In situ Raman spectroscopy was used to monitor the dehydrogenation of ball-milled mixtures of LiNH₂–LiBH₄–MgH₂ nanoparticles. The as-milled powders were found to contain a mixture of Li₄BN₃H₁₀ and Mg(NH₂)₂, with no evidence of residual LiNH₂ or LiBH₄. It was observed that the dehydrogenation of both of Li₄BN₃H₁₀ and Mg(NH₂)₂ begins at 353 K. The Mg(NH₂)₂ was completely consumed by 415 K, while Li₄BN₃H₁₀ persisted and continued to release hydrogen up to 453 K. At higher temperatures Li₄BN₃H₁₀ melts and reacts with MgH₂ to form Li₂Mg(NH)₂ and hydrogen gas. Cycling studies of the ball-milled mixture at 423 K and 8 MPa (80 bar) found that during rehydrogenation of Li₄BN₃H₁₀ Raman spectral modes reappear, indicating partial reversal of the Li₄BN₃H₁₀ to Li₂Mg(NH)₂ transformation.

1. Introduction

The search for materials that match the U.S. Department of Energy’s criteria for hydrogen storage materials to be used in mobile applications has been largely focused on complex hydride materials in the past 10 years. In particular, since the work of Chen et al. [1] and Vajo et al. [2] on mixtures of LiNH₂/LiH and LiBH₄/MgH₂, there have been a number of publications devoted to complex hydrides that are thermodynamically destabilized by ball-milling with other hydrides [3,4]. The advantage of such reactions is that the large enthalpies of complex hydrides can be lowered by providing an alternate reaction pathway that liberates hydrogen. It has also been observed that new phases could be formed during the high-energy ball-milling of different ratios of known hydrides. For example in mixtures of LiNH₂/MgH₂, Mg(NH₂)₂ was found to form, which then reacts with the remaining LiH during dehydrogenation [5,6]. In fact mixtures of LiBH₄ and LiNH₂ yield an entire series of new Li–B–N–H phases [7–10]. It has been recently demonstrated that mixtures of LiH and BN–NHₓ form a compound with a relatively low hydrogen desorption temperature ~373 K [11].

These approaches have been extended into three component systems, and recently Yang et al. [12] reported on the formation of a new “self-catalyzed” complex hydride by the mechanical milling of LiBH₄–LiNH₂–MgH₂ in ratio of 1:2:1. They found that upon ball-milling most of the initial phases were converted into a mixture of the Li₄BN₃H₁₀ and Mg(NH₂)₂. This mixture was shown to release up to 4 wt% hydrogen for temperatures starting at 423 K via multiple reactions. Recently Niemann et al. [13] reported that the onset of hydrogen release of the mixture could be reduced to 353 K via nanoscale engineering of the powders. To do this the LiBH₄ and LiNH₂ were first milled together until the formation of Li₄BN₃H₁₀ was...
completed, and the completed product was then milled with a MgH₂ powder that had an average grain size on the order of 10 nm. To verify the full conversion of the powder during processing, as well as the hydrogen desorption reaction pathway, detailed characterization and in situ structural analysis of the powder is necessary. Raman spectroscopy is a useful measurement technique for studying desorption in complex hydrides. Many complex hydrides and their desorption products are Raman active, and the position of their Raman modes is sensitive to the local environment of the chemical bonds [14–16]. This allows for tracking the formation of new phases during desorption, as well as providing qualitative information about the amount of the phase present.

In the present article we will report on a series of in situ Raman spectroscopic measurements on mixtures of LiBH₄–LiNH₂–MgH₂ where the constituents have been ball-milled to nanometer-scale grain sizes individually and then milled together sequentially. It will be shown that the as-milled powders show no detectable traces of LiNH₂ or LiBH₄. Further, we will demonstrate that in these powders the decomposition of Mg(NH)₂ begins at 363 K, and is completed by 415 K. This reaction will be shown to occur concurrently with the decomposition of LiₓBN₃H₁₀ and is shown to be directly related to the release of hydrogen via desorption kinetics measurements using a Sieverts apparatus. Subsequent in situ rehydrogenation at 423 K and 8 MPa (80 bar) reveals the reformation of LiₓBN₃H₁₀, the decomposition of which to form LiₓMg(NH)₂ was previously described as being irreversible [12].

