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First-principles study of a double-cation alkali metal borohydride $\text{LiK}(\text{BH}_4)_2$

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Abstract

Metal borohydrides have been attracting great interest as potential candidates for use as advanced hydrogen storage materials because of their high gravimetric hydrogen densities. In the present study, first-principles calculations have been performed for the newly reported dual-cation alkali metal borohydride $\text{LiK}(\text{BH}_4)_2$, using density functional theory (DFT) within the generalized gradient approximation and the projected augmented wave method. $\text{LiK}(\text{BH}_4)_2$ is found to have an orthorhombic structure in the space group $Pnma$ (No 62) with nearly ideal tetrahedral shape. It is an insulating material having a DFT-calculated wide band gap of 6.08 eV. Analysis of the electronic structure shows an ionic interaction between metal cations and $(\text{BH}_4)^-$ and the covalent B–H interaction within the $(\text{BH}_4)^-$ tetrahedron. The enthalpy of the formation reaction from primary elements is calculated and found to be $-449.8 \text{ kJ mol}^{-1}$. The decomposition temperature (T_{dec}) of $\text{LiK}(\text{BH}_4)_2$ lies between those of LiBH_4 and KBH_4 , which suggests that the hydrogen decomposition temperature of metal borohydrides can be precisely adjusted by the appropriate combination of cations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The growing worldwide demand for energy, the limited supply of fossil fuels, and the adverse effect of fossil fuels on the environment have made it necessary to search for alternative energy sources that are renewable, abundant, secure, environmentally friendly, and cost effective [1]. Hydrogen is viewed as the most promising alternative energy carrier of the future [2–4] because of its abundance, easy synthesis, the highest heating value per mass and its nonpolluting nature during combustion. However, there are many scientific and technological challenges to overcome in its production, distribution, storage, and use in fuel cells. Foremost among these is the issue of hydrogen storage. Existing technology for hydrogen storage is limited to compressed gas and liquefaction, both of which are used now in demonstration vehicles. Solid state storage

is seen as the safest and most effective way of routinely handling hydrogen in the future. An ideal solid hydrogen storage material for practical applications should meet the requirements of high gravimetric ($>6.0 \text{ wt\%}$) and volumetric densities ($>45 \text{ kg m}^{-3}$), fast absorption–desorption kinetics, favorable thermodynamics and low cost. Up to now, there has been no storage material known to meet simultaneously all of the above requirements.

Alkali complex hydrides have attracted growing interest as potential candidates for use as advanced hydrogen storage materials due to their high gravimetric hydrogen densities (lithium borohydride (LiBH_4) has a theoretical hydrogen capacity of $\sim 18.3 \text{ wt\%}$). Complex hydrides generally consist of a lattice of metal cations and complex anions such as $(\text{AlH}_4)^-$ or $(\text{BH}_4)^-$, where the hydrogen is located in the corners of a tetrahedron with boron or aluminum in the center, respectively. On heating, these materials decompose via intermediate complex hydrides into bulk metals, elemental hydrides, and hydrogen gas. Unfortunately, they are very

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stable and are dehydrogenated only at elevated temperatures. Bogdanović and Schwickardi [5] reported for the first time in 1997 that the Ti-catalyzed NaAlH₄ system could reversibly absorb and desorb hydrogen up to 4.2 wt% and the mechanism of the two-step reaction was described. A more detailed study of NaAlH₄ with an improved catalyst by Bogdanović *et al* was published in 2000 [6]. Following the discovery of reversible H₂ storage in Ti-doped sodium alanate, there has been a strong interest in NaAlH₄ and other high density alanates. In the past few years, the attention has gradually shifted from alanates toward boranates because of higher gravimetric hydrogen density in the latter. However, most of the commonly known borohydrides are found to be unsuitable for on-board hydrogen storage applications. This is primarily attributable to the high stability resulting in very high decomposition temperatures or complete irreversibility of hydrogen desorption [7]. In principle, a large variety of boranates can be synthesized by changing the metal cations, which can be used to tune the formation energy [8]. More recently, a mixed alkali metal borohydride LiK(BH₄)₂ has been synthesized by Nickels *et al* [9]. The observed decomposition temperature (T_{dec}) of LiK(BH₄)₂ lies between that of LiBH₄ and KBH₄. This finding of a genuine, dual-cation single-phase material offers the real prospect of chemical control of T_{dec} by the manipulation of multi-cation combinations.

