Raman studies on eutectic melting in metal borohydride systems

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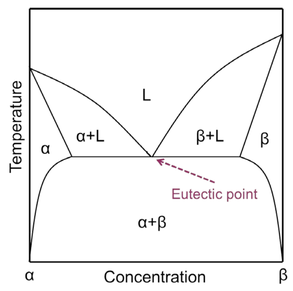
Introduction

A safe and efficient way of storing hydrogen is a crucial challenge for the realization of low-carbon transport within a renewable energy-based society. The borohydrides of light metals are being pursued as potential hydrogen storage media, due to their relatively high gravimetric and volumetric hydrogen storage capacities. However, their high dehydrogenation temperature and limited reversibility have so far prevented their use in real applications [1]. Eutectic melting occurs in mixtures of alkali, alkali earth and transition metal based borohydrides, which may facilitate hydrogen release at a temperature lower than that of the individual compounds [2].

The aim of this project is to promote the decomposition (and recombination) reactions for the eutectic mixtures and facilitate hydrogen desorption (and reabsorption). This poster describes studies of dehydrogenation processes in $LiBH_4$ and the effect of surface containment on phase nucleation, using Raman spectroscopy.

Eutectic melting

A eutectic system describes a liquid phase transition between two solid components with a specific atomic ratio at the eutectic temperature. The eutectic temperature is the lowest melting temperature possible among the different mixing ratios at equilibrium.

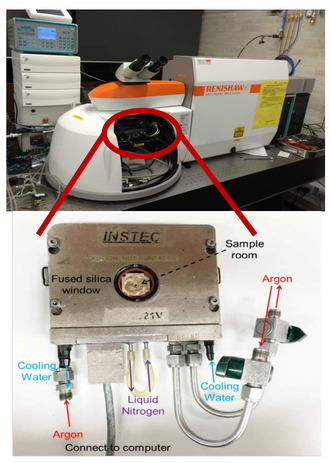


In the research for solid state hydrogen storage materials, eutectics in alkali and alkali earth metal borohydrides been investigated: $0.62LiBH_4$-$0.38NaBH_4$ [2], $0.725LiBH_4$-$0.275KBH_4$ [3], $0.6LiBH_4$-$0.4Mg(BH4)_2$ [4], and $0.68LiBH_4$-$0.32Ca(BH4)_2$ [5]. The melting and decomposition temperatures were found to be lower than that of the pure components.

Raman Spectroscopy

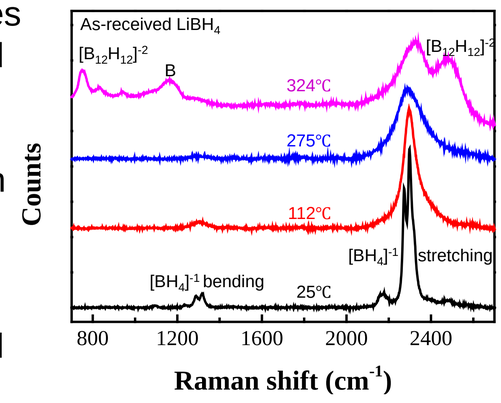
Raman spectroscopy is a powerful technique that allows the vibrational, rotational, and other low-frequency modes of compounds to be determined. It provides information on the chemical structure of phases in the solid (crystalline and amorphous forms), liquid and gaseous form [6].

The Raman spectrometer used in this project is a Renishaw inVia Raman microscope. All in situ Raman measurements were operated under 1 bar of flowing Ar and measured using a 488 nm laser and a 2400 l/mm grating system.



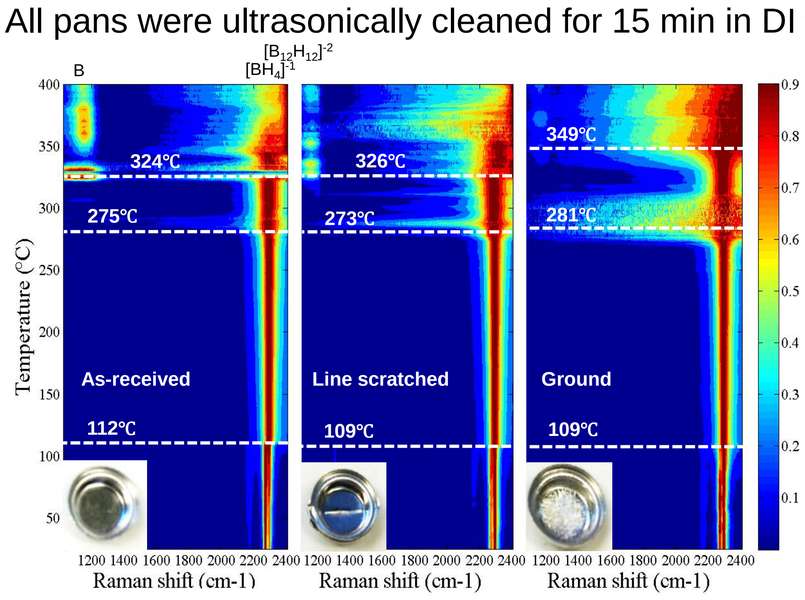
Effect of Surface Containment on molten $LiBH_4$