2. Experimental

2.1. Preparation of nano LiₓBN₃H₁₀–MgH₂ powders

The parent compounds LiBH₄ and LiNH₂ were purchased from Sigma Aldrich with a purity of at least 95% [17]. The MgH₂ used was purchased from Alfa Aesar with a purity of 98%. All materials were kept in an inert atmosphere in a glove box and used without further purification. The investigated samples were created in 4 g batches with a constant molar ratio of 2LiNH₂:LiBH₄:MgH₂ by employing high-energy ball-milling. LiₓBN₃H₁₀ was formed first by milling the LiBH₄ and LiNH₂ together for 5 h at 300 rpm. The MgH₂ was subsequently added and the mixture was milled for an additional 5 h. The crystallite size for each phase was estimated from X-ray diffraction experiments and was found to be 30 nm for LiₓBN₃H₁₀ and 10 nm for MgH₂ [13]. The resulting compound is hereafter referred to as nano LiₓBN₃H₁₀–MgH₂. As-received LiBH₄ and LiNH₂ and portions of the as-milled LiₓBN₃H₁₀ and nano MgH₂ were retained for use as reference Raman spectra.

The prepared powders were stored inside an Ar filled glove box with water concentrations less than 1.11 × 10⁻⁷ mol H₂O/mol Ar (0.05 ppm). The samples were loaded and sealed into a high-pressure high-temperature in situ optical cell inside the glove box, and the cell was then back-filled to a static pressure of 0.49 MPa (5 bar) with ultra high purity (UHP) Ar (purity >99.999%) for initial desorption measurements.

A positive pressure of Ar was chosen here because previous works on LiₓBN₃H₁₀ have shown that it melts prior to releasing hydrogen; therefore during measurements in static or dynamic vacuum the material will spit and accumulate on the window of the optical cell. The UHP Argon used yields a similar hydrogen partial pressure as one would expect from static vacuum, providing a near best case kinetic desorption curve. However, as the powder releases hydrogen during desorption the thermodynamics, and thus the reaction pathway, could be affected by the increased hydrogen partial pressure. This was partially circumvented by using small quantities of the powder (~3–6 mg), which after complete dehydrogenation increases the hydrogen partial pressure in the cell to about 0.00194 MPa (0.0194 bar). This is on the edge of sensitivity for typical charging measurements, and is appreciably below the reported desorption plateau pressure of the nano LiₓBN₃H₁₀–MgH₂ powder (~0.5 MPa). It was therefore concluded that the effect of hydrogen release in the statically pressurized cell on the thermodynamics of the powder was minimal.

2.2. In situ Raman and volumetric characterization

The in situ optical cell will be described in more detail in a future publication. Briefly, the chamber body is made from a 4.5” 316 steel conflat (CF) nipple, and is sealed on each end by CF flanges. One CF flange was machined to allow optical access to the powder through a circular sapphire window with a radius of 60 mm and a thickness of 9 mm. The window is seated on a 50 mm × 0.3 mm Au o-ring that acts as a seal and prevents point contact of the flange to the window. The optical cell was designed to operate at pressures up to 10 MPa (100 bar).

The powder was packed in a 6.5 mm diameter Mo set screw, which was then mounted into a 46 mm radius Mo plate that served as a heat bath. The plate was mounted to a 38.1 mm BN substrate heater from Bluewave Semiconductor capable of reaching a maximum temperature of 1073 K in reactive environments. The use of BN as the heating stage material prevents chemical attacks from the hydrogen gas during high-temperature high-pressure rehydrogenation. The bottom of the Mo set screw was in direct contact with the substrate heater to ensure good temperature uniformity during temperature ramping. The Mo plate can accommodate up to 19 Mo set screws, so that up to 19 different powders can be measured in series. The powder-to-window distance is adjustable from 1 mm to 2 cm and for this study the distance was set to ~1 mm. During desorption studies the temperature was ramped at 5 K/min up to 593 K with the Raman spectra being taken at every 10 K.

Raman spectroscopic measurements were performed in a backscattering geometry using 514.5 nm radiation from an argon ion laser. Approximately 50 mW of laser radiation was focused onto the powder with a 300 mm focal length spherical lens. Scattered radiation was collected and collimated with a f/4 achromatic lens located at infinite conjugate ratio. A holographic notch filter (150 cm⁻¹ nominal spectral edge width and 6.0 nominal optical density) was placed in the collected, collimated radiation. An achromatic lens was used to couple radiation into a 0.5 m focal length, f/6.5 imaging spectograph equipped with an 1800 groove/mm holographic grating (optimized for use in the visible region of the
3. Results and discussion

