

Dehydrogenation Thermodynamics of Hydrogen Storage Material Manganese Borohydride: First-Principles Study

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Abstract

Ab initio calculations using DFT were performed to establish a stable crystal structure of $\text{Mn}(\text{BH}_4)_2$. The crystal structure of $\text{Mn}(\text{BH}_4)_2$ is found to be orthorhombic with space group $Fddd$ (No. 70). The electronic density of states shows that manganese borohydride is of metallic nature without a band gap. Our calculations showed that the interaction between Mn atoms and BH_4 complexes has an ionic character while the internal bonding of BH_4 is essentially covalent. The reaction enthalpy was also found for the reaction $\text{Mn}(\text{BH}_4)_2 = \text{Mn} + 2\text{B} + 4\text{H}_2(\text{g})$ to be 135.026 kJ/f.u. at 0 K including zero point energy (ZPE) corrections.

Introduction

Light weight, low cost, highly reversible hydrogen storage systems are essential for low temperature PEM fuel cell powered vehicles¹. Complex hydrides of alkali and alkaline earth elements are promising candidates for hydrogen storage, but typically have heats of reaction that are too high to be of use for fuel cell vehicles. So, transition metal borohydride complexes as hydrogen storage materials have recently attracted great interest. $\text{Mn}(\text{BH}_4)_2$, among all other transition complex borohydrides, is stable at room temperature², and is considered to be a potential candidate for on-board applications as it has high theoretical hydrogen storage capacity of 10 wt% and also a reasonably low decomposition temperature compared to complex alkali and alkaline earth borohydrides. To be a viable candidate, a hydride must have a reaction free energy that lies in a range of values to allow reversible H_2 storage at practical temperatures and pressures. Thermodynamic data such as standard enthalpy of formation and Gibbs energy of dehydrogenation reaction required to assess the usability of the candidate material for practical applications are not available.

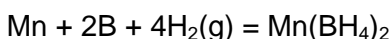
A combined theoretical and experimental approach can better lead us to design a suitable complex material for hydrogen storage. Here, we explore the complex hydrides using density functional theory (DFT) to provide information at the electronic level that is hard to obtain by experimental methods. Such calculations can also unravel the transition states of the molecules undergoing chemical transformation at complex solid surfaces. Phonon spectrum helps us to calculate the finite temperature thermodynamics and such calculations are performed in this work.

Computational details and methodology

First-principle calculations were performed in this work on $\text{Mn}(\text{BH}_4)_2$ using DFT within the generalized gradient approximation (GGA) and projector augmented wave (PAW) method and a plane wave basis set to calculate the total energies, as implemented in

the Vienna *Ab initio* Simulation Package (VASP).³⁻⁵ We started our calculations from known similar complex formula units $X(YZ_4)_2$ ⁶ for $Mn(BH_4)_2$ to find a stable crystal structure. Based on the optimized crystal structure from DFT, lattice dynamics based on the harmonic approximation using the direct force constant method in the PHONON⁷ code was used to calculate the phonon density of states (DOS) to confirm the finite temperature crystal stability and then calculated finite temperature thermodynamics.

The standard enthalpy of formation is an important predictor of decomposition temperature for the decomposition reaction with its associated standard thermodynamic parameters. For a complex hydride, when the material is being heated, the effect of standard entropy starts dominating the standard enthalpy and at the decomposition temperature and constant pressure the standard Gibbs energy is zero. As during heating the entropy change of solid materials is very small compared to the gas, we can consider that the entropy change during the decomposition reaction is primarily due to H_2 evolution. We have calculated the enthalpy for the formation equation of $Mn(BH_4)_2$ from its elemental components as given below:



The calculated results indicated that those for space group *Fddd* gives the stable structure. We have also calculated the electronic total density of states (DOS) and Electron Localization Function (ELF) of $Mn(BH_4)_2$ to gain insights into the nature of the material and bonding between the elements.

Results/Discussion

The above methods were used to establish the stable crystal structure with appropriate lattice parameters & atomic positions and the electronic structure of the high theoretical hydrogen storage capacity material $Mn(BH_4)_2$. The minimum total energy for $Mn(BH_4)_2$ was found to be -49.510 eV/mol at a unit cell volume of 816.10 Å³. The final optimized crystal structure with atomic positions is shown in Table 1.

