Nano-Phases of NaBH₄ and KBH₄

P. Vajeeston*, P. Ravindran, and H. Fjellvåg

Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315, Oslo, Norway

Phase stability and chemical bonding of β-NaBH₄ and β-KBH₄ derived nano-structures and possible low energy surfaces of them from thin film geometry have been investigated using ab initio projected augmented plane wave method. Structural optimizations based on total energy calculations predicted that, for β-NaBH₄ and β-KBH₄ phases, the (011) and (101) surfaces are more stable among the possible low energy surfaces. The predicted critical size of the nano-cluster for β-NaBH₄ and β-KBH₄ is 1.35 and 1.8 nm, respectively. The corresponding critical diameter for the nano-whisker is 2.6 and 2.8 nm respectively for β-NaBH₄ and β-KBH₄. Structural optimization based on total energy calculations show that the bond distances in the surfaces of nano-whisker are found to be higher than that in the bulk material and the calculated H site energies and bond overlap population analysis suggesting that it is considerably easier to remove hydrogen from the surface of the clusters and nano-whiskers than that from the bulk crystals.

Keywords: NaBH₄, KBH₄ Nanosphere.

1. INTRODUCTION

Hydrogen is viewed as a new clean energy source. For applications of hydrogen as energy source, especially as an on-board power source, hydrogen storage is one of the key enabling technologies. The target set by the U.S. Department of Energy (DOE) for an automobile on-board storage system is that the hydrogen storage capacity should be higher than 6% of the system weight by 2010. For achieving the DOE’s target, considerable work has been carried out on the research and development of new types of hydrogen storage materials, in which the boro-hydrides are one of the potential candidates. However, it suffers from unfavourable thermal stability and requires elevated temperature to desorb hydrogen. NaBH₄ and KBH₄ are characterized as hydrogen storage materials having both high volumetric and gravimetric (10.66 and 7.47 wt% for NaBH₄ and KBH₄ respectively) hydrogen density. Unfortunately, the decomposition temperature for both NaBH₄ and KBH₄ is close to 400 and 500 °C, respectively which is well above the temperature for any practical application as a hydrogen storage material in a mobile hydrogen storage system, e.g., automotive PEM fuel cell or a combustion engine. However, in the past 10 years, it has become clear that nanostructurization of solid state hydrides, which is usually achieved by mechanical alloying/milling, improves enormously the kinetics of their hydrogen desorption. Due to high stability, nonvolatility, and high hydrogen content, both NaBH₄ and KBH₄ are considered as potential systems for fuel cell applications. In order to use boro-hydrides as energy carrier in mobile applications one has to find the possible ways to decrease the hydrogen desorption temperature. Numerous studies have been focused on to improve the problematic sorption kinetics including mechanical ball milling, react with other complexes (like MgH₂, SiO₂, etc.), and chemical alloying. However, the required absorption and desorption kinetics has not yet been reached. In the present study we have investigated the role of particle size and nanophase effect on stability, electronic structure, and chemical bonding in NaBH₄ and KBH₄.

2. COMPUTATIONAL METHOD

The quantum-mechanical calculations have been performed in the frame of density functional theory using the generalized gradient approximation (GGA) as implemented in the VASP code. The interaction between the ion and electron is described by the projector augmented wave method. For the present calculations we have used a plane-wave cutoff energy of 500 eV. The k-points were generated using the Monkhorst-Pack method with a grid size of 8×8×12, 8×8×1, for the bulk and surfaces, respectively. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 1 meV/cell. With this criterion, the forces generally acting on the atoms were found to...
Na/BH₄ stoichiometry was always maintained. For the whisker construction the vacuum is included only in the x and y directions. The vacuum thickness was considered wide enough to prevent whisker-to-whisker/cluster-to-cluster interactions and we found that a width of 14 Å was sufficient to ensure that the energy was converged to less than 0.1 eV/Å. Different size of the nano-clusters and nano-whiskers have been constructed from optimized bulk phases through different supercell sizes. The k-points were generated using the Monkhorst-Pack method with a grid size of 1×1×1 and 1×1×2, for structural optimization for nano-clusters and nano-whiskers, respectively. During the nanoclusters/whisker construction the Na/BH₄ stoichiometry was always maintained. The optimized stable nano-whiskers and clusters of both NaBH₄ and KBH₄ are displayed in Figure 1. To gauge the bond strength the bond overlap population (BOP) values are calculated on the basis of the Mulliken population analysis using CASTEP code. For the CASTEP computation we have used the optimized VASP structures as input with Norm-conserving pseudopotentials and the generalized gradient approximation (GGA) exchange correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE).

