IV.I.15 Influence of Pressure on Physical Property of Ammonia Borane and its Re-Hydrogenation

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Accomplishments

Characterization of the High Pressure Phase Discovered During the First Year

The newly discovered high pressure phase (at $P > 1.3$ GPa) has been indexed with a monoclinic symmetry. Table 1 shows the result of indexing. All the diffraction data of the new phase collected at 1.3, 1.6, 2.1, 3.2, 4.3 GPa were analyzed using Le Bail fitting. An example of the Le Bail analyses is shown in Figure 1. The derived molecular volumes of the new phase (with monoclinic structure and Z=3) at different pressures and those of tetrahedral ammonia borane before the phase transition are plotted in Figure 2. The high pressure phase is about 7% denser and nearly twice incompressible than the low pressure phase. The bulk modulus of the new high pressure phase is K=21±5 GPa while low pressure phase has K=9.6±0.9 GPa.

TABLE 1. Indexing of the pressure phase of ammonia borane at 4.3 GPa with monoclinic unit cell: a=6.8551 Å, b= 4.5495 Å, c=5.0612 Å, β=95.516°, V=157.13 $Å^3$

h	k	l	d_{cal}	d_{obs}	d_{obs}-d_{cal}
0	1	1	3.3766	3.3909	0.0143
2	0	0	3.4120		-0.0211
1	1	-1	3.1062	3.1147	0.0085
2	0	-1	2.9590	2.9651	0.0061
2	0	1	2.7078	2.7159	0.0081
2	1	1	2.3269	2.3210	-0.0059
3	0	-1	2.1514	2.1467	-0.0048
0	2	1	2.0732	2.0735	0.0003
1	2	-1	2.0057	2.0066	0.0009
2	1	2	1.7847	1.7847	0.0000
3	2	0	1.6085	1.6000	-0.0084

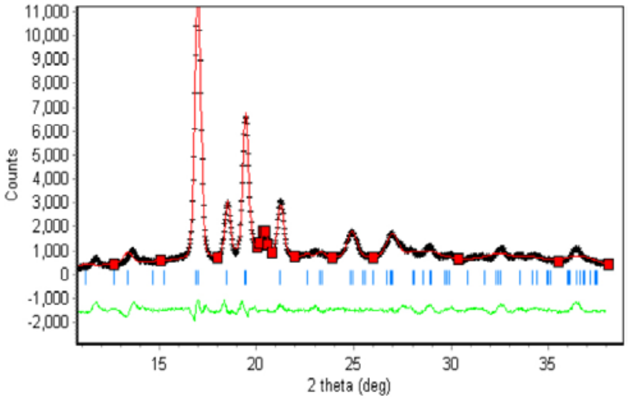

FIGURE 1. Le Bail fiting of the X-ray diffraction pattern of H_3BNH_3 at 5.3 GPa. Crosses: observed data; red line: calculated data, bars: expected diffraction lines, green line: difference between observed and calculated data

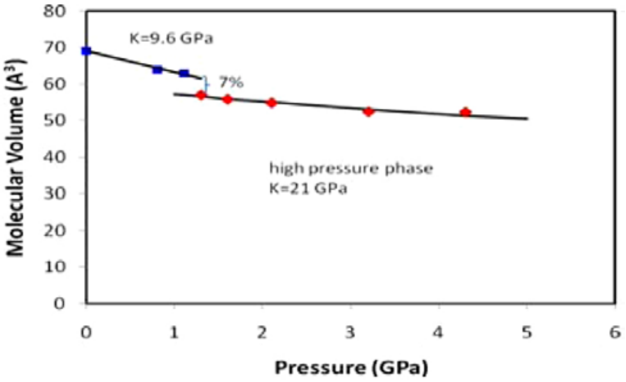

FIGURE 2. Derived molecular volume of H_3BNH_3 as a function of pressure. Z=3 for the high pressure monoclinic phase.