Density functional theory (DFT) has become a valuable tool in the effort to explore possible hydrogen storage materials [10]. It has greatly expanded our understanding of the properties of known hydrides, including the electronic structure, hydrogen bonding character, enthalpy of formation, elastic behavior, and vibrational energetics. LiK(BH₄)₂ is a novel double-metal-cation borohydride; very little is known about its structural and thermodynamic properties. In this paper, we wish to study the structure and thermodynamics of the formation reactions for the mixed alkali metal borohydride using a first-principles DFT approach. The electronic structure in relation to the crystal structure is used to analyze the bonding of LiK(BH₄)₂. We obtain the thermodynamic properties by calculating total energies of all compounds involved in possible formation reactions of LiK(BH₄)₂.

2. Computational methods

In the present study, first-principles computations were performed using the Vienna *ab initio* simulation package (VASP) code [11] with the projector augmented wave (PAW) [12, 13] method. A kinetic energy cutoff of 500 eV was used for the plane wave basis set. The GGA exchange–correlation energy functional [14–16] generally yields lattice constants and electronic total energies that are in more favorable agreement with experiment than the LDA values. Hence, we had used GGA of ‘Perdew–Wang 91’ [17] to describe the exchange–correlation interaction. The k space integrals were performed using the sampling generated by the Monkhorst–Pack procedure [18]. A total of $8 \times 12 \times 4$, $8 \times 12 \times 8$ and $8 \times 8 \times 8$ k -points were used to model the Brillouin zone for LiK(BH₄)₂, LiBH₄ and KBH₄, respectively. A $19 \times 19 \times 19$ k -point mesh was utilized for the bcc Li and K. The calculation

for boron is carried out using the stable β phase containing 105 atoms in unit cell and with the single Γ point for the k -point sampling. The energy of the H₂ molecule was calculated in an orthorhombic box large enough to ensure isolation. The valence electronic configurations were taken to be $1s^2 2s^1 2p^0$ for Li, $3s^2 3p^6 4s^1$ for K, $2s^2 2p^1$ for B, and $1s^1$ for H. In order to get the precise crystal structures and total energies, all structural degrees of freedom including unit-cell volume and shape as well as atomic positions were relaxed simultaneously. Ground state geometries were determined by minimizing stresses and Hellmann–Feynman forces with the conjugate gradient algorithm, until the forces on all atomic sites were less than 10^{-2} eV \AA^{-1} . The self-consistent calculations were considered to be converged when the difference in total energy of the crystal did not exceed 10^{-6} eV at consecutive steps. When the optimized crystal structures were obtained, the total energies were calculated using the tetrahedron method with Blöchl corrections which could give very accurate total energy in bulk materials.

