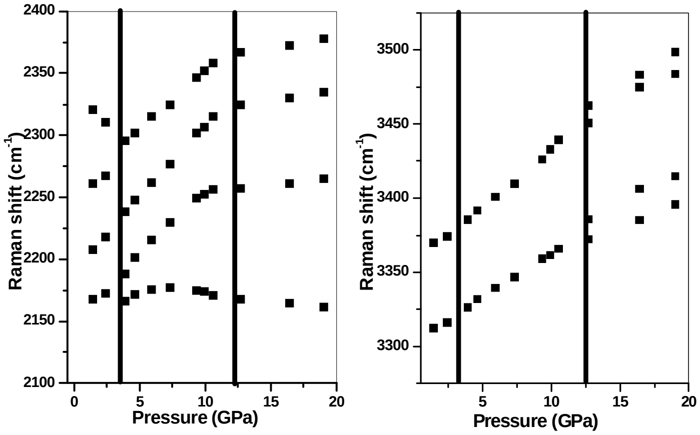

Figure 9. Pressure dependence of Raman peaks of lithium amidoborane. Bold lines indicate the phase boundaries where change of slope, merging or splitting of peaks occurs.

- *Dehydrogenation mechanism of lithium amidoborane*

Lithium amidoborane has attracted significant attention as hydrogen storage material. It releases ~10.9 wt% hydrogen, which is beyond the Department of Energy target, at remarkably low temperature (~90 °C) without borazine emission. It is essential to study the bonding behavior of this potential material to improve its dehydrogenation behavior further and also to make rehydrogenation possible. The high-pressure behavior of lithium amidoborane in a diamond anvil cell was studies using in situ Raman spectroscopy (Najiba and Chen 2012). The study indicated that there is no dihydrogen bonding in this material, as the N-H stretching modes show blueshift with pressure instead of redshift a characteristic feature of dihydrogen bounding in ammonia borane (Figure 10). The absence of the dihydrogen bonding in this material is an interesting phenomenon, as the dihydrogen bonding is the dominant bonding feature in its parent compound ammonia borane. This observation may provide guidance to the improvement of the hydrogen storage properties of this potential material and to design new material for hydrogen storage application.