3.1. Room temperature Raman spectrum

Fig. 1 shows the Raman spectrum of the as-prepared nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ powder at room temperature in 0.49 MPa of Ar. The four peaks in the 3200 cm$^{-1}$–3350 cm$^{-1}$ range, the broad feature centered at ~2300 cm$^{-1}$, and the weak feature at ~380 cm$^{-1}$ are attributed to the powder while the peaks observed at 418 cm$^{-1}$, 432 cm$^{-1}$, 451 cm$^{-1}$, 581 cm$^{-1}$, and 751 cm$^{-1}$ originate from the optical cell’s sapphire window [21]. The powder spectral features in the 3200 cm$^{-1}$–3350 cm$^{-1}$ range and the features centered at ~2300 cm$^{-1}$ are attributed to N–H stretching modes and B–H stretching modes, respectively, based on the reported infrared spectral assignments for a Li$_3$BN$_3$H$_{10}$/Mg(NH)$_2$ mixture obtained by ball-milling a LiNH$_2$, LiBH$_4$, and MgH$_2$ [12]. More specific peak assignments can be inferred from a comparison of the mixed powder spectrum to spectra of various reference compounds.

Fig. 2 shows the Raman spectra in the N–H stretching spectral region of the studied nano Li$_3$BN$_3$H$_{10}$–MgH$_2$ (shown in Fig. 1), and two reference materials Li$_4$BN$_3$H$_{10}$, and LiNH$_2$ at room temperature in 0.49 MPa of Ar. The Li$_4$BN$_3$H$_{10}$ Raman spectrum exhibits two peaks at 3246 cm$^{-1}$ and 3305 cm$^{-1}$, in agreement with the N–H stretching frequencies observed at 3243 cm$^{-1}$ and 3303 cm$^{-1}$ in the infrared spectrum of Li$_3$BN$_3$H$_{10}$ [7]. The mixed powder Raman spectrum exhibits four N–H stretching features at 3243 cm$^{-1}$, 3274 cm$^{-1}$, 3300 cm$^{-1}$, and 3329 cm$^{-1}$. The two peaks at 3243 cm$^{-1}$ and 3300 cm$^{-1}$ are attributed to the Li$_4$BN$_3$H$_{10}$ phase. The two peaks at 3274 cm$^{-1}$ and 3329 cm$^{-1}$ are attributed to the Mg(NH)$_2$ phase, the N–H stretching modes of which have been observed at 3277 cm$^{-1}$ and 3326 cm$^{-1}$ in an infrared spectrum of Mg(NH)$_2$ [22]. The three peaks observed in the LiNH$_2$ Raman spectrum at 3259 cm$^{-1}$, 3310 cm$^{-1}$, and 3320 cm$^{-1}$ are in agreement with the reported spectrum of this compound [23] but do not correspond to any features observed in the spectra of Li$_4$BN$_3$H$_{10}$ or nano Li$_3$BN$_3$H$_{10}$–MgH$_2$.

Fig. 3 shows the Raman spectra in the B–H stretching spectral region of nano Li$_3$BN$_3$H$_{10}$–MgH$_2$ (shown in Fig. 1), Li$_4$BN$_3$H$_{10}$, and LiBH$_4$ at room temperature in 0.49 MPa of Ar. The nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ and Li$_4$BN$_3$H$_{10}$ spectra both exhibit a peak in the ~2286 cm$^{-1}$ to ~2289 cm$^{-1}$ range superimposed on broader, weaker, unresolved features extending from ~2275 cm$^{-1}$ to ~2400 cm$^{-1}$. The appearance of the B–H stretching modes in these Raman spectra are similar to the appearance of the broad B–H stretching modes reported in an infrared spectrum of a Li$_3$BN$_3$H$_{10}$/Mg(NH)$_2$ mixture obtained by ball-milling LiNH$_2$, LiBH$_4$, and MgH$_2$ [12]. The LiBH$_4$...
spectrum exhibits two relatively intense, resolved features at ~2275 cm$^{-1}$ and ~2300 cm$^{-1}$ with a shoulder at ~2320 cm$^{-1}$, and weaker features in the ~2140 cm$^{-1}$ to ~2220 cm$^{-1}$ and ~2380 cm$^{-1}$ to ~2595 cm$^{-1}$ ranges, in agreement with the reported LiBH$_4$ Raman spectra [24,25]. The most intense B–H stretching modes in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$, Li$_4$BN$_3$H$_{10}$, and LiBH$_4$ spectra are all observed in a similar wavenumber range. This observation is consistent with the BH$_4$ tetrahedra remaining intact in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ and Li$_4$BN$_3$H$_{10}$ powders after ball-milling, as has been reported to be the case [7,12]. While the appearance of the B–H stretching modes is similar in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$, Li$_4$BN$_3$H$_{10}$, and LiBH$_4$ Raman spectra (see Fig. 3), there are some differences in the spectra. Compared to the B–H stretching modes in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ and Li$_4$BN$_3$H$_{10}$ spectra, the B–H stretching modes in the LiBH$_4$ spectrum tend to be more resolved and to exhibit higher signal-to-noise ratios. In addition, compared to the B–H stretching modes in the Li$_4$BN$_3$H$_{10}$–MgH$_2$ spectrum, the B–H stretching modes in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ spectrum exhibit a peak at a lower wavenumber (~2286 cm$^{-1}$ and ~2289 cm$^{-1}$ in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ and Li$_4$BN$_3$H$_{10}$ spectrum, respectively) and a lower relative intensity of the peak to the broad, underlying B–H modes. These spectral differences indicate that the Raman scattering environments of the BH$_4$ tetrahedra are different in all three of these materials. However, the similarity of the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ spectrum to the Li$_4$BN$_3$H$_{10}$ spectrum and the differences of both spectra compared to the LiBH$_4$ spectrum indicate that the scattering environment in nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ and Li$_4$BN$_3$H$_{10}$ are more similar to each other than the environment in either is to LiBH$_4$. It will be shown later that the presence of LiBH$_4$ is also not observed as a reaction product during temperature cycling.