3. RESULT AND DISCUSSION

NaBH₄ exhibits a cubic structure (α-NaBH₄) under ambient conditions. Experimental studies have shown that it has either the Fm̅3m (Ref. [21]) or the F43m (Refs. [22, 23]) space group. These two structural models are essentially identical; therefore, the higher symmetry space group Fm̅3m has been commonly accepted for α-NaBH₄. At low temperature, it shows a phase transition into a tetragonal P–421c phase (β-NaBH₄). Similar to NaBH₄, KBH₄ also exhibits a cubic structure (α–KBH₄) under ambient conditions. At low temperature this cubic structure transforms into a tetragonal P4₀/nmc symmetry structure. According to the theoretical finding this low temperature phase (β–KBH₄) is having lower total energy than the cubic α-modification. This is the one of the reasons why we have studied the size dependent property of nanophases derived from β-modification rather than that from the α-phase.

3.1. Active Low Energy Surfaces

For the surface calculations the unrelaxed slabs have been cleaved from the optimized bulk crystal in different possible low indexes, where bulk structures have been fully relaxed with respect to stress and strain. Sufficient number of vacuum layers were created and the convergence of total energy with respect to vacuum layers were studied. All atoms in such created slabs have been allowed to relax using the minimization of forces acting on them. For the considered surface models we have included an integer number of Na/KBH₄ formula units and are thus stoichiometric. The surface energy of a crystal can be calculated using the following equation

\[ E_{\text{surf}}(n) = \frac{E_{\text{tot}}(n) - E_{\text{bulk}}(n)}{2A} \]

where \( E_{\text{tot}} \) and \( A \) are the total energy and total surface area, respectively. \( E_{\text{bulk}} \) refers to the energy of the bulk \( \beta-\text{Na/KBH}_4 \) system containing the same number of molecular units as that in the slab. Since the constructed supercell of the slab has two surfaces, the energy difference is normalized by twice the area of each surface in Eq. (1). From the calculated surface energy as a function of layer thickness in all the studied thin film geometries we have found that 8 to 9 layers supercell (depending upon the surface) is sufficient to achieve well converged surface energy. The calculated surface energies for the \( \beta-\text{NaBH}_4 \) vary from 0.24 to 1.89 J/m² (depending upon the surface) and for the \( \beta-\text{KBH}_4 \) surfaces the surface energies are between 0.3 and 1.67 J/m² (see Table I). In both phases the (011) and (101) surfaces having same or almost the same surface energy. The possible reason is that in \( \beta-\text{KBH}_4 \) both (011) and (101) surfaces have almost a similar atomic arrangement. In (011) and (101) surfaces K and BH₄ tetrahedral units are arranged as an alternative layers and within the BH₄ layers the tetrahedral are arranged alternatively in an up and down manner. The low surface energy value for these surfaces indicates that the energy costs will be smaller to create these surfaces through only
Table I. Calculated surface energy (in J/m²) for NaBH₄ and KBH₄ in different possible low energy surfaces.

<table>
<thead>
<tr>
<th>Direction</th>
<th>β-NaBH₄</th>
<th>β-KBH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>1.89</td>
<td>1.64</td>
</tr>
<tr>
<td>(010)</td>
<td>1.36</td>
<td>1.29</td>
</tr>
<tr>
<td>(011)</td>
<td>0.24</td>
<td>0.30</td>
</tr>
<tr>
<td>(100)</td>
<td>1.36</td>
<td>1.29</td>
</tr>
<tr>
<td>(101)</td>
<td>0.24</td>
<td>0.31</td>
</tr>
<tr>
<td>(110)</td>
<td>1.75</td>
<td>1.67</td>
</tr>
<tr>
<td>(111)</td>
<td>0.82</td>
<td>0.73</td>
</tr>
</tbody>
</table>

breaking H–Na/K bonds in bulk Na/KBH₄ and are much lesser than α-MgH₂. These values are much closer to the corresponding surface energy for the α-LiBH₄ surfaces and one could expect a similar value for the other poly-morphs of Li/Na/KBH₄ systems. One may also expect a similar value for RbBH₄ and CsBH₄ in the rest of the ABH₄ (A is any one of the alkali element) series and for them such studies are under investigation.