3. Results and discussion

Understanding the structural properties of hydrides is the primary step toward their experimental characterization, and also a prerequisite for finding or designing materials with specific storage thermodynamics [19]. The structure of the mixed alkali metal borohydride LiK(BH₄)₂ has been characterized using high resolution x-ray diffraction [9]. At room temperature, LiK(BH₄)₂ exhibits an orthorhombic $Pnma$ (No 62) structure with 48 atoms in the primitive unit cell. Its approximate lattice parameters are $a = 7.9134$ \AA , $b = 4.4907$ \AA , and $c = 13.8440$ \AA , and the b -axis lattice parameter is very similar to that of orthorhombic LiBH₄ (4.436 86 \AA) [20], suggesting a degree of structural similarity between the phases. Starting from the experimental results, the structural optimization with the full relaxation of the unit-cell volume and shape as well as atomic positions is performed. The optimized structure is in excellent agreement with the experimental data. The cell parameters $a = 7.8240$ \AA , $b = 4.4263$ \AA , $c = 13.6950$ \AA are only slightly underestimated (errors of $\approx 1\%$). The calculated atomic positions are also in good agreement with the experimental data. The optimized lattice parameters and atomic positions are given in table 1. Figure 1 shows the optimized orthorhombic ($Pnma$) crystal structure of LiK(BH₄)₂. Our calculation results have shown a nearly ideal tetrahedral shape where the bond lengths are almost constant and the bond angles are close to the ideal value $\theta_{\text{H-B-H}} = 109.5^\circ$. The bond lengths and the bond angles of the BH₄ complexes are $d_{\text{B-H}} = 1.2237$ – 1.2272 \AA , $\theta_{\text{H-B-H}} = 105.85^\circ$ – 111.66° , respectively. We have, in detail, summarized the bond lengths and the bond angles of tetrahedral BH₄ complexes in table 2. In our calculations, the bond lengths of BH₄ complexes in LiK(BH₄)₂ are very close to the B–H distances in orthorhombic LiBH₄ and cubic KBH₄, where the B–H distances within the BH₄ complexes are 1.2224–1.2278 \AA and 1.2280 \AA , respectively.

The total and partial densities of states for LiK(BH₄)₂ are calculated and shown in figure 2. From the figure, it can be seen

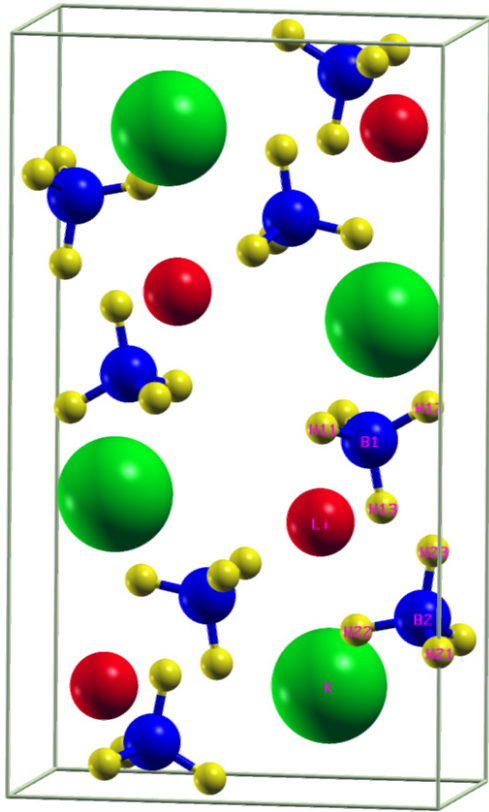


Figure 1. Crystal structure of $\text{LiK}(\text{BH}_4)_2$. Hydrogen atoms (small yellow spheres) form tetrahedra around the boron atoms (blue spheres). The red (middle) spheres and green (large) spheres denote lithium atoms and potassium atoms, respectively.

Table 1. Optimized crystal structure of $\text{LiK}(\text{BH}_4)_2$. The space group is $Pnma$ (No 62) and the optimized lattice parameters are $a = 7.8240 \text{ \AA}$, $b = 4.4263 \text{ \AA}$, $c = 13.6950 \text{ \AA}$. All the atomic positions are given by Wyckoff letters and the number of formula units in the unit cell $Z = 4$.