![Fig. 3](image1.png)  
Fig. 3 – The Raman spectra in the B–H stretching spectral region of nano Li$_4$BN$_3$H$_{10}$–MgH$_2$, Li$_4$BN$_3$H$_{10}$, and LiBH$_4$ at room temperature in 0.49 MPa of Ar. The spectra are offset on the vertical scale for clarity.

![Fig. 4](image2.png)  
Fig. 4 – The Raman spectra in the low frequency spectral region of the mixed nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ (shown in Fig. 1), Li$_4$BN$_3$H$_{10}$, and LiBH$_4$ at room temperature in 0.49 MPa of Ar. The spectra are offset on the vertical scale for clarity.

attributed to the optical cell window. This feature is not evident in either of the other spectra. Hence, it is tentatively attributed to an external mode of Mg(NH$_2$)$_2$. The three features observed in the LiBH$_4$ Raman spectrum at ~195 cm$^{-1}$, ~260 cm$^{-1}$, and ~295 cm$^{-1}$ are attributed to external modes of this compound [24,25].

No evidence of either LiNH$_2$ or LiBH$_4$ phases is observed in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ or Li$_4$BN$_3$H$_{10}$ spectra. The spectra of LiNH$_2$ and LiBH$_4$ show relatively intense peaks in the N–H spectral region (see Fig. 2) and B–H spectral region (see Fig. 3), respectively. Hence, the absence of any features related to either LiNH$_2$ or LiBH$_4$ phases in the nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ or Li$_4$BN$_3$H$_{10}$ spectra indicates that either 1) neither phase is present or 2) any of these phases that is present in a crystalline form in relatively small amounts with concomitant low Raman scattering intensity and/or in a disordered form with concomitant broad, unresolved Raman features. No evidence of a MgH$_2$ phase is observed in the as-prepared nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ Raman spectrum: no spectral feature is observed at ~950 cm$^{-1}$, the reported wavenumber of the most intense MgH$_2$ Raman-active mode [26]. This result is in contrast to X-ray diffraction results obtained from the similarly prepared nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ powders, which show diffraction peaks of MgH$_2$ [10]. A partial reason for the apparent insensitivity to MgH$_2$ of these Raman spectroscopic measurements may be due to a luminescent and/or incandescent background, although a feature could be identified at ~950 cm$^{-1}$. Due to this background, the overall Raman scattering signal-to-background ratio in the spectra was low, in contrast to the LiNH$_2$ and LiBH$_4$ spectra. In addition, during the formation of Mg(NH$_2$)$_2$, the MgH$_2$ is partially consumed and the reduced presence of MgH$_2$ would further hinder its ability to be observed via Raman spectroscopy.
3.2 Temperature dependent in situ Raman spectrum

