

High-pressure storage of hydrogen fuel: ammonia borane and its related compounds

Yu Lin^{1,*}, Wendy L Mao^{1,2}

¹Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, USA

²Photon Science, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

E-mail: lyforest@stanford.edu

Abstract

As a promising candidate material for hydrogen storage, ammonia borane (NH_3BH_3) has attracted significant interest in recent years due to its remarkably high hydrogen content. Subjecting this material to high pressure not only enables the formation of novel phases and compounds with exotic properties, but also improves our basic understanding of materials behavior at different levels of atomic and molecular interactions. This review focuses on the perspective of high-pressure chemical hydrogen storage related to NH_3BH_3 -based materials. Four main aspects are discussed: the structures and bonding of NH_3BH_3 over a wide pressure-temperature space, thermolysis of NH_3BH_3 at high pressure, the formation of a novel high-pressure H-rich compound as a result of storage of additional molecular H_2 in NH_3BH_3 , and the potential rehydrogenation of the thermally decomposed NH_3BH_3 under the extreme of pressure.

1. Introduction

Hydrogen has been touted for its potential to be an environmentally clean and efficient energy carrier [1, 2]. Hydrogen has a high energy content per mass compared to gasoline (120 MJ/kg for hydrogen versus 46 MJ/kg for gasoline). However, hydrogen has a poor energy content per volume (0.01 MJ/L at standard temperature and pressure (STP) and 8 MJ/L for liquid hydrogen versus 34 MJ/L for gasoline). For the most fuel-efficient vehicle to drive 500 km without refueling, a minimum of 5 kg of H₂ needs to be stored on-board, which corresponds to a volume of nearly 60 m³ at STP. To meet the updated United States Department of Energy (US DOE) 2017 targets (5.5 wt% system gravimetric capacity and 0.04 kg H₂/L system volumetric capacity), a minimum of 90.9 kg of the hydrogen storage material, or a minimum of 125 L of the storage system will be needed for light-duty fuel cell vehicles [3]. Therefore, one of the greatest challenges to a hydrogen economy is the discovery and development of materials and compounds capable of storing enough hydrogen on-board for transportation applications.

Many materials with high gravimetric and/or volumetric hydrogen densities have been studied over the last decade, with the significant interest being generated by B–N compounds, especially ammonia borane (NH₃BH₃). Both B and N are light elements capable of bonding with multiple H atoms. B–H and N–H bonds tend to be hydridic and protonic, respectively, which results in the relatively easy release of H₂, because H₂ can be more readily produced by the local combination of H atoms with both positive (H in N–H) and negative (H in B–H) charges. In addition, NH₃BH₃ satisfies the stability requirements necessary for safe storage of hydrogen.

As appropriate materials will be one of the central focuses to achieving a hydrogen economy, exploration over a vast pressure-temperature-composition (*P-T-x*) space allows us to access new phases and compounds that are not available at ambient conditions. Among these

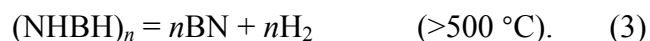
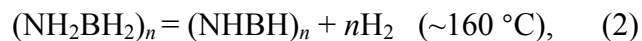
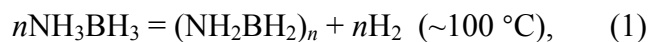
tuning parameters, pressure allows access to a much wider energy landscape that enables the formation of novel phases with exotic properties. In addition, pressure, which serves as a smooth and clean thermodynamic parameter, can dramatically alter a material's physical and chemical properties. Investigating existing materials at high pressure could thus improve our basic understanding of the materials' accessible range of properties and failure mechanisms and further guide us in the design of improved hydrogen storage materials for practical applications.

In this review, we focus on the unique perspective of high-pressure hydrogen storage associated with NH_3BH_3 and its interaction with H_2 . We first discuss the structures and bonding of NH_3BH_3 at high pressure and varying temperatures, followed by understanding the thermolysis of NH_3BH_3 at high pressure, and finally we look into the interaction of NH_3BH_3 in the presence of excess H_2 pressure and the potential rehydrogenation of decomposed NH_3BH_3 at high pressure.