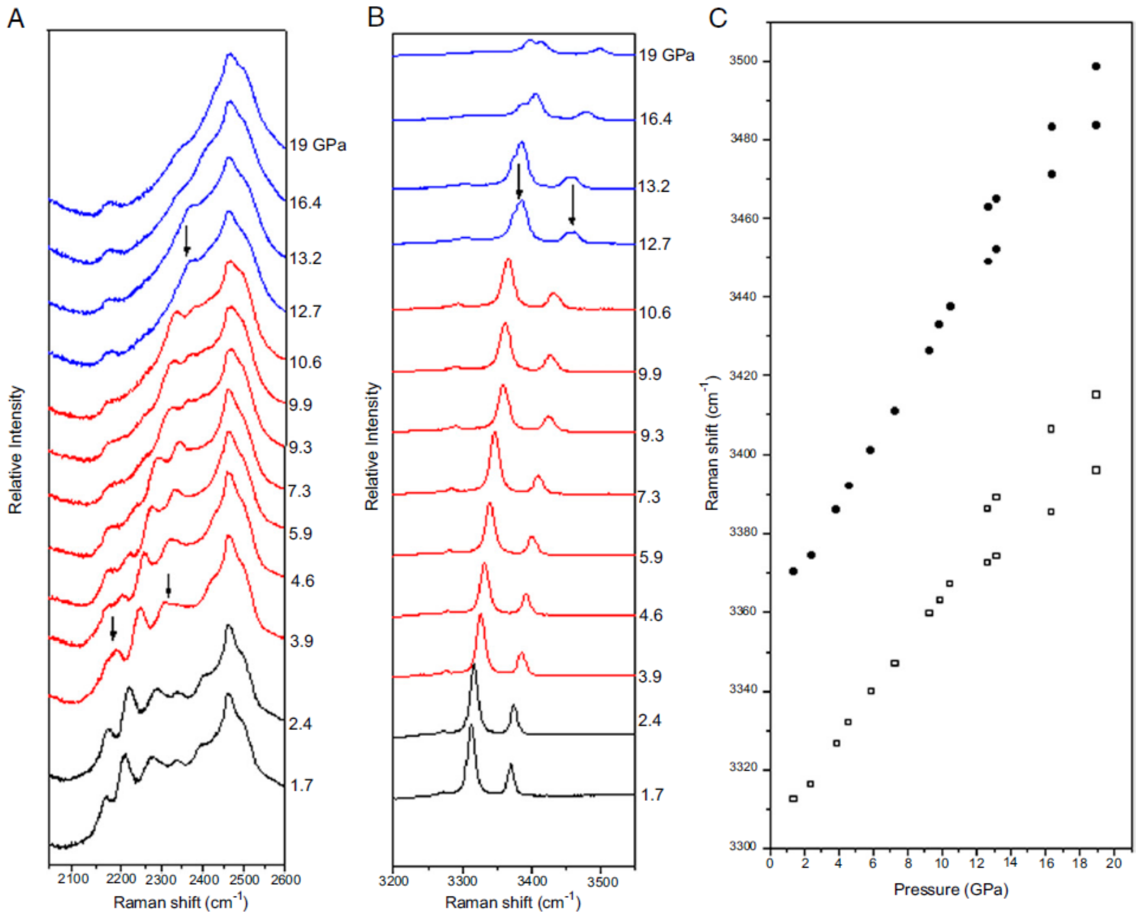

Figure 10. Evolution of N-H and B-H stretching modes at high pressure: B-H (A) and N-H (B) stretching modes, arrow (↓) indicates the position of merging and/or splitting of Raman modes. (C) Pressure dependence of Raman shift of N-H stretching modes.

- *Behavior of decomposed ammonia borane at high pressure*

High pressure behavior of ammonia borane after thermal decomposition was studied by Raman spectroscopy at high pressure up to 10 GPa using diamond anvil cell (DAC). The ammonia borane was decomposed at around 140 degree Celsius under the pressure of ~0.7 GPa. Raman spectra show the hydrogen was desorbed within 1 hour. The hydrogen was sealed in DAC well and cooled down near to room temperature. Raman shift of N-H stretching of the decomposed product as a function of pressure up to ~10 GPa indicates loss of dihydrogen bonding after the decomposition (Sun *et al.* 2015) by the evidence of their pressure-induce blueshift (Figure 11).

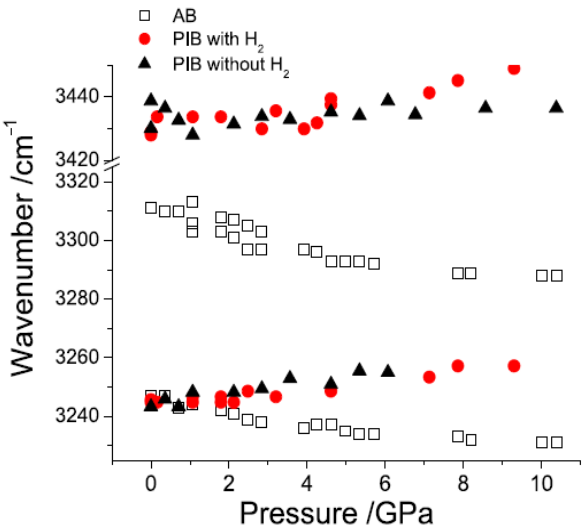

Figure 11. Pressure dependence of the N-H stretching Raman modes of ammonia borane and its first step decomposition product poly-amidoborane (PAB) and second step decomposition product poly-imidoborane (PIB). N-H stretching mode of ammonia borane shows a refshift with increasing pressure, a characteristic feature for dihydrogen bounding, whereas those of PAB and PIB show blueshift.

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