In situ Raman spectra of the mixed nano Li$_4$BN$_3$H$_{10}$–MgH$_2$ powder in the N–H stretching, B–H stretching, and external mode spectral region, respectively, are plotted as a function of temperature in 0.49 MPa of Ar in Figs. 5–7. For clarity only Raman spectra measured at selected temperatures are plotted in these figures. In the N–H stretching spectral region (see Fig. 5) in the spectra recorded at temperatures from 303 K to 353 K, the two peaks at 3243 cm$^{-1}$ and 3300 cm$^{-1}$ (attributed to the Li$_4$BN$_3$H$_{10}$ phase) and the two peaks at 3274 cm$^{-1}$ and 3329 cm$^{-1}$ (attributed to the Mg(NH)$_2$ phase) are clearly observed, as described previously (see Fig. 2). In the spectrum recorded at 383 K, the overall intensity of these four features is weaker than in the spectra recorded at lower temperatures, with the 3274 cm$^{-1}$, 3300 cm$^{-1}$, and 3329 cm$^{-1}$ peak intensities being especially weak. In addition, the 3243 cm$^{-1}$ feature exhibits a broader FWHM than the corresponding feature in the spectra recorded at 353 K and lower temperatures. Further, a broad, weak feature is observed at $\sim$ 3180 cm$^{-1}$. The appearance of the $\sim$ 3180 cm$^{-1}$ feature is attributed to the presence of a metal imide phase, the infrared spectra of which has been reported to exhibit a relatively broad peak at $\sim$ 3180 cm$^{-1}$ (intense) [27]. Although the metal imide phase observed in this work is impossible to definitively identify, it is tentatively identified as Li$_2$Mg(NH)$_2$, based on the work of Yang et al. [12].

In the spectra recorded at temperatures from 413 K to 573 K, of the four peaks at 3243 cm$^{-1}$, 3274 cm$^{-1}$, 3300 cm$^{-1}$, and 3329 cm$^{-1}$, only a feature at $\sim$ 3243 cm$^{-1}$ is observed and this feature again exhibits a broader FWHM than the corresponding feature in the spectra recorded at 353 K and lower temperatures. This could indicate a mixture of the Li$_4$BN$_3$H$_{10}$ and Li$_2$Mg(NH)$_2$ in this temperature region, and makes it difficult to distinguish when the former phase has completely reacted. In addition, in the spectra recorded at temperatures from 413 K to 573 K, the broad $\sim$ 3180 cm$^{-1}$ feature is more intense. These trends indicate that the metal imide phase has more developed crystallinity then and/or is present in greater amounts in the Raman scattering volume at temperatures above 383 K than at lower temperatures.

In the B–H stretching spectral region (see Fig. 6) in the spectra recorded at temperatures from 313 K to 353 K, the broad B–H stretching mode features are nominally identical to those observed at room temperature with a peak at $\sim$ 2286 cm$^{-1}$ superimposed on broader, weaker, unresolved features extending from $\sim$ 2275 cm$^{-1}$ to $\sim$ 2400 cm$^{-1}$, as described previously (see Fig. 3). In the spectra recorded at temperatures from 393 K to 553 K, the $\sim$ 2286 cm$^{-1}$ feature is no longer observed. Again, this suggests that the phase responsible for B–H stretches observed in the spectra recorded at temperatures above 353 K is not related to LiBH$_4$. In the spectrum recorded at 613 K, no B–H stretching features are observed.

In the external mode spectral region (see Fig. 7) in the spectra recorded at temperatures from 303 K to 363 K, the weak feature at $\sim$ 380 cm$^{-1}$ is nominally identical to that observed at room temperature, as described previously (see Fig. 4). In the spectra recorded at temperatures from 393 K to 423 K, the intensity of this feature decreases, making it difficult to observe this feature at all.

![Fig. 5 – The Raman spectra in the N–H stretching spectral region as a function of temperature. The spectra are offset on the vertical scale for clarity.](image1)

![Fig. 6 – The Raman spectra in the B–H stretching spectral region as a function of temperature. The spectra are offset on the vertical scale for clarity.](image2)

![Fig. 7 – The Raman spectra in the low frequency spectral region as a function of temperature. The spectra are offset on the vertical scale for clarity.](image3)
3.3. Reaction pathways

It is evident from Figs. 5–7 that the Raman spectra can give a qualitative indication of the species present as the mixed nano Li$_4$BN$_3$H$_{10}$-MgH$_2$ powder is heated. Further insight into the reaction pathways can be obtained by plotting the normalized intensities of selected Raman spectral modes as a function of temperature. Fig. 8 shows the temperature dependence of the N-H stretching modes at 3180 cm$^{-1}$, 3243 cm$^{-1}$, and 3274 cm$^{-1}$ as a function of temperature and compared to a hydrogen desorption kinetics plot, which was taken separately. The Raman spectral intensities were determined by fitting the respective peak at each temperature with a Lorentzian line shape. The peak intensities thus obtained were normalized by the maximum peak intensity (in counts/sec) of Li$_2$Mg(NH)$_2$ (reached at 553 K).