2. NH_3BH_3

NH_3BH_3 was first synthesized by Shore and Parry [4] over half a century ago by the reaction of lithium borohydride or diamoniato of borane with ammonia salts at room temperature in diethyl ether solution. It contains a total of 19.6 wt% hydrogen content. Through step-wise thermolysis, one third of its total H_2 (6.5 wt%) can be released during each heating step. The amount of H_2 released at every single step has already achieved the US DOE 2017 target of 5.5 wt% gravimetric H_2 density for onboard hydrogen storage systems for light-duty vehicles. While the release of all the H_2 is only accomplished at above 500 °C, the first two steps happen at moderately elevated temperatures. The evolution of the thermolysis reactions is summarized in

eq. (1)~(3), where NH_3BH_3 , upon heating, transforms to polyaminoborane $(\text{NH}_2\text{BH}_2)_n$, and then polyiminoborane $(\text{NHBH})_n$, and ultimately boron nitride BN while progressively releasing H_2 .



A myriad of studies have been conducted on how to effectively dehydrogenate NH_3BH_3 , including lowering the decomposition temperatures [5, 6] and increasing the rate of H_2 release through the use of acid- [7, 8] or transition metal- catalysts [9, 10], ionic liquids [11], nanoscaffolds [12, 13], etc.

NH_3BH_3 belongs to a family of inorganic analogs of simple hydrocarbons where carbon atoms are replaced by nitrogen and boron atoms. NH_3BH_3 is a solid at room temperature with a high melting point of $104\text{ }^\circ\text{C}$ when compared to compounds like isoelectronic C_2H_6 which melts at $-183\text{ }^\circ\text{C}$. This is primarily due to dipole-dipole interactions and a network of dihydrogen bonding. The short-range cooperative dipole-dipole interactions in the molecular NH_3BH_3 crystal result in the length of B–N dative bond being significantly shorter in the solid state (1.58 \AA) than in the gas phase (1.66 \AA) [14–16]. Meanwhile, bonding in the NH_3BH_3 crystal also represents a unique class of unconventional hydrogen bonds which are considered as dihydrogen bonds where both protonic H ($\text{H}^{\delta+}$) and hydridic H ($\text{H}^{\delta-}$) are present, and can be described as $\text{N}^{\delta-} - \text{H}^{\delta+} \cdots \text{H}^{\delta-} - \text{B}^{\delta+}$. Theoretical work estimated the $\text{H} \cdots \text{H}$ bond strength to be in the range of 3–6 kcal/mol per hydrogen bond [17–19], which is in the range of conventional hydrogen bonds.

At ambient conditions, NH_3BH_3 crystallizes in a tetragonal space group $I4mm$ with a unit cell containing two molecules [20, 21]. At about 225 K, a first-order rotational order-disorder phase transition occurs where the body-centered tetragonal (bct) $I4mm$ structure transforms into

the orthorhombic $Pmn2_1$ phase, as first revealed from the neutron diffraction structure determination [22]. This low-temperature modification of NH_3BH_3 was found to display three short $\text{N-H}\cdots\text{H-B}$ interactions with the shortest $\text{H}\cdots\text{H}$ distance of 2.02 Å which is still shorter than the sum of the van der Waals radii of H (2.4 Å). A large number of experiments and theoretical calculations have been performed to investigate the nature of the structural changes as a function of temperature, as well as the dihydrogen bond network [23–25]. The existence of an intermediate phase near 225 K has also been suggested.

2.1 Structures and bonding of NH_3BH_3 at high pressure

The effect of pressure on the behavior of NH_3BH_3 expands our fundamental understanding of this system and further guides us in the design of improved materials for hydrogen storage applications. As molecular solids with weak/medium intermolecular interactions tend to be very sensitive to external forces, in-situ high-pressure vibrational spectroscopy studies can provide unique insight into the nature of intermolecular bonding such as dihydrogen bonding as well as intramolecular interactions. Two early Raman spectroscopy studies investigated the evolution of vibrational modes in NH_3BH_3 as a function of pressure up to 4 GPa at room temperature [26, 27]. However, while Trudel and Gilson [26] reported two phase transitions at 0.5 and 1.4 GPa, Custelcean and Dreger [27] only observed one pressure-induced disorder-order phase transition around 0.8 GPa. Later, Lin et al. [28] revisited the effect of pressure on the Raman spectra of NH_3BH_3 but up to a much higher pressure of 23 GPa, and confirmed one phase transition at 2 GPa and found two new transitions at 5 and 12 GPa. Subsequent Raman spectroscopy study up to 60 GPa by Chellappa et al. [29] and combined Raman and synchrotron infrared measurements

up to 14 GPa by Xie et al. [30] also suggested similar phase transformations in NH_3BH_3 at high pressure.

