

IV.H.19 Influence of Pressure on Physical Property of Ammonia Borane and its Re-Hydrogenation

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Objectives

- Understand pressure influence on the structure, phase stability, dehydrogenation of ammonia borane and its derivative through in situ study using X-ray diffraction and Raman spectroscopy.
- Study pressure influence on the rehydrogenation after thermolysis of ammonia borane and its derivative to explore the possibility of pressure induced rehydrogenation.

Technical Barriers

Ammonia borane-based chemical hydrogen storage materials have high hydrogen density (gravimetric and volumetric) with slow discharge rate and nearly irreversibility. Characterizing the materials under high pressure so that we can understand the stability of the materials and reversibility of their discharge process is not trivial.

Abstract

Behavior of ammonia borane under high pressure up to 20 GPa and temperature from 80–350 K has been studied using Raman spectroscopy/X-ray diffraction and diamond anvil cell. 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 ~ 0.5 GPa and ~ 9.7 GPa respectively, and the temperature induced transformation from 217 K to 195 K 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.

Progress Report

Improved in situ X-ray diffraction patterns of ammonia borane have been collected at high pressure up to 15 GPa and room temperature. These data are of much higher quality with respect to our earlier diffraction study, and confirm two structural phase transitions at pressures about 1 GPa ($I4mm$ to $Cmc2_1$) and 12 GPa ($Cmc2_1$ to $P2_1$) respectively (Figure 1) (Lin et al. 2012). All other phase changes (e.g. at 5 GPa and 8 GPa) (Lin et al. 2008; Xie et al. 2009) observed in Raman spectroscopy are apparently of second order transition.

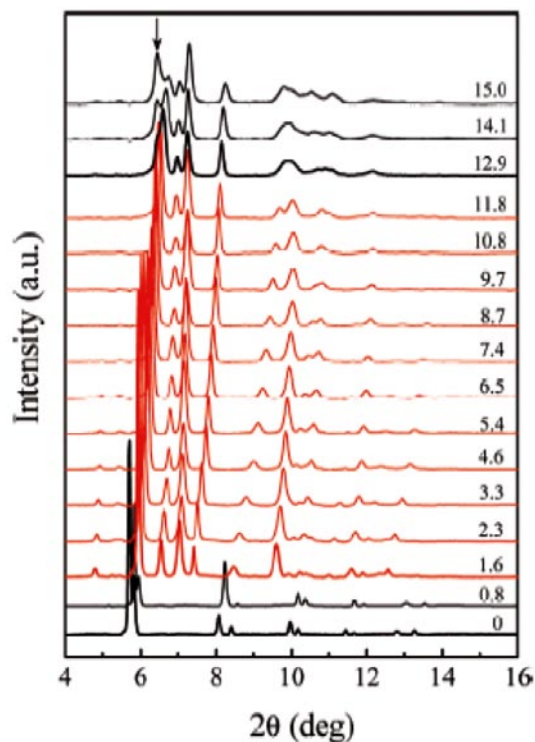


FIGURE 1. X-ray diffraction of ammonia borane at high pressures collected at APS (Lin et al. 2012)

In situ Raman spectra of ammonia borane have been collected at high pressure up to 12 GPa and temperature from 80 K to 350 K. Figure 2 and Figure 3 show the phase relation above and below room temperature respectively. Within the orthorhombic ($Cmc2_1$) structure stability field, there are two possible second order phase transitions above room temperature (Figure 2). At low temperature, four new phases are observed in the Raman scattering (Figure 3). 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.

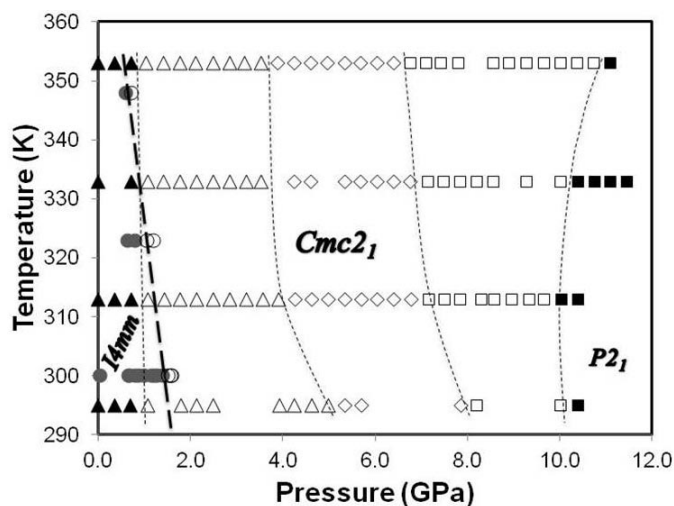


FIGURE 2. Phase boundary of ammonia borane at high pressure and elevated temperature. Solid and open circles represent $I4mm$ and $Cmc2_1$ phases respectively, determined by X-ray diffraction. Solid triangles and squares represent $I4mm$ and $P2_1$ phases respectively, determined by Raman spectroscopy. Open symbols between $I4mm$ and $P2_1$ phases represent $Cmc2_1$ phase.