As previously discussed, the 3180 cm$^{-1}$, 3274 cm$^{-1}$, and 3243 cm$^{-1}$ features are attributed to the Li$_2$Mg(NH)$_2$ phase, the Mg(NH)$_2$$_2$ phase, and the Li$_4$BN$_3$H$_{10}$, respectively. The N-H stretching modes were selected for this comparison because these modes exhibit the highest signal-to-noise ratios in the nano Li$_4$BN$_3$H$_{10}$-MgH$_2$ Raman spectrum. As shown in Fig. 8, the peak intensity of the Li$_4$BN$_3$H$_{10}$ phase exhibits a slight increase from 303 K to ~313 K, a decrease from ~313 K to ~343 K, a little change from ~343 K to ~493 K, and a decrease from ~493 K to approximately zero at ~600 K. The peak intensity for Mg(NH)$_2$$_2$ shows a small initial increase between 303 K and 343 K, and a decrease from 353 K to 413 K, where it goes to zero. Finally, the peak intensity for Li$_2$Mg(NH)$_2$ is approximately zero from 303 K to 373 K, it increases in intensity up to 453 K, is roughly constant between 453 K and 473 K, increases in intensity again between 473 K and 553 K, then decreases to zero by 593 K.

The slight initial decrease in the Li$_4$BN$_3$H$_{10}$ intensity for temperatures below 333 K is observed simultaneously with an increase in the Mg(NH)$_2$$_2$ mode intensity. This was previously attributed to the reaction of Li$_4$BN$_3$H$_{10}$ with MgH$_2$ [12,28]. Above 353 K the peak intensities of both the Li$_4$BN$_3$H$_{10}$ and Mg(NH)$_2$$_2$ phases decrease, while the peak intensity of the Li$_2$Mg(NH)$_2$ phase increases. This corresponds to the beginning of the hydrogen desorption as indicated by the hydrogen desorption curve. Previous reports have found experimentally that Mg(NH)$_2$$_2$ will desorb hydrogen at temperatures as low as 453 K [5]. Further, ball-milling with MgH$_2$ has been found to lower the onset of hydrogen desorption to 378 K, consistent with what has been observed in the present study [29].

Above 413 K the intensity of the Mg(NH)$_2$$_2$ N-H stretching mode approaches zero signifying that the majority of the amide has been consumed by this temperature. The similarity in the N-H stretching mode peak of Mg(NH)$_2$$_2$ with the temperature dependence of the 380 cm$^{-1}$ peak (Fig. 5) is consistent with the assignment of the latter mode to Mg(NH)$_2$$_2$. Both peak intensities show an initial increase in intensity as the temperature is raised to 363 K. Above this temperature, the intensities of both peaks decrease and approach zero by ~413 K. However, the peak intensities for Li$_4$BN$_3$H$_{10}$ and Li$_2$Mg(NH)$_2$ continue to decrease and increase, respectively, until 453 K where they both reach a plateau. The source of this increase is either a continuation of the self-catalytic effect whereby the Li$_4$BN$_3$H$_{10}$ is transformed directly to Li$_2$Mg(NH)$_2$ or a two step reaction where it transforms first to Mg(NH)$_2$$_2$ and then rapidly decomposes to the metal imide phase. The hydrogen desorption curve during this temperature range shows a rapid release of hydrogen starting at 363 K that continues up until 453 K, at which point hydrogen release stops. Above 493 K the direct decomposition of the Li$_4$BN$_3$H$_{10}$ phase to the metal imide begins, and is associated with further hydrogen release and continues to ~600 K, which was shown previously for these powders in ref. [13]. It should be pointed out that above 600 K the peak centered around 2300 cm$^{-1}$ also vanishes (see Fig. 6). Finally, above 573 K the Li$_2$Mg(NH)$_2$ peak intensity rapidly decreases, signifying its decomposition.

One potential concern when performing Raman on reactive powders is the effect of laser heating, which could lower the reaction temperatures observed from their actual values. To mitigate this a relatively low power density was obtained using a low laser power (50 mW) in conjunction with a fairly large spot size (∼0.25 mm). This yields a relatively low power density delivered to the powder.