To unveil the crystal structures as well as the dihydrogen bonding networks associated with these high-pressure phases, a number of research groups have further devoted extensive experimental and theoretical efforts. It is now generally agreed that the transition at below 2 GPa is where NH_3BH_3 in the low-pressure $I4mm$ structure transforms into an ordered high-pressure orthorhombic $\text{Cmc}2_1$ phase, as initially determined by Filinchuk et al. using powder X-ray diffraction and density functional theory (DFT) calculations [31]. This phase transition was further confirmed by the following structural studies including an X-ray study by Chen et al. [32], combined X-ray and neutron diffraction and DFT calculations by Kumar et al. [33], molecular dynamics (MD) simulations by Wang et al. [34], and the most recent X-ray and DFT studies by Lin et al. [35]. Although consensus has been reached on the transition from $I4mm$ to $\text{Cmc}2_1$ at pressures below 2 GPa, disagreements still exist regarding how NH_3BH_3 evolves with further compression which is partially a result of the increased difficulty in solving the crystal structure of this H-rich material as pressure increases. Kumar et al. [33] observed a structural transition from $\text{Cmc}2_1$ to triclinic $P1$ phase above 8 GPa experimentally, while the DFT study by Ramzan et al. [36] suggested a second orthorhombic-to-tetragonal phase transition occurring at around 11.5 GPa and another MD study by Wang et al. [34] proposed that $\text{Cmc}2_1$ transformed into a $P2_1$ phase at above 12 GPa and further into a different $P2_1$ phase at 50 GPa. Most recently, Lin et al. [35] observed experimentally that $\text{Cmc}2_1$ phase developed into a $P2_1$ phase at above 12 GPa, and the structure of the high-pressure $P2_1$ phase has also been optimized by DFT simulations which included van der Waals forces.

In addition to the exploration of the structures of NH_3BH_3 at high pressure and room temperature, a few studies have discussed the behavior of NH_3BH_3 at low temperature down to 90 K and high pressure up to 15 GPa [37–40]. The study by Andersson et al. [37] reported the boundaries between, and the range of stabilities of $I4mm$, $Cmc2_1$, and $Pmn2_1$ phases using in-situ thermal conductivity measurements in the pressure and temperature ranges of 0–1.5 GPa and 110–300 K, respectively, while another study by Najiba et al. [40] which covered a much wider P - T space suggested that they observed four new low-temperature and high-pressure phases as evidenced by the changes in the Raman spectra. It was found that the geometric characteristics of individual NH_3BH_3 molecules in all the known phases are comparable, while the intermolecular dihydrogen bonding networks associated with each phase are distinct.

2.2 Thermolysis of NH_3BH_3 at high pressure

At ambient pressure, NH_3BH_3 decomposes upon heating with step-wise releasing of H_2 , and the first decomposition temperature is lower than its melting temperature. As the intermolecular distances decrease and the structures and bonding networks modify with pressure, it is of considerable interest to investigate how the thermal decomposition of NH_3BH_3 changes at high pressure. Wang et al. [41] reported that up to 0.7 GPa and 140 °C, NH_3BH_3 decomposes into $(\text{NH}_2\text{BH}_2)_n$, and heating NH_3BH_3 at 0.7 GPa and at temperatures of 120–140 °C was similar to heating NH_3BH_3 at ambient pressure and 90 °C. Meanwhile, Nylen et al. [42, 43] studied the thermal decomposition of NH_3BH_3 at high pressure in greater details and found that in contrast to the three-step thermolysis at ambient pressure, compressed NH_3BH_3 released almost its entire H_2 content in two distinct steps. While $(\text{NH}_2\text{BH}_2)_n$ was observed both in the ambient-pressure and high-pressure thermolysis after the first heating step, the residual after the second

decomposition step, $(\text{BNH}_x)_n$, was unique at high pressure. $(\text{BNH}_x)_n$ with much lower H content ($x < 0.5$) than $(\text{NHBH})_n$ was most likely to be composed of large fragments of graphitic-layered hexagonal BN terminated by H atoms, as suggested by Raman spectroscopy and X-ray diffraction. As the decomposition temperature increased with pressure, a new high-pressure and high-temperature phase was also observed prior to decomposition. This phase, which was determined to be Pnma space group, were evolved from and closely related to the known high-pressure Cmc2₁ structure. The high-temperature phase can be recovered upon cooling and only return to the I4mm structure upon further decompression. Liang et al. [44] also performed first-principles MD calculations to investigate the mechanisms associated with H₂ formation in NH₃BH₃ at ambient and high pressure, and intra- and inter-molecular decomposition pathways were found at ambient and 6 GPa, respectively.