3.2. Nano-Clusters and Whiskers

From the variation in the interatomic distances compared with bulk materials it should be anticipated that nanophase materials have different physical and chemical property than the bulk materials. Once we reduce the particle size beyond certain range (called critical size), all atoms will be exposed to the surface. It is at this region where the properties of the material begins to differ drastically from that of the bulk materials. In order to identify the critical particle size we have calculated the total energy as a function of the cluster size and that are shown in Figure 2. From Figure 2 it is evident that if the cluster size decreases the total energy becomes more positive (i.e., the formation energy decreases with decrease of cluster size). In particular there is a steep increase in the total energy when the size of the cluster is below 1.35 and 1.8 nm for NaBH₄ and KHB₄, respectively. Similarly, the calculated total energy as a function of nano-whisker diameter shows that (see Fig. 3) when we reduce the diameter below certain critical value (2.6 nm for NaBH₄; the corresponding value for KBH₄ is 2.9 nm) the total energy increase drastically. If one reduce the cluster size and nano-whisker diameter, the relative energy of the clusters/nano-whiskers becomes less negative, which indicates the destabilization of small particles. This also suggests that the thermodynamical properties and in particular the hydrogen sorption temperature is expected to reduce in nanophases compared with that in bulk materials.

Further, the surface-to-volume ratio increases upon decreasing the cluster/nano-whisker size. Since the surface atoms have lower coordination than that in bulk materials, the average number of bonds between constituents is lower for smaller clusters. It should be noted that a similar trend has also been observed in LiBH₄ where the critical size of the cluster was 1.75 nm. On the other hand, the calculated critical diameter for the nano-whisker of LiBH₄ was found to be almost half the value than the Na/KBH₄ whiskers. Moreover, in ultra small clusters and whiskers, the hydrogen atoms are generally found to occupy the less stable top and bridge sites at the surfaces compared with the more stable three-dimensionally coordinated sites commonly found in thicker clusters/whiskers (diameter above the critical size) as well as in corresponding bulk materials. In both phases, the calculated B–H distances versus number of bonds (see Fig. 4) for the biggest clusters/whiskers indicate that the values were scattered compared with that in the corresponding bulk phase. Especially most of the
Fig. 4. Calculated interatomic distances between B–H, K/Na–H in the optimized Na/KBH₄ nanoclusters and whiskers. Arrow mark indicates the theoretical B–H and K/Na–H (red arrow mark corresponds to NaBH₄ and black corresponds to KBH₄ cluster/whisker) distance for the bulk NaBH₄ and KBH₄ phase.

B–H bonds have longer bond distances than that in the bulk. Moreover, the calculated Na–H and K–H distance for the nanophases are found to be very much scattered than the B–H distances. This type of structural arrangement is expected in nano- and amorphous-phases with no three dimensional crystallinity owing to reduction in coordination number of atoms.

It should be noted that when we increase the cluster/nano-whisker size above the critical size these objects have core Na/KBH₄ structural units that makes these systems become quite stable. Hence, one must reduce the particle size beyond the critical size to easily remove the H from the Na/KBH₄ particles. In order to strengthen this argument we have calculated the H site energy (HSE; \(\Delta E\)) in these particles. In nano-clusters/whiskers the H is situated in four different configurations such as H1 (in between Na/K), H2 (in between Na/K and B), H3 (H is connected with B) and H4 (center of the cluster). The H site energy is calculated in the following manner; \(\Delta E = (E_{\text{Hvac}} + 1/2E_{\text{Hmol}}) - E_{\text{nano}}\), where \(E_{\text{Hvac}}\) and \(E_{\text{Hmol}}\) refer to the energy of the nano object with and without H vacancy and \(E_{\text{Hmol}}\) is the total energy of a free H₂ molecule calculated in a large box (the calculated energy is \(-6.789\) eV). The calculated HSE for \(\beta\)-NaBH₄ and \(\beta\)-KBH₄ derived clusters/whiskers are scattered in a wide energy range (see Fig. 5); which is highly depending upon the environment of the H sites. The calculated H1, H2, H3 and H4 site energy values are 0.65, 0.82, 1.30, and 2.2 eV, for \(\beta\)-NaBH₄ and 0.73, 0.90, 1.32, and 2.31 eV for \(\beta\)-KBH₄ derived clusters. Similarly, for nano-whiskers, the calculated HSE value in \(\beta\)-NaBH₄ is 0.78, 1.09, 1.38 and 2.19 and that in \(\beta\)-KBH₄ whiskers 0.68, 1.14, 1.33, and 2.30 eV for H1, H2, H3 and H4 sites, respectively. The corresponding HSE value for the bulk phases are 2.21 and 2.32 eV for \(\beta\)-NaBH₄ and \(\beta\)-KBH₄, respectively. This finding clearly indicates that the required energy to remove H from the center of the nano objects (nano-clusters/nano-whisker) will be similar to that of bulk phase. Also, substantially reduction in energy is expected to remove hydrogen in nanophases below their critical size. Further, the small energy require to remove from the surface layers of complex hydrides indicates that the nano-phases of hydrogen storage materials will be more advantageous to use for practical applications since they substantially reduce the hydrogen sorption temperature and improve the kinetics.