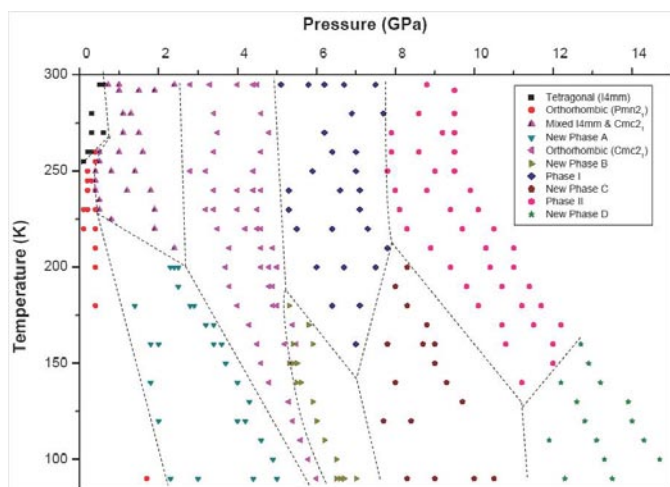


FIGURE 3. Phase boundary of ammonia borane at high pressure and low temperature determined by Raman spectroscopy

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 borane (Xiong et al. 2008) 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. Compared to the result with MCM-41 (Kim et al. 2009), 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 nanoconfinement on pressure induced phase transitions is also observed using Raman spectroscopy. The phase boundary between the 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.

Remarkably, confining ammonia borane makes it possible to reverse its thermolysis process by applying high pressure to the system. The result is more promising for the case of lithium amidoborane (to be published). In situ Raman spectroscopy study on lithium amidoborane indicates that the sample experiences two phase transition at high pressure up to 19 GPa (Figure 4). The first transition is observed about 3 GPa for peak splitting at $2,175$ cm^{-1} and peak merging at $2,300$ cm^{-1} , and the second phase transition is observed at about 12 GPa for peak splitting at $3,375$ cm^{-1} and 3450 cm^{-1} (Figure 5).

Future Directions

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.

References

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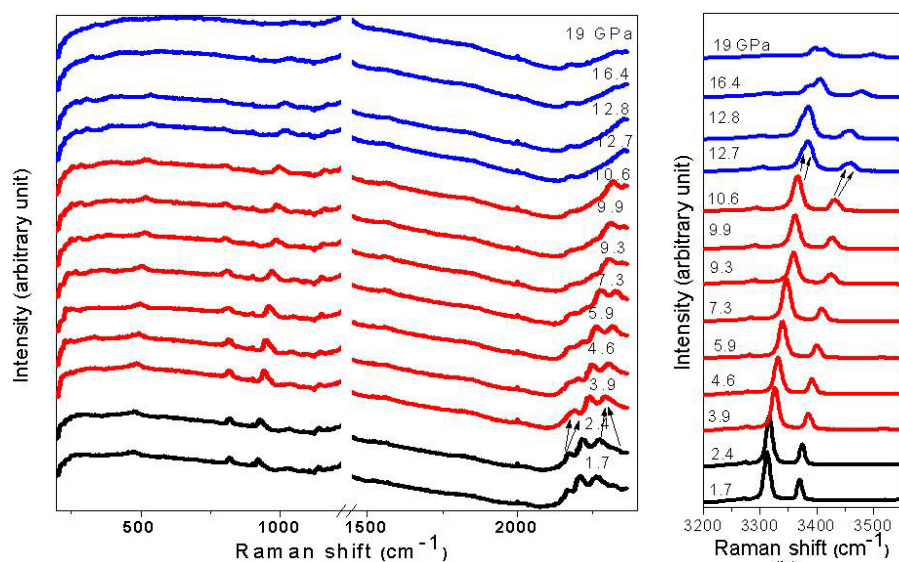


FIGURE 4. High Pressure Raman Spectra of lithium amidoborane. Numbers next to the spectra indicate the pressure in GPa.

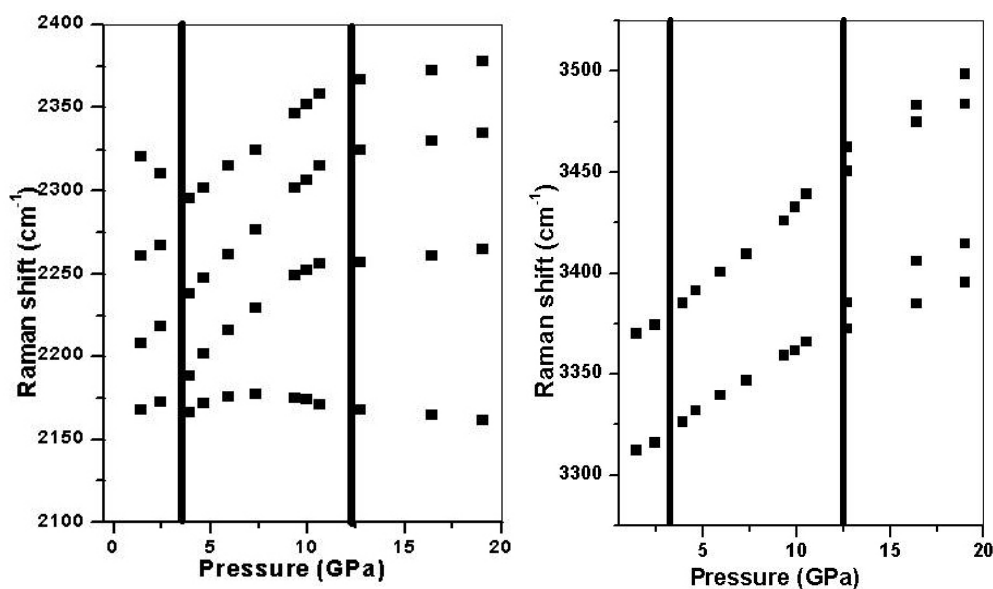


FIGURE 5. Pressure dependence of Raman peaks of lithium amidoborane. Bold lines indicate the phase boundaries where change of slope, merging or splitting of peaks occurs.

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