Behavior of Decomposed Ammonia Borane at High Pressure

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Abstract: 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 at ~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. Applying higher pressure up to ~10 GPa indicates interactions between the products and loss of dihydrogen bonding. No rehydrogenation was detected in the pressure range investigated.

Keywords: Inorganic compounds; Raman spectroscopy; Phase transitions; Thermodynamic properties; High pressure

Introduction

Ammonia borane [1] [2] is considered to be a very promising on-board hydrogen storage material because of its high hydrogen density (19.6 wt% of hydrogen) and mild hydrogen releasing conditions [1, 3]:

However, there are several barriers to overcome to take this hydrogen storage material into application. One of the barriers is the low hydrogen desorption rate. Recently, hydrolysis [4-7], nano confinement [8-16], acid initiation [17], ionic liquids [6], and other methods have been reported to decrease the decomposition temperature and increase the hydrogen desorption rates.

Another barrier is low or non-rechargeability of ammonia borane after dehydrogenation. Pressure is an important tool for hydrogen storage [18-20]. Although it has been reported that ammonia borane can hardly be rehydrogenated directly after decomposition by high pressure [21], Lin's group successfully used high pressure put more extra hydrogen into ammonia borane at room temperature [19]. On the other hand, interactions between BNH compounds and hydrogen under high pressure [22-24] were detected by Raman studies, which impose possibilities to recharge hydrogen back into decomposed ammonia borane. To study the mechanism of decomposition and interaction between NBH compounds and hydrogen, some fundamental research should be conducted first. While a lot of work has already been reported, many issues such as the detailed decomposition mechanism, the rehydrogenation property, and the dihydrogen bonding effect still remain unclear. So study the behavior between the NBH compounds and hydrogen at high pressure is still meaningful. Previous studies of ammonia borane has been focused on infrared (IR) and Raman spectroscopy [19, 20, 25-28], X-Ray diffraction [29-31], nuclear magnetic resonance (NMR) [14, 32], theoretical computation [30, 33-35], neutron scattering [36-39], and anelastic spectroscopy [40], etc. Pressure influence on the crystal structure evolution of ammonia borane has been recently reviewed [41]. Here we report our study on the high pressure behavior between decomposed ammonia borane, which are first-step decomposition product poly-amidoborane (PAB) and second step decomposition product poly-

imidoborane (PIB), interacted with hydrogen in DAC using in situ Raman spectra.

Experiment

The ammonia borane, NH_3BH_3 , sample was purchased from Sigma-Aldrich Co. and was used without any additional purification. The sample was loaded in the Mao-Bell type diamond anvil cell (DAC) with a culet size of 400 μm . Sample chamber was a hole of 150-200 μm in diameter and 60-80 μm in thickness in the stainless steel or beryllium-copper alloy foil. No pressure transmitting medium was used [21]. Ruby chips were loaded in the sample chamber as well for pressure calibration. Ruby fluorescence method with temperature correction [42, 43] was used to determine the pressure inside the DAC.

Fig. 1 The experimental system used in the high pressure and high temperature experiments. a: asbestos; b: heater; c: DAC cylinder; d: DAC piston; e: Diamond anvil seats; f: first thermocouple; g: asbestos; h: gasket; i: sample; j: diamond anvil; k: second thermocouple.

As shown in fig. 1, high temperature in DAC was achieved using a resistive nichrome toroidal-type heater surrounding the outside of DAC. The temperature was measured using two K-type thermocouples: the first one is positioned near the sample chamber in contact with the diamond anvil, and the second one was positioned near the heater for temperature control. The sample temperature is reflected by the first thermocouple, which is 20-40 $^{\circ}\text{C}$ lower than the second one due to the temperature gradient between the heater and diamond. The temperature was controlled using a Delta DTB4824 thermal controller. The cell was isolated from surrounding using several layers of thermal insulation (asbestos) and kept at the desired temperatures within $\pm 2^{\circ}\text{C}$. Raman spectra were recorded in the back-scattering configuration. An argon ion laser (Ar^+) operated at ~ 108 mW of power was used to excite the sample. The scattering signals were collected with an exposure time of 2 min using a high throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Andor).