Atom	Wyckoff	Present			Experiment ^a		
		x	y	z	x	y	z
Li	4c	0.1953	0.25	0.1389	0.1885	0.25	0.1349
K	4c	0.3371	0.25	0.8714	0.33814	0.25	0.86851
B ₁	4c	0.2475	0.25	0.5481	0.2508	0.25	0.5460
B ₂	4c	0.9335	0.25	0.2394	0.9292	0.25	0.2397
H ₁₁	8d	0.3336	0.4712	0.5258	0.324	0.456	0.5288
H ₁₂	4c	0.2180	0.25	0.6361	0.206	0.25	0.614
H ₁₃	4c	0.1126	0.25	0.5025	0.140	0.25	0.498
H ₂₁	8d	0.9958	0.4787	0.2040	0.976	0.452	0.2057
H ₂₂	4c	0.7802	0.25	0.2214	0.789	0.25	0.218
H ₂₃	4c	0.9563	0.25	0.3280	0.960	0.25	0.316

^a Reference [9].

that $\text{LiK}(\text{BH}_4)_2$ is an insulating material with a fundamental band gap of 6.08 eV. The bandwidth of $\text{LiK}(\text{BH}_4)_2$ is narrower than the band gaps of LiBH_4 (6.86 eV) and KBH_4 (6.26 eV) in our calculations, which are in good agreement with other calculation [21]. The valence band splits into two separate regions (region I: -6.8 to -5.7 eV, region II: -2.1 to E_F) with a 3.6 eV gap between these regions. The occupied states are primarily dominated by B 2s and H 1s orbitals and B 2p and

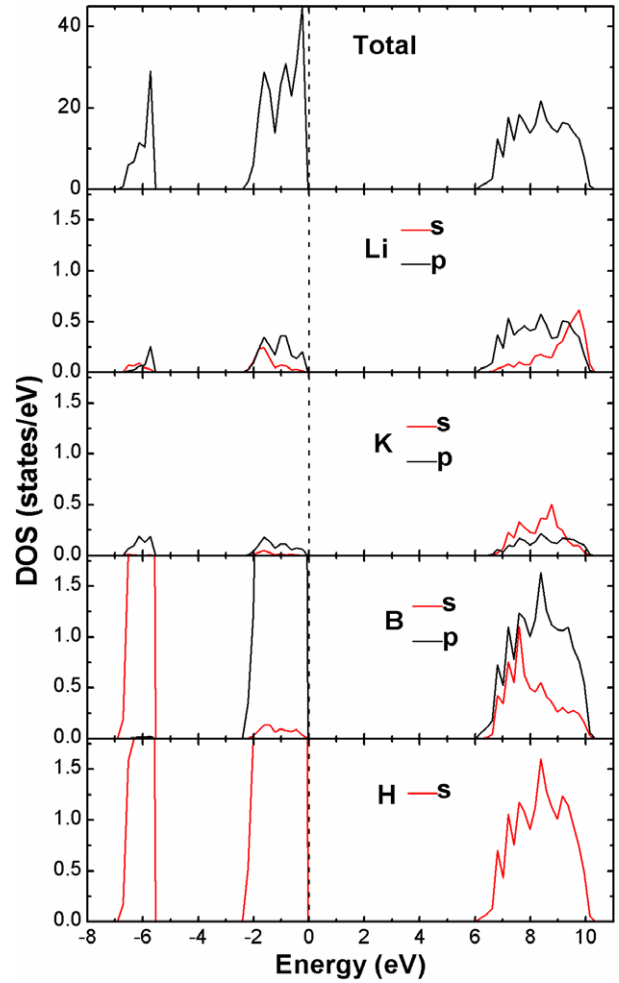


Figure 2. Total and partial densities of states for $\text{LiK}(\text{BH}_4)_2$. The zero of the energy scale is set at the Fermi level.

Table 2. Bond lengths $d_{\text{B-H}}$ (\AA) and bond angles $\theta_{\text{H-B-H}}$ (deg) of BH_4 complexes in orthorhombic $\text{LiK}(\text{BH}_4)_2$.