Rehydrogenation of Ammonia Borane at High Pressures

Possibility of pressure induced rehydrogenation for decomposed ammonia borane was investigated using in situ Raman spectroscopy and X-ray diffraction. Ammonia borane sample was loaded in a diamond anvil cell. The pressure was slightly raised to generate a close system (sealed system) to retain the hydrogen released during decomposition. The sample temperature was then increased to start the thermolysis of ammonia borane. The decomposed products were quenched to ambient temperature, and then subject to further pressurization.

Figure 3 shows the X-ray diffraction patterns collected during the experiment. The sample was

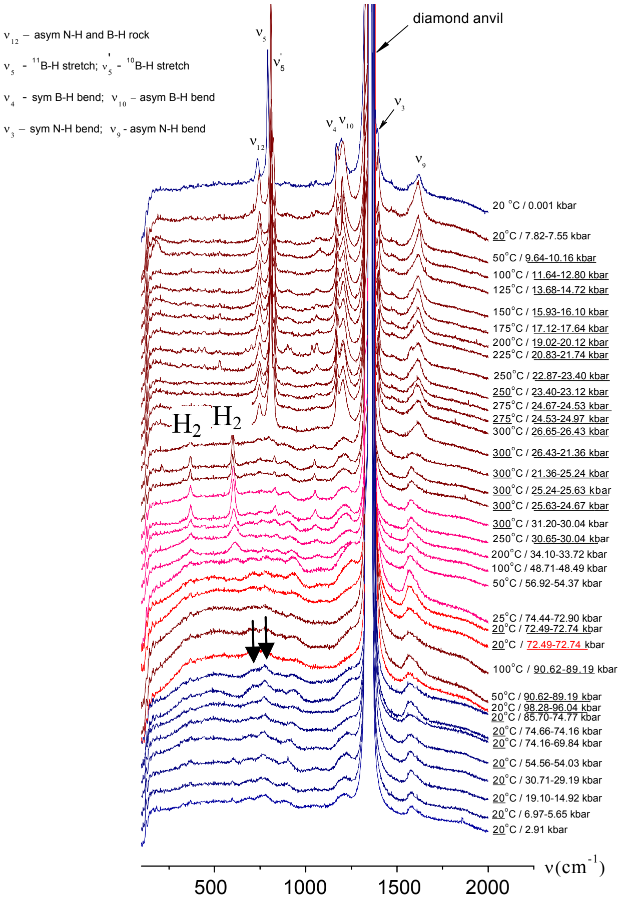

FIGURE 3. Raman spectra of ammonia in a close system (DAC cell) during heating and compression. Data sequence starts from the top spectrum at ambient conditions, and follow by increasing in temperature at 0.8 GPa to 300°C, and then compression after cooling. (: vibration modes from ammonia borane, H_2: vibration from molecular hydrogen)

heated at 0.3 GPa up to 150°C, at which diffraction peaks from ammonia borane phase totally vanished. The sample was then quenched and compressed up to 9 GPa. At 8.1 GPa, weak peaks appeared at the location where ammonia borane diffraction peaks are expected. Nevertheless, intensities of these peaks were very weak comparing to the diffraction from initial ammonia borane sample in the cell. Similar experiments were conducted using Raman spectroscopy. Figure 4 shows the Raman spectra of B-H and N-H vibration regions during the heating and compression. The strongest peak at about 1,350 cm^{-1} is from diamond anvil. The sample was heated at 0.8 GPa (8 kbar), up to 300°C. B-H and N-H rocking (12), B-H stretching peaks (5 and 5') totally disappeared when temperature was increased to 300°C, companied by appearance of H_2 molecule vibration. Upon compression to about 10 GPa (~98 kbar), these peaks came back with significantly weakened intensities.

These experiments indicate that pressure might promote the reversal of the thermolysis process.