After the closure of the DAC, the ammonia borane sample was heated to $\sim 140^{\circ}\text{C}$ to make sure the first equivalent of hydrogen molecule was released but sealed in the gasket by initial pressure at $\sim 0.7\text{GPa}$. Then the sample was cooled down to room temperature and the pressure was increased step

by step with an interval of ~ 0.7 GPa. At each compression step, pressure was held for a few minutes before any measurement. Ruby fluorescence from ruby chips at different location in the sample chamber indicates that the pressure in the cell is nearly hydrostatic although we did not use any pressure medium. The Raman spectra of the sample at room temperature and ambient pressure agree well with previous study.

Result and discussions

Similar to the previous work[20, 28], the Raman spectra we collected were analyzed separately in several regions: NH stretching (NH str.) region (3150 cm^{-1} - 3350 cm^{-1}), BH stretching (BH str.) region (2250 cm^{-1} - 2550 cm^{-1}), BN stretching (BN str.) region (700 cm^{-1} - 1000 cm^{-1}), BH bending (BH ben.) region (1150 cm^{-1} - 1300 cm^{-1}), NH bending (NH ben.) region (1450 cm^{-1} - 1700 cm^{-1}).

As shown in fig. 2, ammonia borane was decomposed after heated to $\sim 140^\circ\text{C}$ for 1 hour. The second spectrum from top shows the Raman shifts of decomposed products cooled to room temperature, which contains first step decomposition product poly-amidoborane (PAB), second step decomposition product poly-imidoborane (PIB) and molecular hydrogen. It has been declared that the byproducts (such as diborane, borazine and ammonia) could be decomposed from ammonia borane at ambient pressure, but we did not see obvious peaks of these by products from our Raman study at $\sim 0.7\text{GPa}$. At $\sim 140^\circ\text{C}$, 1 equivalent of hydrogen molecule was estimated to be decomposed from ammonia borane and we did see the strong hydrogen peaks (S and Q modes) at ~ 580 and $\sim 4300\text{ cm}^{-1}$, however, while the growing of N-H stretching mode $\nu_s(\text{NH}_2)$ from PAB, we also found the N-H stretching mode $\nu_s(\text{NH})$ mode from PIB [23, 24] indicating the occurrence of the second step decomposition. After the second spectrum, the spectra from top to bottom show the Raman shifts of the products dependent as a function of pressure. No rehydrogenation (reappearance of characteristic Raman peak) of ammonia borane was observed. But a new peak near the Q(1) mode of hydrogen was observed at high pressure, in addition to the intensity decrease of the hydrogen peaks. This new peak did not disappear even after the pressure was decreased near to ambient pressure when the cell was opened. The location of this new peak is consistent with previous reports[23, 24]. As we estimated, the peak was due to interaction between hydrogen and decomposed ammonia borane in their interface, which indicates even though the products of PAB and PIB cannot be rehydrogenated by chemistry reaction, they can still absorb hydrogen physically. The physic-sorption effect can be quenched to very low pressure that near ambient condition.

Another important finding that should be mentioned here is the dihydrogen bonding effect, which has been discussed in many Raman studies under high pressure [20, 27, 33, 44, 45]. As a result of B-H $\cdots$ H-N dihydrogen bond [26, 27], the frequency of B-H stretching shifts positively and the frequency of N-H stretching shifts negatively when pressure increases. As a comparison, the high pressure Raman spectra study of neat ammonia borane was also conducted at room temperature up to $\sim 10\text{ GPa}$, as shown in fig. 3, where the N-H stretching region and N-H bending region show negative pressure dependence due to dihydrogen bonding effect. This study was highly consistent with previous reports [18, 20] in terms of Raman peaks position of different modes, and phase transitions were also observed at similar pressures. Contrarily, the peaks in the N-H stretching region (3150 cm^{-1} - 3350 cm^{-1}) and NH bending region (1450 cm^{-1} - 1700 cm^{-1}) of PAB and PIB show positive pressure dependence (fig. 4) within a hydrogen circumstance, other than negative dependence (fig. 3) of neat ammonia borane or no dependence as previous reported[23, 24]. The previous reports which declared no dependence may due to lack of high pressure data since they only compressed the sample up to 3 GPa. This phenomenon shows the di-hydrogen effect was lost after the decomposition of ammonia borane.