One can approximate a worst-case scenario for laser heating if it is assumed that the packed powder behaves as isolated particles, which absorb the incident laser power in an infinitely thin layer at their surface. An analytical solution of a similar case was previously described by Lax [30], however the solution requires values for the thermal conductivity and refractive index of the material. Unfortunately, values of these quantities for the two primary phases in the current powder (Li$_4$BN$_3$H$_{10}$ and Mg(NH)$_2$$_2$) have not been reported in the literature. As a first approximation one can assume all of the laser power is absorbed (perfect absorber) and use the values for thermal conductivity reported for other borohydrides such as LiBH$_4$ and NaBH$_4$ (1–2 W m$^{-1}$ K$^{-1}$) and LiNH$_2$/LiH mixes (∼0.1–0.4 W m$^{-1}$ K$^{-1}$) [31,32]. The relatively low values for the thermal conductivities of these materials bolsters the assumption that the particles behave as isolated particles. The assumption of isolated particles implies that the incident laser power on a 30 nm particle is in the order of 2 nW, yielding an upper bound to the change in temperature due to laser heating if it is assumed that the packed powder behaves as isolated particles, which absorb the incident laser power in an infinitely thin layer at their surface. An analytical solution of a similar case was previously described by Lax [30], however the solution requires values for the thermal conductivity and refractive index of the material. Unfortunately, values of these quantities for the two primary phases in the current powder (Li$_4$BN$_3$H$_{10}$ and Mg(NH)$_2$$_2$) have not been reported in the literature. As a first approximation one can assume all of the laser power is absorbed (perfect absorber) and use the values for thermal conductivity reported for other borohydrides such as LiBH$_4$ and NaBH$_4$ (1–2 W m$^{-1}$ K$^{-1}$) and LiNH$_2$/LiH mixes (∼0.1–0.4 W m$^{-1}$ K$^{-1}$) [31,32]. The relatively low values for the thermal conductivities of these materials bolsters the assumption that the particles behave as isolated particles. The assumption of isolated particles implies that the incident laser power on a 30 nm particle is in the order of 2 nW, yielding an upper bound to the change in temperature due to laser heating.
heating of approximately 0.17 K. This is experimentally supported by the close correlation between normalized Raman intensity data and the kinetic desorption curve taken during separate micro-sieverts measurements (Fig. 8). Additionally, the correlation of the Raman and kinetic desorption properties of the powder were verified via simultaneous optical/volumetric measurements using a specially designed cell (Fig. 9). From the calculation of the laser heating and a comparison of the two results, the laser heating of the powder was deemed to be negligible.

Yang et al. [12] previously proposed the following reaction pathways for the decomposition of mixtures of LiBH₄, LiNH₂, and MgH₂:

1. \[2\text{Li}_{4}\text{BN}_3\text{H}_{10} + 3\text{MgH}_2 \rightarrow 3\text{Mg}[(\text{NH})_2]_2 + 2\text{LiBH}_4 + 6\text{LiH} \quad (1)\]
2. \[2\text{Li}_{4}\text{BN}_3\text{H}_{10} + 3\text{MgH}_2 \rightarrow 3\text{Li}_2\text{Mg}[(\text{NH})_2]_2 + 2\text{LiBH}_4 + 6\text{H}_2 \quad (2)\]
3. \[\text{Mg}[(\text{NH})_2]_2 + 2\text{LiH} \rightarrow \text{Li}_2\text{Mg}[(\text{NH})_2]_2 + 2\text{H}_2 \quad (3)\]

Here reaction 1 is proposed to occur during the ball-milling and during initial heating (temperatures less than 373 K). From a combination of X-ray diffraction and Fourier transform infrared spectroscopy it was inferred that above 373 K the \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) melted and reacted with residual \(\text{MgH}_2\) to form \(\text{Li}_2\text{Mg}[(\text{NH})_2]_2\), which acted as a seed for the decomposition of \(\text{Mg}[(\text{NH})_2]_2\). This was termed the self-catalytic step. The subsequent reaction of \(\text{Mg}[(\text{NH})_2]_2\) began for temperatures higher than 473 K. Further, the reaction of \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) was deemed to have been irreversible, based on the shifting of the temperature programmed desorption (TPD) plot of the cycled powders to higher temperatures.