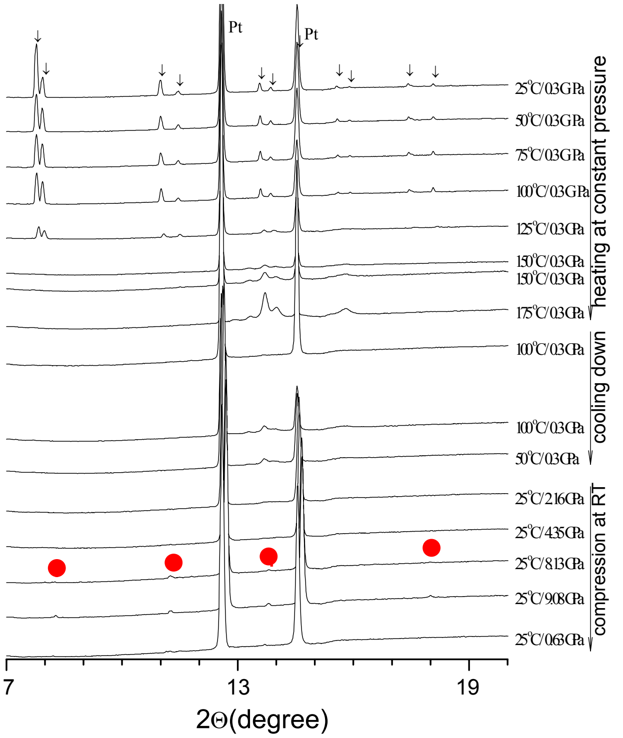

FIGURE 4. X-ray diffraction patterns of ammonia borane during heating (starts from top spectrum) and compression. Arrows represent peaks from ammonia borane. Dots indicate possible re-occurrence of the ammonia borane peaks.

Possible leak of the released hydrogen (evidenced by weakening of the H_2 molecule vibration peaks) may give rise to the extremely weak signal of the reversed process.

Study of Possible Formation of New Phase that Contains Higher Hydrogen Content than Ammonia Borane at High Pressure

To explore possible phase that may contain more hydrogen than ammonia borane, we have conducted experiments to study the reaction of ammonia borane and hydrogen at high pressures (Part of the work was led by Wendy Mao of the Stanford University team). Ammonia borane was loaded in a diamond anvil cell with high pressure hydrogen gas (~2 kbar). The sample was them compressed to high pressures. Figure 5 show comparison of the X-ray diffractions between the samples loaded with and without hydrogen gas (labeled as AB-H_2 and pure AB respectively) at about 9 GPa. A significant difference in the diffraction patterns between the two samples was observed, indicating a possible reaction between ammonia borane and H_2 at high pressure. This reaction is anticipated to produce a phase with higher hydrogen content than ammonia borane. Raman spectroscopy conducted at FIU also indicates some changes in the spectra when mixture of ammonia borane and H_2 undergoes high pressure (Figure 6). The broad peak at 2,900 cm^{-1} is expected

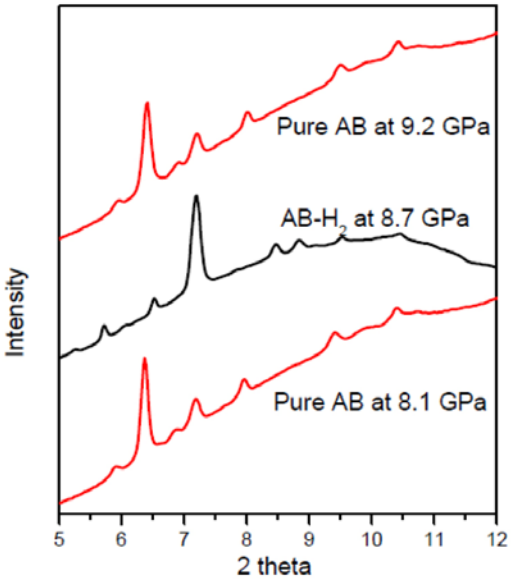

FIGURE 5. Comparison of X-ray diffraction patterns from ammonia borane + hydrogen gas and from pure ammonia borane in a diamond anvil cell at high pressure.