By systematically combining previous data [37, 42, 45], a schematic *P-T* phase diagram of NH₃BH₃ is shown in Fig. 1. It mainly includes the five known phases that are the parent I4mm phase, its low-temperature modification Pmn2₁ phase, two high-pressure Cmc2₁ and P2₁ phases, and one high-pressure and high-temperature Pnma phase prior to the decomposition. The boundaries of the two-step thermolysis processes at high pressure are also shown in Fig. 1.

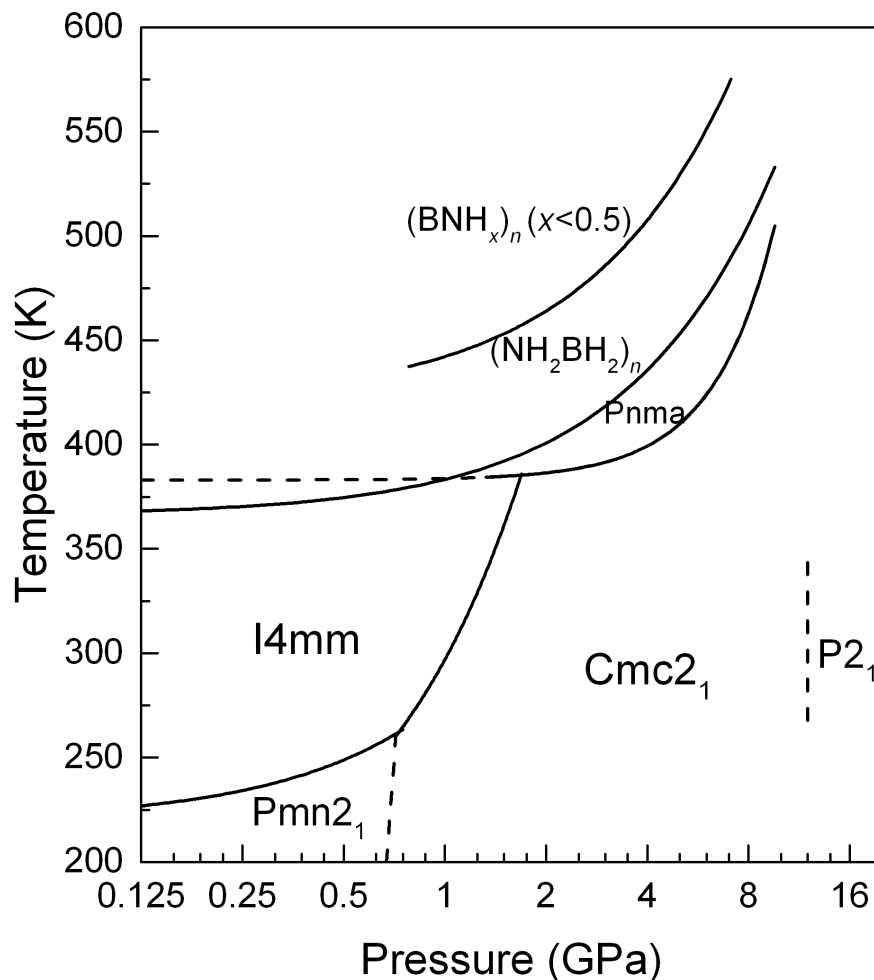


Fig. 1 Schematic P - T phase diagram of NH_3BH_3 in the pressure range of 0–16 GPa (in log₂ scale) and temperature range of 200–573 K

3. $\text{NH}_3\text{BH}_3\text{-H}_2$

NH_3BH_3 shows very rich structural variations upon compression. High pressure is also found to stabilize new phases which can hold additional molecular H_2 in a number of second-row hosts, like H_2O [46, 47] and CH_4 [48]. These extra H_2 molecules that are bound by weak van der Waals interactions to the host structures can be easily released for practical applications. A number of studies have focused on investigating whether NH_3BH_3 can serve as a host material for storing

additional amounts of H₂ and the potential H₂ release-uptake cycle in NH₃BH₃ with excess H₂ pressure.