	$d_{\text{B-H}}$ (\AA)		$\theta_{\text{H-B-H}}$ (deg)	
B ₁ -H ₁₁	1.2237	H ₁₁ -B ₁ -H ₁₁	111.66	
B ₁ -H ₁₂	1.2246	H ₁₁ -B ₁ -H ₁₂	108.09	
B ₁ -H ₁₃	1.2267	H ₁₁ -B ₁ -H ₁₃	109.51	
		H ₁₂ -B ₁ -H ₁₃	109.93	
B ₂ -H ₂₁	1.2272	H ₂₁ -B ₂ -H ₂₁	105.85	
B ₂ -H ₂₂	1.2266	H ₂₁ -B ₂ -H ₂₂	110.18	
B ₂ -H ₂₃	1.2269	H ₂₁ -B ₂ -H ₂₃	110.38	
		H ₂₂ -B ₂ -H ₂₃	109.80	

H 1s orbitals in region I and region II, respectively, and there is little contribution from Li and K orbitals. This supports an ionic picture for the interaction between metal atoms and $(\text{BH}_4)^-$ complexes [8, 22]. The Li and K atoms donate electrons to the $(\text{BH}_4)^-$ complexes and are ionized as Li^+ and K^+ cations. The B 2p and H 1s orbitals are energetically degenerate in region II, which clearly facilitates the formation of the hybridization prerequisite for the occurrence of the covalent bond in $(\text{BH}_4)^-$ complexes. The conduction band is dominated by the s and p electrons of Li, K and B, and H 1s electrons. Although H 1s electrons are prominent in the

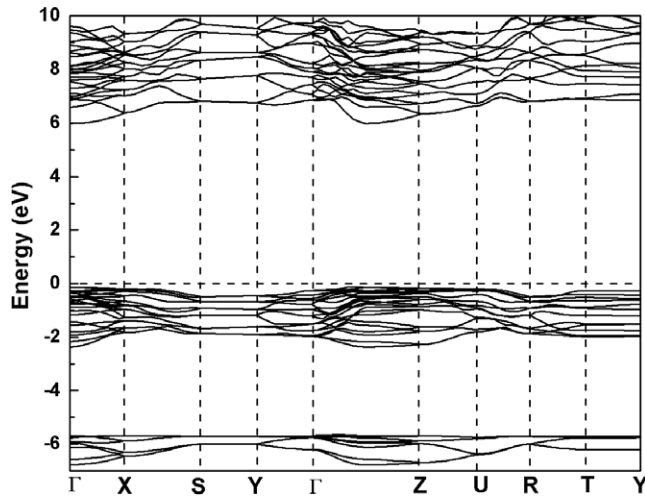


Figure 3. Band structure of orthorhombic $\text{LiK}(\text{BH}_4)_2$ along some high symmetry direction. The zero of the energy scale corresponds to the Fermi energy.

valence band, some H 1s states is also found in the conduction band which may indicate charge transfer to H atoms.

The calculated band structures of orthorhombic $\text{LiK}(\text{BH}_4)_2$ along the selected high symmetry directions of the Brillouin zone are presented in figure 3. The selected high symmetry points of the Brillouin zone for orthorhombic $\text{LiK}(\text{BH}_4)_2$ are labeled Γ (0, 0, 0), X (0.5, 0, 0), S (0.5, 0.5, 0), Y (0, 0.5, 0), Z (0, 0, 0.5), U (0.5, 0, 0.5), R (0.5, 0.5, 0.5) and T (0, 0.5, 0.5). It can be seen that the band gap is an indirect one because the maximum of the valence band does not coincide with the minimum of the conduction band. The maximum of the valence band is located at the Γ point of the Brillouin zone, whereas the minimum of the conduction band can be observed along the Γ -X and Γ -Y directions. The width of the valence band is equal to 6.64 eV with the internal gap equal to 3.6 eV, and the top of valence bands has a very flat character along selected symmetry lines. As far as we know, there are no theoretical and experimental results on the electronic band structure of the orthorhombic phase of $\text{LiK}(\text{BH}_4)_2$ to compare with.