Fig. 2 Raman spectra of H₂ and Polyiminoborane (PIB) at 20 °C. From top to bottom: the neat ammonia borane and decomposed ammonia borane at different pressures. All the spectra are measured at room temperature in a Mao-Bell type diamond anvil cell. Different modes from ammonia borane (AB), H₂, pAB and diamonds are marked in the first spectrum. pAB: poly-amidoborane; AB: ammonia borane; Ben.: bending; Str.: stretching.

Fig. 3 Raman spectra of ammonia borane as pressure increases from bottom to top. PT1: phase transition 1; PT2: phase transition 2.

For further comparison, we compressed the decomposed PAB and PIB after we open the DAC to release the decomposed molecular hydrogen, as shown in fig. 4. Here, without the hydrogen circumstance, the N-H stretching mode $\nu_s(\text{NH}_2)$ from PAB still shows positive pressure dependence but the slope is much lower, while the N-H stretching mode $\nu_s(\text{NH})$ mode from PIB shows no big difference, which indicates hydrogen indeed interact with PAB and it will affect the N-H bonding of PAB while the similar effect between hydrogen and PIB was not detected. Fig. 5 shows the detailed pressure dependence of the N-H stretching mode from PAB, PIB and ammonia borane. These phenomenon could also be evidences of that the PIB is thermodynamically more difficult to be rehydrogenated than that of PAB.

If we compare the two spectra of neat ammonia borane (fig. 3) and decomposed PAB and PIB (fig. 2 and fig. 4), another interesting phenomena can be detected: while the peaks in the NH stretching region (3150 cm^{-1} - 3350 cm^{-1}) and NH bending region (1450 cm^{-1} - 1700 cm^{-1}) shows only slightly shift with pressure, the peaks in BH stretching region (2250 cm^{-1} - 2550 cm^{-1}) and BH bending region (1150 cm^{-1} - 1300 cm^{-1}) are almost disappeared completely. By these phenomena, we can conclude that the B-H bond is much weaker than N-H bonds and the hydrogen that comes from ammonia borane to form hydrogen molecule are mostly from the broken of B-H bonds. Or there may be another possibility that an intermediate phase, the ionic dimer diammoniate of diborane (DADB)[2, 46], is favored to let B-H bonds other than N-H bonds to be broken first. The Raman spectra showed similar decomposition pathway now that we applied initial pressure at $\sim 0.7\text{ GPa}$, compared to other experiments at near ambient pressures or higher pressures [21, 47, 48]. This uneven decomposition between B-H bonds and N-H bonds is strongly related to the dative bonds in ammonia borane structure due to the difference of the electro-negativity of borane and nitrogen atoms, which is also the reason that the dihydrogen bonding is formed. The broken of B-H bonding can also explain the disappearance of dihydrogen bonding from this view.

Fig. 4 Raman spectra of Ploy-amidoborane and Poly-imidoborane (without H_2) during compression (from bottom up) and decompression.

Fig. 5 Pressure dependence of the N-H stretching mode from PAB, PIB and ammonia borane.

Conclusion

Ammonia borane sample was decomposed at 0.7 GPa and 140 degree Celsius and the decomposed molecular hydrogen, PAB and PIB were detected. Compressing on the decomposed products up to 10 GPa at ambient temperature did not revise the decomposition reaction. We found the PAB and PIB can storage extra hydrogen by physic-sorption. The di-hydrogen bonding effect on pressure dependence of B-H Raman modes was not found whether with or without hydrogen circumstance after decomposition of ammonia borane. Ammonia borane is a promising on-board hydrogen materials and still need to be further studied.

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