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 \( K=21\pm5 \) GPa while low pressure phase has \( K=9.6\pm0.9 \) GPa.

<table>
<thead>
<tr>
<th>( h )</th>
<th>( k )</th>
<th>( l )</th>
<th>( d_{\text{cal}} )</th>
<th>( d_{\text{obs}} )</th>
<th>( d_{\text{obs}}-d_{\text{cal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3.3766</td>
<td>3.3909</td>
<td>0.0143</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3.4120</td>
<td>-0.0211</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>3.1062</td>
<td>3.1147</td>
<td>0.0085</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>-1</td>
<td>2.9590</td>
<td>2.9651</td>
<td>0.0061</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>2.7078</td>
<td>2.7159</td>
<td>0.0081</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2.3269</td>
<td>2.3210</td>
<td>-0.0059</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>2.1514</td>
<td>2.1467</td>
<td>-0.0048</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>1</td>
<td>2.0732</td>
<td>2.0735</td>
<td>0.0003</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>-1</td>
<td>2.0057</td>
<td>2.0066</td>
<td>0.0009</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1.7847</td>
<td>1.7847</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0</td>
<td>1.6085</td>
<td>1.6000</td>
<td>-0.0084</td>
</tr>
</tbody>
</table>

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...
Possible leak of the released hydrogen (evidenced by weakening of the \( \text{H}_2 \) 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 then compressed to high pressures. Figure 5 shows 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 \( \text{H}_2 \) 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 \( \text{H}_2 \) undergoes high pressure (Figure 6). The broad peak at 2,900 cm\(^{-1}\) is expected...
to be caused vibrations of \( \text{NH}_4^+ \) group. If such an assignment is valid, this indicates that the reaction between ammonia borane and molecular hydrogen yields \( \text{NH}_4^+ \) 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 189 K.

**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. \( \text{NH}_4^+ \) indicate possible formation of \( \text{NH}_4^+ \) species in the sample.

**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, \(-\text{H$_2$BNH$_2$}\). 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$_2$BNH$_2$, LiH (1:1 mole ratio), H$_2$BNH$_2$ and NaH (1:1 mole ratio), H$_2$BNH$_2$, NaH and LiH (2:1:1 mole ratio), H$_2$BNH$_2$, 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$_3$BNH$_3$ and LiH produces LiH$_2$BNH$_3$. In the case of H$_3$BNH$_3$ and NaH, NaH$_2$BNH$_3$ can be produced by ball milling, but decomposition NaH$_2$BNH$_3$ may occur during over time (>1 hr) ball milling. An unreported phase was produced from the mixture of H$_3$BNH$_3$, LiH and MgH$_2$. Chemistry and structure of this new phase is under investigation.

Thermogravimetric measurements (Figure 9) show that LiH$_2$BNH$_3$ releases hydrogen at a lower temperature with regard to H$_3$BNH$_3$. The new phase formed from H$_3$BNH$_3$, 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
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:

\[
B(OCH_3)_3(l) + 3NH_3(l) + 3H_2(g) \rightarrow 200\text{MPa}, 320\text{K} \rightarrow \text{NH}_3BH_3 + \text{CH}_3OH
\]

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$_2$N$_2$H$_4$ and metal hydrides e.g. Mg$_2$FeH$_6$ 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} + 26.75 x 10^{-8}T, 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](image1.png)

**FIGURE 11.** Derived phase diagram of NaBH$_4$ from in situ X-ray diffraction and Raman spectroscopy.

![Figure 12](image2.png)

**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](image3.png)

**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:


Presentations:


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%)

*The experiments were conducted at the Advanced Photon Source of Argonne National Lab, National Synchrotron Light Source of Brookhaven National Lab, Cornell High Energy Synchrotron Source (CHESS) in Cornell University, Los Alamos National Lab, Stanford University and Florida International University by the collaboration team of the project.

*References are not listed due to the space limit