Table 1: Optimized crystal structure of $Mn(BH_4)_2$. The space group is *Fddd* (# 70) with lattice parameters $a = 9.1562$ Å, $b = 12.8508$ Å and $c = 6.9358$. All the atomic positions are given by Wyckoff letter and the number of formula units in the unit cell $Z=8$.

Element	Wyckoff letter	X	Y	Z
Mn	8a	0.0000	0.0000	0.0000
B	16f	0.0000	0.1917	0.0000
H1	32h	0.8959	0.7493	0.4659
H2	32h	0.9648	0.6399	0.6414

The crystal structure of $Mn(BH_4)_2$ is consist of metal cation Mn^{2+} and nearly ideal tetrahedral $[BH_4]^-$. Each Mn^{2+} is surrounded by six octahedrally coordinated $[BH_4]^-$ anions and each $[BH_4]^-$ has three Mn^{2+} neighbors. Therefore this structure satisfies the electrostatic valence rule. The shortest Mn-H bond distance is 2.02 Å and the B-B nearest neighbor distance is 3.345 Å and Mn-B distance is 2.464 Å. The B-H bond lengths and the H-B-H bond angles are $d_{B-H} = 1.228 - 1.229$ Å and $\theta_{H-B-H} = 106 - 112^\circ$, respectively. The geometry of the BH_4 tetrahedron is similar to that found in isolated

$[\text{BH}_4]^-$ ions, an ideal tetrahedral structure with a constant bond length of 1.24 Å for B-H bonds, and tetrahedral angles of 109.5°, where the B and H atoms are covalently bonded.

From electronic structure calculations, ionic interaction between Mn and $[\text{BH}_4]^-$ and strong ionocovalent B–H interaction within the $[\text{BH}_4]^-$ tetrahedral structure are revealed. Electronic density of states studies reveal that this phase has no band-gap which suggests that the $\text{Mn}(\text{BH}_4)_2$ is a metallic hydrogen storage material.

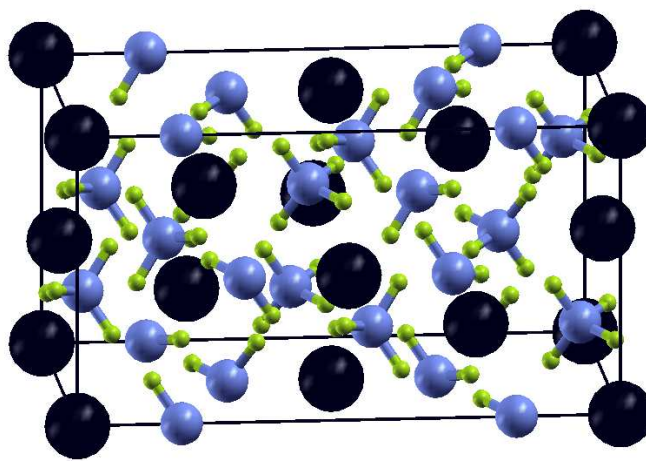


Figure 1. Crystal structure of $\text{Mn}(\text{BH}_4)_2$. Black (large), blue (middle) and green (small) spheres represent Mn, B and H atoms, respectively.

Conclusion

We have used density functional theory and lattice dynamics calculations to predict the crystal structure of the candidate material, the reaction enthalpies and identify suitable dehydrogenation reaction thermodynamics. It was found that $\text{Mn}(\text{BH}_4)_2$ exists as an orthorhombic structure of space group of *Fddd*. The electronic density of states shows that manganese borohydride is a metallic hydrogen storage material without having any band gap between valence and conduction bands. The electronic structure analysis also implies polar covalent bonds both between Mn and H and between B and H, with the lowest degree of polarity between Mn and H. The enthalpy of formation was calculated for the $\text{Mn}(\text{BH}_4)_2$ to be -135.026 kJ/f.u. at 0 K including zero point energy (ZPE) corrections. The simulated standard enthalpy of formation and dehydrogenation reaction for the complex $\text{Mn}(\text{BH}_4)_2$ shows that the most favorable dehydrogenation reaction is found to be $\text{Mn}(\text{BH}_4)_2 = \text{Mn} + 2\text{B} + 4\text{H}_2$, which is an endothermic reaction.

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