3.1 Interactions of NH₃BH₃ with H₂ at high pressure and room temperature

By subjecting NH₃BH₃ in excess H₂ pressure, Lin et al. [49] discovered a new solid phase NH₃BH₃(H₂)_x, where $x = 1.3\text{--}2$. This new NH₃BH₃–H₂ compound that can form slowly at 6.2 GPa is capable of storing an estimated 8–12 wt% of additional molecular H₂. As a consequence, this phase can hold a total of approximately 30 wt% gravimetric H₂ density including the original H in NH₃BH₃, which makes it one of the most H-rich materials currently known (Fig. 2). Raman spectroscopy and X-ray diffraction results of the new phase suggested the probable presence of several or a continuum of NH₃BH₃ frameworks that can hold H₂ and the complex structure of the new compound. The reaction kinetics and the bonding variations, although complex and sensitive to the pressure environments, also shed light upon designing alternative chemical pathways to recover this new H-rich material to more practical conditions for applications. Concurrently, Chellappa et al. [29] studied the pressure-induced complexation and intermolecular interactions in NH₃BH₃ and H₂ mixtures up to 60 GPa. The results suggested that two NH₃BH₃–H₂ complexes were formed at 6.7 and 10 GPa, and the NH₃ group played a dominant role in the interactions. The observed strengthening in dihydrogen bonding associated with the interactions between NH₃BH₃ and H₂ may imply that there may be low temperature routes for stabilizing the complexes at more practical conditions based on the fact that the strengthening effect has also been observed in NH₃BH₃ at low temperatures.

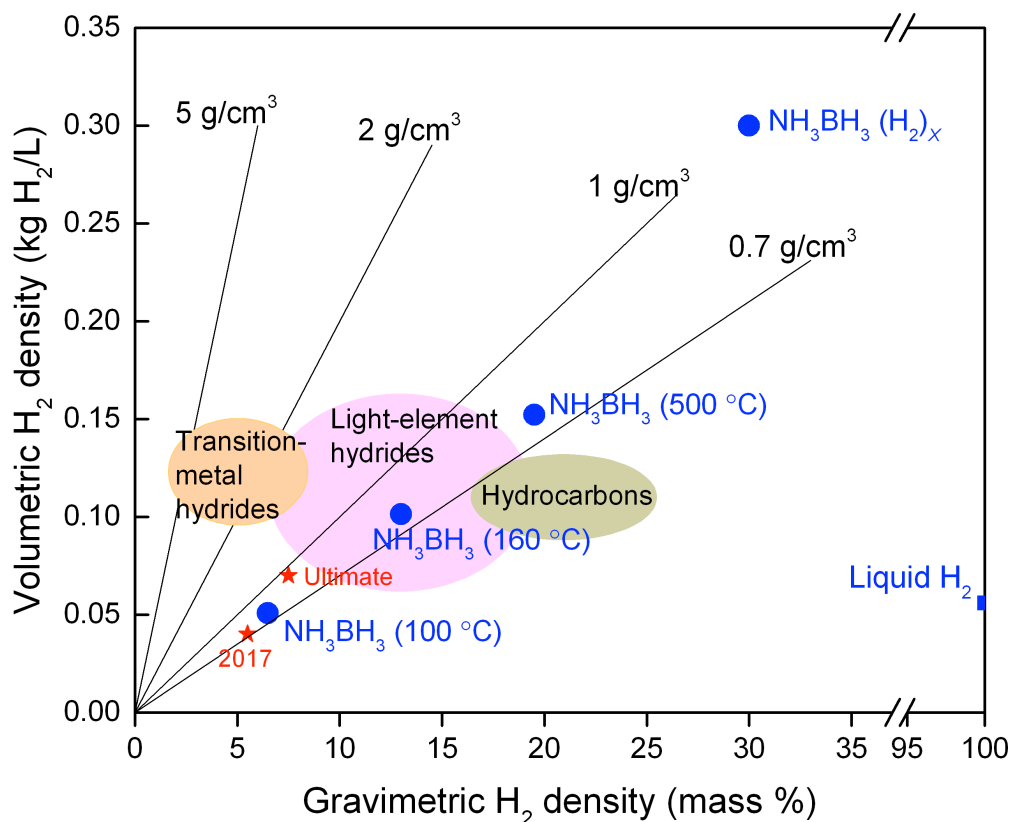


Fig. 2 Comparison of gravimetric and volumetric H₂ densities of various hydrogen storage materials including transition-metal hydrides, light-element hydrides, hydrocarbons, NH₃BH₃, and the new NH₃BH₃-H₂ compound. The straight lines indicate the total density of the storage materials. Stars show the updated US DOE target by the year 2017 and an ultimate target of 7.5 wt% H₂ or 0.07 kg H₂/L for on-board hydrogen storage for light-duty fuel cell vehicles. The figure illustrates the tremendous potential of the NH₃BH₃-H₂ compound. (Adapted from Mao *et al.* [51])