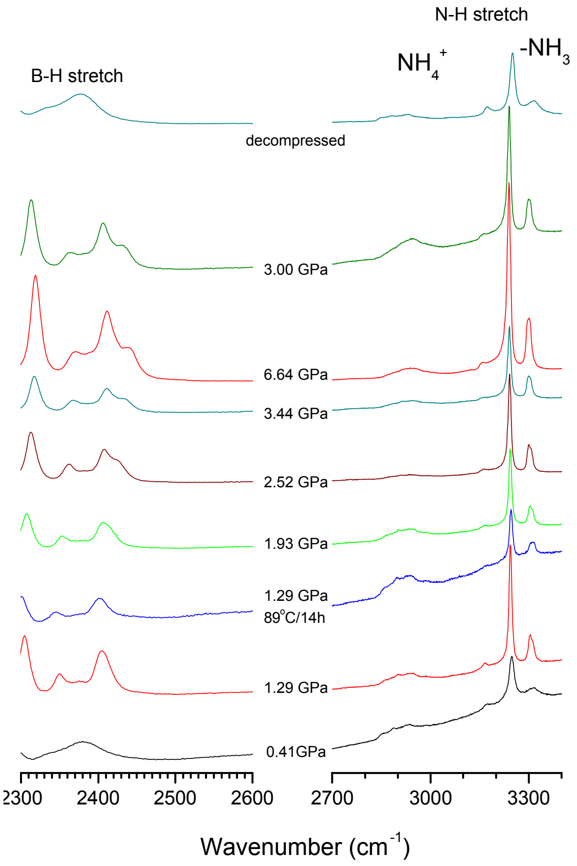

FIGURE 6. Raman spectra of ammonia borane + hydrogen gas in a diamond anvil cell at high pressure. Sample was heated up to 89°C after initial loading. NH_4^+ indicate possible formation of NH_4^+ species in the sample.

to be caused vibrations of NH_4^+ group. If such an assignment is valid, this indicates that the reaction between ammonia borane and molecular hydrogen yields NH_4^+ containing species.

Study of Ammonia Borane at Low Temperature and High Pressure

Stability of ammonia borane at low temperature and high pressure was investigated using in situ X-ray diffraction. A diamond anvil cell loaded with ammonia borane sample was placed in a helium cryostat. The whole cell is cooled from ambient temperature down to 9.5 K. X-ray diffraction from ammonia borane sample was collected during cooling. Phase transition from the tetragonal to orthorhombic structure was observed at