3.3. Chemical Bonding

For the bulk phases the theoretical charge-density maps clearly demonstrated the striking ionic character between Na/K and H with noticeable covalent bond within the BH₄ units. The substantial difference in the electronegativity between Na/K and H suggests the presence of strong ionic character (i.e., the Na/K valence electrons transferred to the H sites) and the small difference in the electronegativity between B and H suggests the presence of strong covalent character. In order to gain further understanding about the bonding situation in nano objects of \(\beta\)-Na/KBH₄, we turn our attention to the charge density analysis. According to the charge-density distribution at the Na and K sites in the center of the nano-phases (Figs. 6(a–f)), it is evident...
that the highest charge density resides in the immediate vicinity of the nuclei. The spherical charge distribution at the Na and K sites (Figs. 6(b, c, e and f)) clearly reflects the ionic character. On the other hand, due to the covalent interaction a finite charge density was present in between B and H. In order to more insight into the chemical bonding we have visualized the charge density with the isosurface value of 0.6 e [1(a) for dot and (d) for whiskers], only the iso-surfaces with value of 0.6 e [1(b) for dot and (e) for whiskers], and two dimensional view [1(c) for dot and (f) for whiskers].

In order to have a better understanding about the bonding interaction between the constituents the bond overlap population (BOP) values are calculated on the basis of Mulliken population analysis. The BOP values can provide useful information about the bonding property between atoms. A high BOP value indicates a strong covalent bond, while a low BOP value indicates an ionic interaction. For the practical use of NaBH₄ and KBH₄ as hydrogen storage materials, one must weaken their B–H bonds. The calculated BOP values for the B–H bonds in different modifications of NaBH₄ and KBH₄ are presented in Table II. Table II shows that the BOP values for the B–H bonds are considerably weaken in the nano-phases. This finding is consistent with the present HSE study. It is interesting to note that the BOP value for B–H bond in bulk phase is around 1.13, which is almost equivalent to that of covalent C–C bond in diamond (the BOP value is 1.08). This might be one of the reasons why these phases can only release H only at elevated temperature (above the melting point). In all the considered phases the calculated Na/K–H BOP values are almost zero owing to the high degree of the ionic character.

### Table II. Calculated B–H distance (in Å) and bond overlap population (BOP) values for bulk, low energy surfaces, nano-clusters, and nano-whiskers of β-NaBH₄ and β-KBH₄.

<table>
<thead>
<tr>
<th>Modification</th>
<th>B–H distance</th>
<th>BOP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>β-NaBH₄</td>
<td>β-KBH₄</td>
</tr>
<tr>
<td>Bulk</td>
<td>1.207</td>
<td>1.204</td>
</tr>
<tr>
<td>Surface</td>
<td>1.206–1.23</td>
<td>1.22–1.24</td>
</tr>
<tr>
<td>Cluster</td>
<td>1.20–1.25</td>
<td>1.22–1.25</td>
</tr>
<tr>
<td>Whisker</td>
<td>1.202–1.25</td>
<td>1.23–1.24</td>
</tr>
</tbody>
</table>

### 4. CONCLUSION

In summary, we have studied the possible low energy surfaces and the phase stability of β-NaBH₄ and β-KBH₄ derived nano-clusters and nano-whiskers using the density functional total energy calculations. The calculated surface energy for the low-index surfaces show that due to similar atomic arrangements in (011) and (101) surfaces both the surfaces are more stable among all the surfaces considered in the present calculations. We have predicted that the critical size for the nano-cluster of β-NaBH₄ and β-KBH₄ is 1.35 and 1.8 nm, respectively. The corresponding critical diameter of the nano-whiskers are 2.6 and 2.8 nm, respectively. If one reduces the size below the critical size, the stability of the cluster/nano-whisker reduce drastically and we have identified that in such objects almost all atoms are exposed to the surface. The bonding interactions in surface layers are considerably weaker than that at the center of the cluster/nano-whisker. As a result, one can expect that the removal of hydrogen from the surface of the nano-phases is much easier than that from the bulk or from the inner part of the cluster/nano-whisker. The present study suggest that, in order to use β-NaBH₄ and β-KBH₄ as a hydrogen storage materials, one must reduce the particles size below the critical size.

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**References and Notes**

Nano-Phases of NaBH$_4$ and KBH$_4$

Vajeeston et al.


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