The enthalpies of formation are the most important thermodynamic parameters used to identify and classify hydrogen storage materials since they determine the heat of the overall hydriding reaction, which, in turn, affects the temperatures of the reversible hydrogenation/dehydrogenation processes. The enthalpy of formation (ΔH) is calculated by taking the difference in total electronic energy of the products and the reactants:

$$\Delta H = \sum E_{\text{tot}}(\text{products}) - \sum E_{\text{tot}}(\text{reactants}) \quad (1)$$

where E_{tot} is the total energy of the bulk structures of interest as calculated from first principles. The zero-point energy corrections are not taken into account in any of the reaction enthalpies in this study. For the following calculations, the phases, lattice constants and total energies per formula unit of all reactants and products appearing in the present study are summarized in table 3.

Table 3. Space group, lattice constants (\AA) and total electronic energy E_{tot} (eV) per formula unit for every reactant and product involved in this study.

Compound	Space group	Lattice constant (\AA)	E_{tot} (eV)
$\text{LiK}(\text{BH}_4)_2$	$Pnma$ (No 62)	$a = 7.8240(7.9134)^a$ $b = 4.4263(4.4907)^a$ $c = 13.6950(13.8440)^a$	-48.144
LiBH_4	$Pnma$ (No 62)	$a = 7.2653(7.17858)^b$ $b = 4.3827(4.43686)^b$ $c = 6.5891(6.80321)^b$	-24.320
KBH_4	$Fm\bar{3}m$ (No 225)	$a = 6.718(6.7306)^c$	-23.818
Li	$Fm\bar{3}m$ (No 225)	$a = 3.4297(3.51)^d$	-1.898
K	$Fm\bar{3}m$ (No 225)	$a = 5.2783(5.328)^d$	-1.039
B	$R\bar{3}m$ (No 166)	$a = b = c =$ 10.1331(10.17) ^e $\alpha = \beta = \gamma =$ 63.17(65.12) ^e	-6.675
H_2	Gas phase	Interatomic distance (\AA) $d = 0.75(0.741)^f$	-6.800

^a Reference [9].

^b Reference [20].

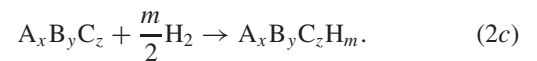
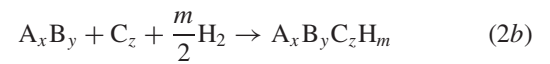
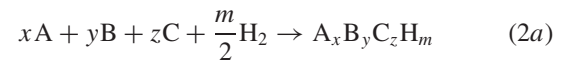
^c Reference [23].

^d Reference [24].

^e Reference [25].

^f Reference [26].

There are many possible reaction pathways for a complex system. For example, the possible formation pathways of quaternary hydrides $\text{A}_x\text{B}_y\text{C}_z\text{H}_m$ have been written as follows:



The enthalpies of formation for the quaternary hydrides $\text{A}_x\text{B}_y\text{C}_z\text{H}_m$ according to the reaction pathways (2a), (2b) and (2c) can be expressed as follows:

$$\Delta H_a = E_{\text{tot}}(\text{A}_x\text{B}_y\text{C}_z\text{H}_m) - \left[xE_{\text{tot}}(\text{A}) + yE_{\text{tot}}(\text{B}) + zE_{\text{tot}}(\text{C}) + \frac{m}{2}E_{\text{tot}}(\text{H}_2) \right] \quad (3a)$$

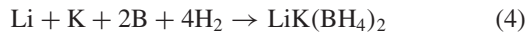
$$\Delta H_b = E_{\text{tot}}(\text{A}_x\text{B}_y\text{C}_z\text{H}_m) - \left[E_{\text{tot}}(\text{A}_x\text{B}_y) + zE_{\text{tot}}(\text{C}) + \frac{m}{2}E_{\text{tot}}(\text{H}_2) \right] \quad (3b)$$

$$\Delta H_c = E_{\text{tot}}(\text{A}_x\text{B}_y\text{C}_z\text{H}_m) - \left[E_{\text{tot}}(\text{A}_x\text{B}_y\text{C}_z) + \frac{m}{2}E_{\text{tot}}(\text{H}_2) \right]. \quad (3c)$$

We assume that the products A_xB_y and $\text{A}_x\text{B}_y\text{C}_z$ are stable (if the products A_xB_y and $\text{A}_x\text{B}_y\text{C}_z$ are unstable, it is obvious that they will decompose and form other products; therefore, the formation reaction pathways (2b) and (2c) are impractical.) Generally speaking, for a stable compound at room temperature the enthalpy of formation is below zero.