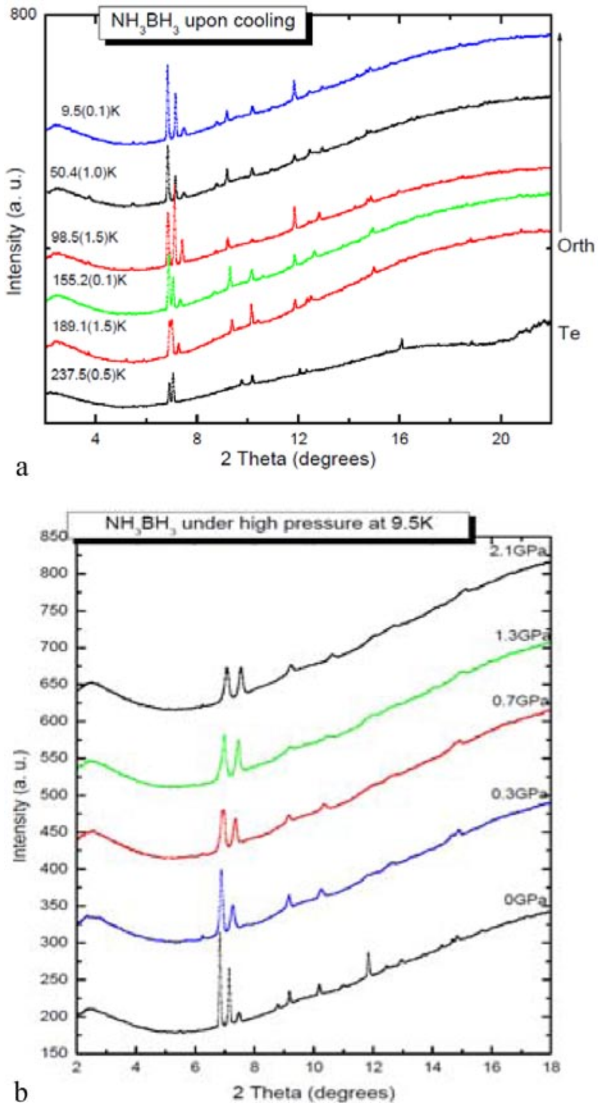

FIGURE 7. X-ray diffraction patterns of ammonia borane in a diamond anvil cell during (a) cooling and (b) compression at low temperature (9.5 K). The phase transition from tetragonal to orthorhombic structure happens at 189 K.

189 K (Figure 7a). The orthorhombic phase is stable till 9.5 K. Compress of the sample at 9.5 K did not produce any other phase transformation up to 2.1 GPa (Figure 7b).

Influence of Metal Substitution in Ammonia Borane

One issue in the reversibility of the thermolysis process is polymerization of decomposed product, -(H_2BNH_2)-$_n$. Substitution of H by alkali metals might be helpful. We have tried to substitute H with Li, Na and Mg by ball milling mixture of H_3BNH_3 and LiH (1:1 mole ratio), H_3BNH_3 and NaH (1:1 mole ratio), H_3BNH_3, NaH and LiH (2:1:1 mole ratio), H_3BNH_3, LiH and MgH_2 (3:1:1 mole ratio). Figure 8 shows the X-ray diffraction patterns of the products. Ball milling (1-2 hr) mixture of H_3BNH_3 and LiH produces LiH_2BNH_3. In the case of H_3BNH_3 and NaH, NaH_2BNH_3 can by produced by ball milling, but decomposition NaH_2BNH_3 may occur during over time (>1 hr) ball milling. An unreported phase was produced from the mixture of H_3BNH_3, LiH and MgH_2. Chemistry and structure of this new phase is under investigation.

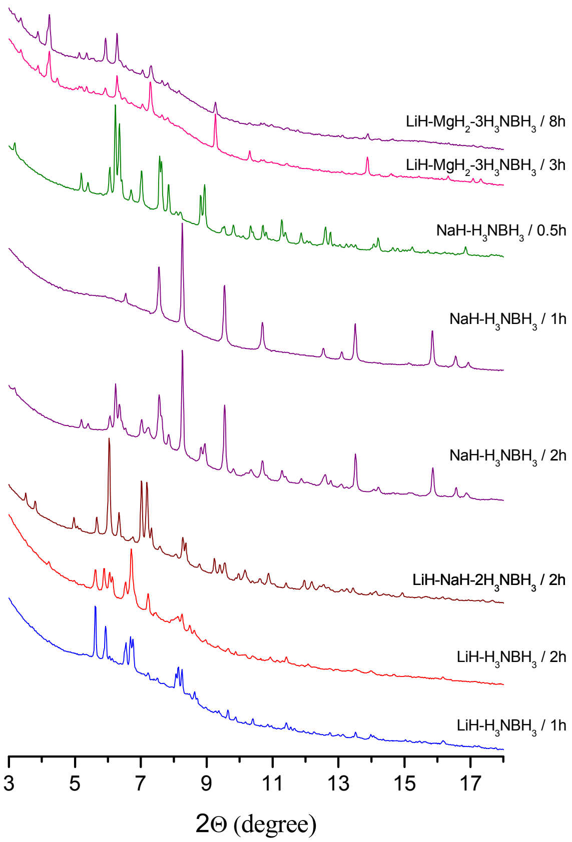

FIGURE 8. X-ray diffraction patterns of samples after ball milling. The starting composition and ball milling time are indicated in the next to the patterns.