Lithium borohydride, $LiBH_4$, has relatively high gravimetric and volumetric hydrogen densities (18.6wt%), and has been extensively studied as a potential hydrogen storage material. At room temperature, it has an orthorhombic structure which undergoes a phase transition to a hexagonal structure in between 108 °C and 115 °C. Fusion occurs around 270-280 °C, followed by decomposition reactions above 320-330 °C. Under 1 bar Ar, $LiBH_4$ will decompose as [7]:



$$LiBH_4 \Leftrightarrow \frac{5}{6}LiH + \frac{1}{12}Li_2B_{12}H_{12} + \frac{13}{12}H_2 \quad \text{and} \quad LiBH_4 \Leftrightarrow LiH + B + \frac{3}{2}H_2$$

Three sample pans with different surface profiles were prepared: As-received (i.e. polished surface), Line-scratched and Ground. The line was scratched using a sharp tweezers, and the ground surface was made using 120 SiC sandpaper. All pans were ultrasonically cleaned for 15 min in DI water and then dried.



➔ The line scratched surface containment does not affect the phase transition, melting and decomposition temperatures. The ground surface containment increases the measured decomposition temperature.

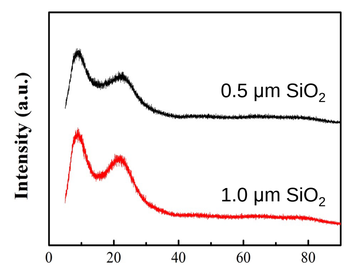
➔ The measured $[B_{12}H_{12}]^{-2}$ to B ratio increased from: As-received, to Line-scratched, to Ground.

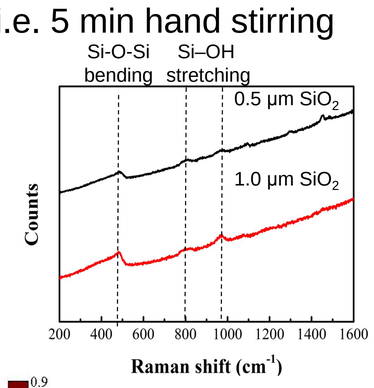
Effect of Nucleation Sites on molten $LiBH_4$

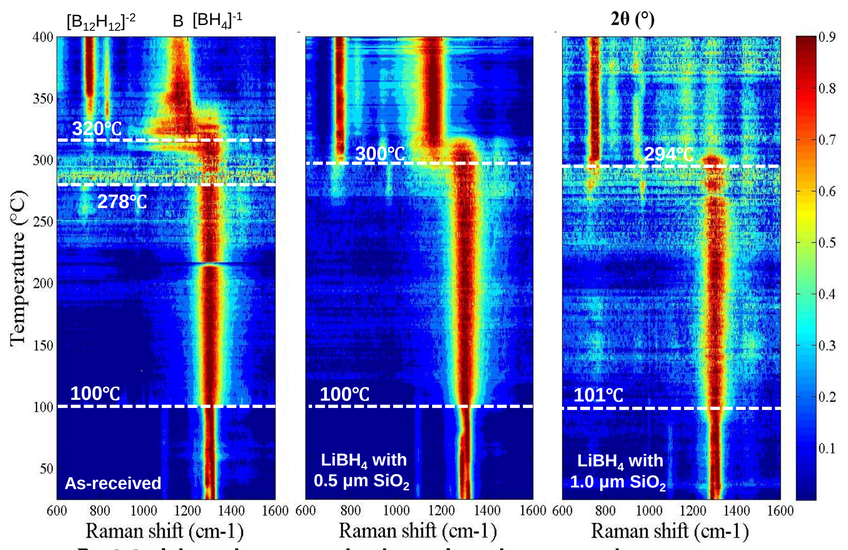
Samples of $0.95LiBH_4$-$0.05SiO_2$ using two different SiO_2 particle sizes (0.5 µm, 1.0 µm) were prepared by gently hand-mixing (i.e. 5 min hand stirring + 5 min hand shaking) 6 times.

As-received SiO_2 particles:

- No sharp peak was detected by XRD.
- Si-O-Si bending and Si-OH stretching modes have been detected [8].







➔ The morphology of decomposed product of $LiBH_4$-SiO_2 is compact, while that of $LiBH_4$ is flake like.

➔ Melting is not obviously observed.

➔ The measured decomposition temperatures for $LiBH_4$-SiO_2 samples are about 20 °C lower than that of as-received $LiBH_4$.

Summary

The *in situ* Raman results show that the ground surface containment increases the measured decomposition temperature by 25 °C (to 349 °C). An increasing of measured $[B_{12}H_{12}]^{-2}$ to amorphous boron ratio is observed. The measured decomposition temperatures for $LiBH_4$-SiO_2 samples are decreased about 20 °C (to 300 °C and 294 °C respectively) in contrast to $LiBH_4$. The morphology of decomposed material for $LiBH_4$-SiO_2 samples is compact, while that of $LiBH_4$ is flake like.

References

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Acknowledgements

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