Hence, we can obtain $\Delta H(A_xB_y) = E_{\text{tot}}(A_xB_y) - [xE_{\text{tot}}(A) + yE_{\text{tot}}(B)] < 0$ (that is $E_{\text{tot}}(A_xB_y) < xE_{\text{tot}}(A) + yE_{\text{tot}}(B)$); consequently $\Delta H_a < \Delta H_b$ according to equations (3a) and (3c). We can also obtain $\Delta H_b < \Delta H_c$; therefore $\Delta H_a < \Delta H_b < \Delta H_c$. On the basis of the above discussion, it is obvious that the formation pathway from pure elements is the lowest energy reaction pathway. If there are no other compelling reasons such as kinetics, the preparation from the pure elements should be the best synthesis route rather than starting from other compounds.

In the present study, we have only considered the formation pathways of $\text{LiK}(\text{BH}_4)_2$ from pure elements and from LiBH_4 and KBH_4 , which is reasonable according to our analysis above. Therefore, the enthalpy of formation (ΔH) has been calculated according to the following reaction equations:



According to the energies given in table 3, the enthalpy changes ΔH (kJ mol^{-1}) for the formation reactions of $\text{LiK}(\text{BH}_4)_2$ (equation (4)), LiBH_4 (equation (5b)) and KBH_4 (equation (5c)) have been displayed in figure 4. In the present calculations, LiBH_4 has orthorhombic symmetry with space group $Pnma$, and KBH_4 has face-centered cubic structure with space group $Fm\bar{3}m$. The enthalpies of formation for LiBH_4 and KBH_4 are calculated on the basis of equation (1) along formation reaction pathways (5b) and (5c), respectively. Our calculation result for LiBH_4 is in excellent agreement with the experimental value, reported as -194 kJ mol^{-1} [27], which indicates that our calculations are reasonable although the zero-point energy is not considered. The obtained enthalpy of formation of reaction pathway 4 for $\text{LiK}(\text{BH}_4)_2$ is $-449.8 \text{ kJ mol}^{-1}$, which shows clearly that $\text{LiK}(\text{BH}_4)_2$ is very stable relative to the elemental constituents. On the other hand, the enthalpy of formation for $\text{LiK}(\text{BH}_4)_2$ from LiBH_4 and KBH_4 is very small (about -0.6 kJ mol^{-1}), which implies that this pathway is unfavorable from a thermodynamic point of view. However, the kinetics is often very important for actual reactions. It usually turns out in practice that the binary and ternary compounds will form anyway, and that the most relevant reaction pathway is the one with the lowest enthalpy of formation. Addition of kinetic barriers to this picture may make the route of $\text{LiK}(\text{BH}_4)_2$ from the ternary borohydrides the best synthesis pathway. Experiments have shown that $\text{LiK}(\text{BH}_4)_2$ can be directly synthesized by heating up together appropriate molar quantities of LiBH_4 and KBH_4 [9].