Thermogravimetric measurements (Figure 9) show that LiH_2BNH_3 releases hydrogen at a lower temperature with regard to H_3BNH_3. The new phase formed from H_3BNH_3, LiH and MgH_2 loses more than 30% weight upon heating to 170°C (Figure 10). Likely certain amount of NH_3 is released during the heating.

Other Related Studies on Boron Compounds and Metal Hydrides

We also investigated regeneration of ammonia borane through other boron compounds. Previous studies showed that the treatment of B–O species with strong reducing agents such as sodium hydride can lead to the formation of B–H bonds, as demonstrated in the well-known Schlesinger process for the synthesis of $NaBH_4$ from $B(OH)_3$. This process is however neither

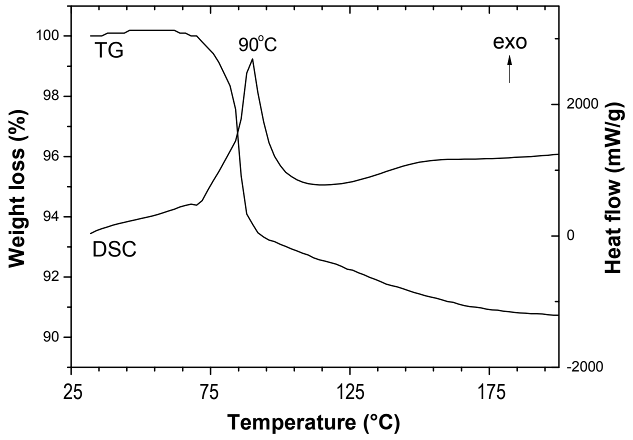

FIGURE 9. Result of thermogravimetric measurement of LiH_2BNH_3. TG curve is plotted on the primary axis and DSC is plotted on the secondary axis.

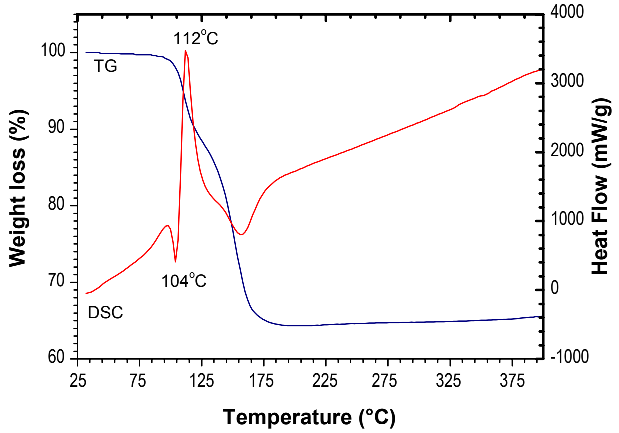

FIGURE 10. Result of thermogravimetric measurement of ball milling product from H_3BNH_3, LiH and MgH2 (3:1:1 mole ratio). Axis note is the same as Figure 9.

efficient nor optimal. An effort led by Yusheng Zhao of the Los Alamos team was made to explore a new approach of ammonia borane regeneration from the $B(OH)_3$ using high H_2 pressure with the reaction shown below:

$$B(OCH_3)_3(l) + 3NH_3(l) + 3H_2(g) \xrightarrow{200MPa,\ 320K} NH_3BH_3 + CH_3OH$$

This work is currently underway, and the reaction product is to be characterized by XRD. We also plan to use catalysis such as Pt to convert the high-pressure H_2 into hydrogen atoms, a process that can conceivably optimize the regeneration reaction.