3.2 Rehydrogenation of decomposed NH₃BH₃ at high pressures

In addition to the study of the uptake of H₂ in NH₃BH₃ and the search for potentially more H-rich materials, rehydrogenation of decomposed NH₃BH₃ still remains to be a critical issue that currently prevents NH₃BH₃ from being an on-board hydrogen storage material. The idea of using

pressure to rehydrogenate the thermally decomposed NH_3BH_3 has been proposed and investigated. Although a few recent studies showed that NH_3BH_3 cannot be recovered by pressurizing $(\text{NH}_2\text{BH}_2)_n$ and/or $(\text{NHBH})_n$ in excess H_2 pressure, the interactions between the decomposed NH_3BH_3 products and H_2 provide insight for recharging NH_3BH_3 . Wang et al. [41] reported that at 0.7 GPa and 140 °C, NH_3BH_3 that was surrounded by H_2 fluid underwent amorphization and decomposition to $(\text{NH}_2\text{BH}_2)_n$. While the heated and decomposed NH_3BH_3 in saturated H_2 environment did not reform NH_3BH_3 during slow cooling to room temperature or upon further application of high pressure up to 3 GPa, during the course of pressurizing from 0.7 to 3 GPa, an additional non-negligible amount of H_2 dissolved into the thermally decomposed NH_3BH_3 and the storage capacity of 3 wt% extra H_2 in heated NH_3BH_3 was estimated at 3 GPa. Another study by Chellappa et al. [50] demonstrated the reactions of H_2 and D_2 with $(\text{NH}_2\text{BH}_2)_n$ and $(\text{NHBH})_n$ in the pressure range of 2–4 GPa and temperatures up to 220 °C, and deuterium labeling experiments further provided insight for understanding their reaction mechanisms. Both $(\text{NH}_2\text{BH}_2)_n$ and $(\text{NHBH})_n$ were capable of interacting with H_2 and forming $(\text{NH}_2\text{BH}_2)_n/(\text{NHBH})_n\text{-H}_2$ complexes. The complexes were stable up to 8.7 GPa and 220 °C and remained stable on recovery to ambient conditions. The faster kinetics of $(\text{NH}_2\text{BH}_2)_n$ and $(\text{NHBH})_n$ complexation with H_2 compared to $\text{NH}_3\text{BH}_3\text{-H}_2$ as well as their wide P - T stability range give us hope to better manipulate and cycle the NH_3BH_3 system for practical purposes.

4. Conclusions and prospects

In recent years, NH_3BH_3 has gained renewed interest as a potential hydrogen storage material. Pressure, a simple but powerful driving force, has opened up a new venue for developing and designing advanced materials. In this article, we have reviewed recent high-pressure activities on

NH_3BH_3 , including its structures at varying pressures and temperatures, the thermolysis process at high pressure, as well as the interactions of NH_3BH_3 and its decomposed products with H_2 . A much richer P - T phase diagram has been constructed for NH_3BH_3 .

High-pressure study leads to the discovery of new phases and simple molecular compounds with unique properties. Once novel materials, for example very H-rich phases, are found at high pressure, we can search for alternative chemical pathways to stabilize the materials near practical conditions. Take the $\text{NH}_3\text{BH}_3\text{-H}_2$ compound as an example, if all the stored H_2 could be fully used, then a minimum of 16.7 kg and 16.7 L of the material is required in a vehicle, assuming the density of the compound is comparable with NH_3BH_3 (approximately 1 kg/L at 6.2 GPa [35]). Even if we only release the additional H_2 in the new compound and the first equivalent of H_2 in NH_3BH_3 , the amount of H_2 is still far beyond the DOE 2017 target. Given its enormous H content, it is also viable to sacrifice some H amount by incorporating promoters or catalysts into the structure in order to improve its synthesis and storage conditions. The strategy of using the extreme of pressure and/or temperature can offer numerous opportunities for searching for new phases or testing the performance limit of current materials. Meanwhile, theory can also serve as guidance for predicting the structures, and assessing the thermodynamic and kinetic stabilities of new molecular compounds that could be potential hydrogen storage materials.

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