From figure 4, we can also obtain the enthalpy changes of the dehydrogenation reactions along opposite directions of reaction pathways (4), (5b) and (5c). The enthalpy of the reaction can be estimated from the difference between the formation enthalpies before and after dehydrogenation. The enthalpy changes for the dehydrogenation reactions of $\text{LiK}(\text{BH}_4)_2$, LiBH_4 and KBH_4 are 112.5, 103.6 and $120.8 \text{ kJ mol}^{-1} \text{ H}_2$. For the dehydrogenation reactions, the

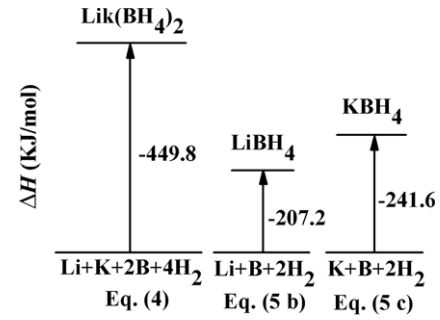


Figure 4. Enthalpy changes ΔH (kJ mol^{-1}) for the formation reactions of $\text{LiK}(\text{BH}_4)_2$ (equation (4)), LiBH_4 (equation (5b)) and KBH_4 (equation (5c)).

associated thermodynamics can be described by $\Delta G = \Delta H_R - T\Delta S$, where ΔG , ΔH_R and ΔS are the standard Gibbs energy, enthalpy and entropy change of the dehydrogenation reaction, respectively. For a complex hydride, when the material is being heated, the entropy factor slowly overcomes the enthalpy contribution. At the decomposition temperature and constant pressure the standard Gibbs energy is zero. So the temperature of dehydrogenation can be estimated using $\Delta H_R = T\Delta S$. During heating the entropy change of solid materials is very small compared to that for gas; we can consider that the entropy change during the decomposition reaction is primarily due to H_2 evolution. At standard pressure and temperature for the simplest metal hydride, $\Delta S \approx \Delta S(\text{H}_2) = 130.7 \text{ J k}^{-1} \text{ mol}^{-1}$ [28]. For most of the dehydrogenation reaction, it is estimated that ΔS is in the range $95 \leq \Delta S \leq 140 \text{ J k}^{-1} \text{ mol}^{-1}$ [29]. Therefore, ΔH_R is, to some extent, a reliable predictor of the dehydrogenation temperature values for various metal hydrides. Our calculation results show that the decomposition temperature (T_{dec}) of $\text{LiK}(\text{BH}_4)_2$ is lower than $T_{\text{dec}}(\text{KBH}_4)$ and higher than $T_{\text{dec}}(\text{LiBH}_4)$, which is agreement with the experiment observing that the decomposition temperature lies between that of the constituent phases [9]. The actual decomposition temperatures of $\text{LiK}(\text{BH}_4)_2$, KBH_4 and LiBH_4 are about 653 K, 773 K and 603 K, respectively. The results offer a viable general route to the chemical control of the decomposition temperatures (T_{dec}) of complex hydrides by the manipulation of multi-cation combinations.

4. Conclusions

We have performed pseudopotential density functional calculations to study the crystal structure, electronic structure and thermodynamics of $\text{LiK}(\text{BH}_4)_2$. We optimize the atomic positions and lattice parameters of all compounds involved in possible reactions; these are in good agreement with experimental results. From electronic structure calculations, the ionic interaction between metal cations and $(\text{BH}_4)^-$ and the covalent B–H interaction within the $(\text{BH}_4)^-$ tetrahedron are revealed. Electronic density of states and band structure studies reveal that $\text{LiK}(\text{BH}_4)_2$ is an insulator with a wide band gap of 6.08 eV. Standard reaction enthalpy calculations reveal that the formation pathway from primary elements is the lowest energy

reaction pathway. This methodology of calculation of the enthalpy of formation can be extended to study other complex hydrogen storage materials. Our calculation results show that the decomposition temperature (T_{dec}) of $\text{LiK}(\text{BH}_4)_2$ lies between those of the constituent phases, which is in qualitative agreement with experimental results. Consequently, the above mentioned results indicate that the appropriate manipulation of multi-cation combinations is an effective method for adjusting the thermodynamic stability of metal borohydrides, similar to the conventional 'alloying' method for hydrogen storage alloys. The criteria for the selection of appropriate cations which can effectively and precisely adjust hydrogen desorption temperature still need to be clarified by future experiments.

Acknowledgments

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