Behavior of boron, boron suboxide, $NaBH_4$, $BH_3N_2H_4$ and metal hydrides e.g. Mg_2FeH_6 and AlH_3 at high pressures were also investigated. Due to the limited space, here we describe a summary for $NaBH_4$ and AlH_3 as examples. We have studied structural stability of $NaBH_4$ under high pressures up to 14 GPa (temperatures up to 425°C) using in situ X-ray diffraction and 27 GPa (ambient temperature) using in situ Raman spectroscopy. An extended high P-T phase diagram is constructed (Figure 11). Bulk modulus, its temperature derivative and thermal expansion coefficient for the cubic phase are found to be 17.5(5) GPa, -0.0137 GPa/K and 12.06 x 10-5+ 26.75x10-8T, respectively. In situ X-ray diffraction of AlH_3 at high pressures revealed a new structural phase transition from γ-AlH_3 at 13.5 GPa (Figure 12). Among the three forms of AlH_3 (α, β, γ) that can be produced at ambient conditions, α-AlH_3 did not transform to this new phase upon compression. Compressibility of the three phases were also measured (Figure 13).

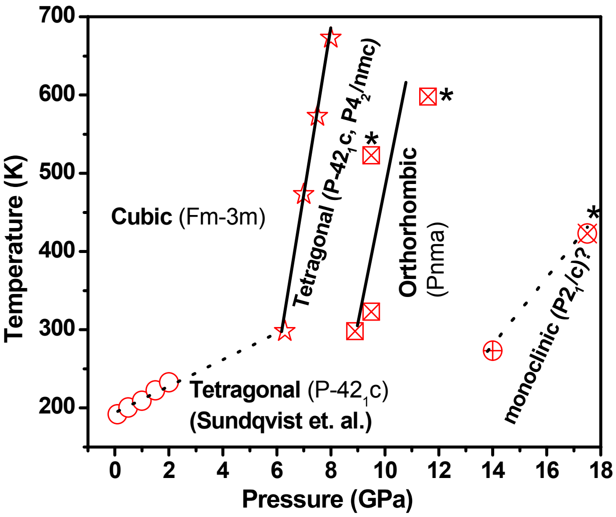

FIGURE 11. Derived phase diagram of $NaBH_4$ from in situ X-ray diffraction and Raman spectroscopy.

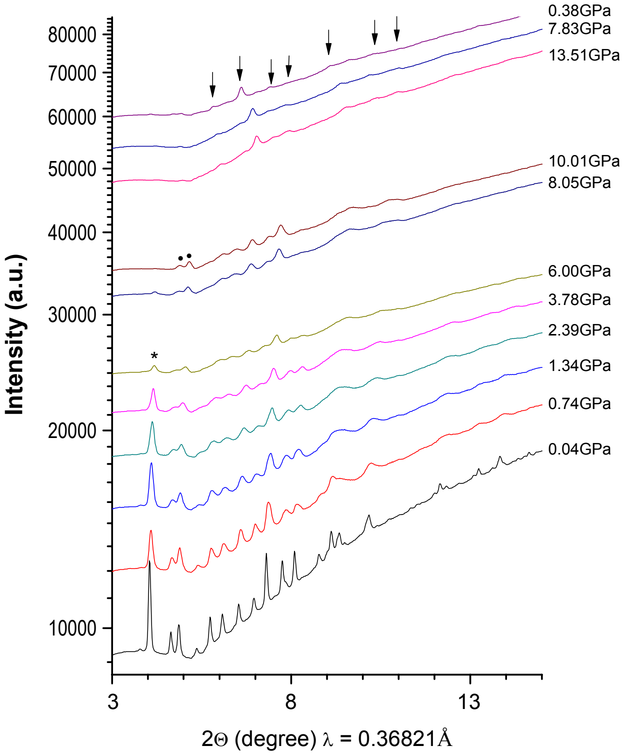

FIGURE. 12. X-ray diffraction of AlH_3 during compression. Symbols "*" and "•" marks the strongest peaks of β-AlH3 and γ-AlH_3 phases, respectively, arrows show peaks of the new high pressure phase.