However, from previous studies on \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) the melting temperature should be higher than 463 K, although it could be possible that extensive ball-milling could reduce the particle size enough to reduce the melting temperature [10]. To confirm that the decrease in the \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) Raman peak intensity is due to its reaction with \(\text{MgH}_2\) and not melting, a \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) powder with a nearly identical grain size as the “self-catalyzed” powder was investigated using the same experimental conditions. Fig. 10 shows the temperature dependence of the intensity of the 3243 cm\(^{-1}\) mode for the \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) powder compared to the same mode for the nano \(\text{Li}_{4}\text{BN}_3\text{H}_{10} \cdot \text{MgH}_2\) powder. The inset of Fig. 10 shows the Raman spectra of \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) in the N–H stretching spectral region as a function of temperature. In Fig. 10, the intensity of the Raman lines for the N–H stretching modes of \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) remain constant for temperatures below 423 K, above which temperature they drop rapidly reaching a plateau at 463 K. Therefore, the decrease in the N–H mode intensity of the nano \(\text{Li}_{4}\text{BN}_3\text{H}_{10} \cdot \text{MgH}_2\) powder above 373 K is attributed to the reaction of \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) with \(\text{MgH}_2\). A similar reduction in the dehydrogenation temperature for \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) was reported by Pinkerton et al. [33], where the dehydrogenation temperature was reduced by 122 K through the addition of NiCl₂.

In the present study the onset of the decomposition of \(\text{Mg}[(\text{NH})_2]_2\) was found to occur at much lower temperature than was previously reported (353 K vs 473 K), although it was pointed out previously that the thermodynamics of the reaction should have yielded a lower decomposition temperature [12, 28, 34]. The discrepancy in the decomposition temperature is likely a result of the nanometer-scale mixing of the starting materials in the current study. The reduced size of the constituents yields a higher surface area for the reactions to occur, while minimizing any diffusional processes required for the reaction of the \(\text{Mg}[(\text{NH})_2]_2\) with the \(\text{LiH}\).

3.4. Reversibility of \(\text{Li}_{4}\text{BN}_3\text{H}_{10}\) decomposition

To detail which of the two initial phases is responsible for the reversible hydrogen storage capacity, an as-milled powder was dehydrogenated at 423 K in 0.5 MPa of UHP Ar for 1 h, until only the imide was observed in the Raman spectra. The

![Fig. 9 – Raman intensity plots for the \(\text{Li}_2\text{Mg}[(\text{NH})_2]_2\) N–H Raman peak (3180 cm\(^{-1}\)) plotted as a function of temperature along with a kinetic desorption plot taken simultaneously using a specially designed optical/volumetric measurement cell.](image-url)
powder was then hydrogenated at 423 K in 8 MPa UHP H₂ (99.999%) for 1 h without being removed from the optical cell. The Raman spectra of the as-milled and rehydrogenated powders are shown in Fig. 11. From the spectra it is clear that the Li₄BN₃H₁₀ phase has reformed during rehydrogenation and that the relative ratio of the Raman peak intensities of Li₄BN₃H₁₀ to the amide is roughly the same as compared to the value of the as-milled powder. These samples were previously shown to be cyclable multiple times without a significant change in the amount of hydrogen released or the onset temperature for release [13]. This is an indication that the phase fraction of Li₄BN₃H₁₀ and Mg(NH₃)₂ is not significantly changing during cycling.

From the previous result it is clear that upon cycling the powder at 423 K and 8 MPa the Li₄BN₃H₁₀ Raman modes return, this includes the B–H modes at 2300 cm⁻¹ (not shown). It was previously proposed, based on the shifting of the TPD to higher temperatures upon cycling, that the reaction of the Li₄BN₃H₁₀ with MgH₂ to form Li₂Mg(NH)₂ was irreversible. However, it was previously reported that in nanocofined Li₄BN₃H₁₀ powders infiltrated into porous carbon, partial reversibility of dehydrogenation was possible [35]. Also, from the calculated value of the enthalpy (≈80 kJ/mol at 300 K) for reaction 2 the reformation of Li₄BN₃H₁₀ does not seem to be thermodynamically inhibited [12]. Therefore it is concluded that reaction (2) is at least partially reversible in this system. To date, near full reversibility of reaction (2) has only been directly observed in powders where the grain size of the constituents have been reduced to <30 nm by high-energy mechanical milling.

4. Conclusions

Variable temperature in situ Raman spectra of a nano Li₄BN₃H₁₀–MgH₂ nano-grained powder were recorded. The hydrogen desorption was observed to start from 353 K, and Raman studies showed that the desorption was accompanied by simultaneous decomposition of both Li₄BN₃H₁₀ and Mg(NH₃)₂. Above 415 K the Mg(NH₃)₂ has been completely consumed, and the remaining hydrogen desorption is due to the decomposition of the Li₄BN₃H₁₀. This temperature is significantly lower than what has been reported in the literature. In situ rehydrogenation studies showed the reappearance of the Raman N–H stretching modes associated with Li₄BN₃H₁₀ indicating that the reaction to form Li₂Mg(NH)₂ is at least partially reversible.

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[17] Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.


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