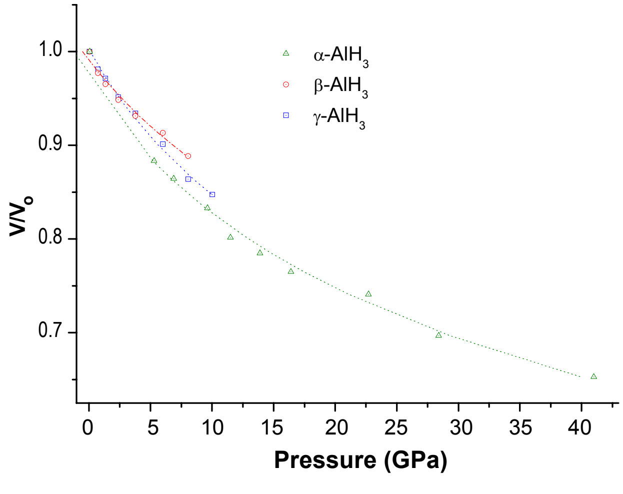

FIGURE 13. Volume (V/V_0) of α-, β- and γ-AlH_3 as a function of pressure, derived from in situ X-ray diffraction.

A List of Papers in which DOE Support is Acknowledged

Journals:

1. Yu Lin, Wendy L. Mao, Vadym Drozd, Jiuhua Chen, and Luke L. Daemen, Raman spectroscopy study of ammonia borane at high pressure, Journal of Chemical Physics 129, 234509 (2008).
2. Jiuhua Chen,YunpengYang, TonyYu, Jianzhong Zhang,Yusheng Zhao and Liping Wang, Strength measurement of boron suboxide B_6O at high pressure and temperature using in situ synchrotron X-ray diffraction, *High Pressure Research*, 28(3), 423-430 (2008).
3. Lyci George, Vadym Drozd, Andriy Durygin, Jiuhua Chen, Surendra K. Saxena, Bulk modulus and thermal expansion coefficient of mechanochemically synthesized Mg2FeH6 from high temperature and high pressure studies, International Journal of Hydrogen Energy 34 (2009) 3410 – 3416.
4. Artem R. Oganov, Jiuhua Chen, Carlo Gatti, Yanzhang Ma, Yanming Ma, Colin W. Glass, Zhenxian Liu, Tony Yu, Oleksandr O. Kurakevych, and Vladimir L. Solozhenko, Ionic high-pressure form of elemental boron, Nature 457, 863-867, doi:10.1038/nature07736 (2009).

Presentations:

1. Jiuhua Chen, Vadym Drozd and Luke Daemen, Pressure Induced Phase Transition in Ammonia Borane, presentation at *Advances in High-Pressure Science Using Synchrotron X-rays Workshop*, Upton, New York, October 4, 2008.
2. Yu Lin, Wendy Mao and Jiuhua Chen, Raman spectroscopic studies of ammonia borane at high pressure, presentation at *2008 COMPRES annual meeting*, Colorado Springs, Colorado, June 25–28, 2008.
3. Jiuhua Chen, Vadym Drozd and Surendra Saxena, Amonia Borane as Hydrogen Storage Material, presentation at Hydrogen Storage Symposium of the Fifth International Meeting of the Study of Matter at Extreme Conditions, Miami - Western Caribbean. March 28 – April 2, 2009.

A List of People Working on the Project – Graduate Students, Postdocs, Visitors, Technicians

Graduate students:

Srinija Rappel (50%)
Jennifer Girard (50%)
Yu Lin (travel support)

Associate:

Jozsef Garai (50%)

Postocs:

Helene Couvy (80%)
Vadym Drozd (80%)

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*References are not listed due to the space limit