

THE EFFECTS OF HYDROSTATIC PRESSURE ON MBH₄ (M = K, Na) STRUCTURES

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ABSTRACT

In recent decades, a lot of efforts has been spent on investigation of metal borohydrides, which can potentially serve as advanced hydrogen storage materials for mobile applications. In this research, we investigate the structure changes under high pressure of the compounds MBH₄ (M = K, Na) as important borohydrides in hydrogen technologies, using ABINIT simulation package based on density functional theory (DFT) and the generalized gradient approximation (GGA). The pressure is in a wide range of 0 GPa to 40 GPa. Structural analysis indicates the phase transformation in the examined range of pressure, which is evidenced by the interaction between metal cations and BH₄⁻, interactive behavior of BH₄ tetrahedron in the simulated cells, change of volume, distance between B and H ions, and enthalpy difference.

Keywords: DFT, KBH₄, NaBH₄, pressure, phase.

1. INTRODUCTION

Hydrogen, a popular element on the Earth, is an energy carrier that has great potential in future applications. Unlike traditional fossil energy sources (*e.g.*, oil, coal, *etc.*), hydrogen has a clean reaction with oxygen, which does not create products that cause the greenhouse effect. It also has a high performance ratio energy/mass. There are examples of current and future applications where hydrogen is used either in fuel cells to provide electricity for electric motors, or used in mobile combustion engines.

In the last decade, research in the both of theoretical and experimental fields has been done in order to look for ideal hydrogen-containing structures. KBH₄, NaBH₄ are compounds that contain elements that are widely available in nature, easily synthesized, and stable in cubic phase at normal conditions. They can contain respectively 7.4 % and 10.6 % hydrogen [1] by weight. For NaBH₄, phase transition from cubic to tetragonal structures were observed under pressure between 5.4 and 6.3 GPa [2], or near 6.8 GPa [3], and the next phase transition to orthorhombic structure occur above 8.9 GPa [2], or near 10 GPa [4]. With KBH₄, previous studies show that when it is under pressure, structural phase transition from cubic structures to tetragonal structures occurred at 3.8 GPa [4], and then to orthorhombic structure about 6.2 and 10 GPa [4].

However, the clear and commonly recognized picture of phase transitions of MBH_4 ($M = \text{K}, \text{Na}$) over the range of pressure is still not available at the present.

By using computational simulation method, we have investigated the influence of pressure in the range from 0 GPa to 40 GPa on borohydride structures, which is wider than one previously reported, *e.g.*, up to 20GPa for KBH_4 [2], and up to 30 GPa [5], 17 GPa [6], or 11.2 GPa [7] for NaBH_4 . By choosing a larger range of pressure and a comparison with experimental data reported recently, we hope to make a more conclusive study on the properties of borohydride structures MBH_4 ($M = \text{K}, \text{Na}$) under high pressure.

2. COMPUTATIONAL METHODS

Lattice structures and total energy were calculated by using density functional theory (DFT) within the generalized gradient approximation (GGA) by using ABINIT program. We used exchange interactive potential that was built by Perdew, Burke, Ernzerhof (PBE). We used k-momentum grids (Monkhost-Pack) as followings, in the first Brillouin zone: $3 \times 3 \times 3$ with cubic structures, $4 \times 4 \times 3$ with tetragonal structures, and $4 \times 6 \times 5$ with orthorhombic structures. The relaxation of structures was estimated by Broyden-Fletcher-Goldfarb-Shanno minimization method and comparing minimization of both force and stress tensor. Structures were relaxed when the value force/stress $< 10^{-5}$ Ha/Bohr. In all calculations, structures were stressed in all directions from 0 to 40 GPa with step 5 GPa at 0 K. Values of volumes as a function of pressure were extracted from Calculated relaxation results. Space group of those structures were determined by FINDSYM, figures of structures were plotted by VESTA. Distance between B and H ions in BH_4 tetrahedral with each pressure value was extracted by VESTA.

3. RESULTS AND DISCUSSION

Firstly, to built calculation models, we used data of lattice constants, Wickoff positions were taken from experiment reports as the following:

α - NaBH_4	(cubic phase Fm-3m) [8]
β - NaBH_4	(tetragonal phase $\text{P4}_2\text{mn}/\text{c}$) [8]
γ - NaBH_4	(orthorhombic phase Pnma) [2]
α - KBH_4	(cubic phase Fm-3m) [8]
β - KBH_4	(tetragonal phase $\text{P4}_2\text{mn}/\text{c}$) [8]
γ - KBH_4	(orthorhombic phase Pnma) [9]

Since α , β , γ phases for KBH_4 and NaBH_4 compounds have the similar space groups, then in Figure 1 we plot only the structure for KBH_4 phases. In Figure 1 potassium atoms are symbolized by big violet balls, boron atoms – by green balls and hydrogen atom – by smallest balls.

After the data analysis we collected some initial information that shows a picture about the changes of structures under pressure. When being stressed in all directions, the size of structure is likely to decrease. Figure 2 shows the calculation results of volume of KBH_4 as a function of pressure which are compared with experimental data from Reference [9]. The volume is taken for the structure cell containing 24 atoms (4 formula units). The comparison between theoretical calculation and experimental data shows a good matching.

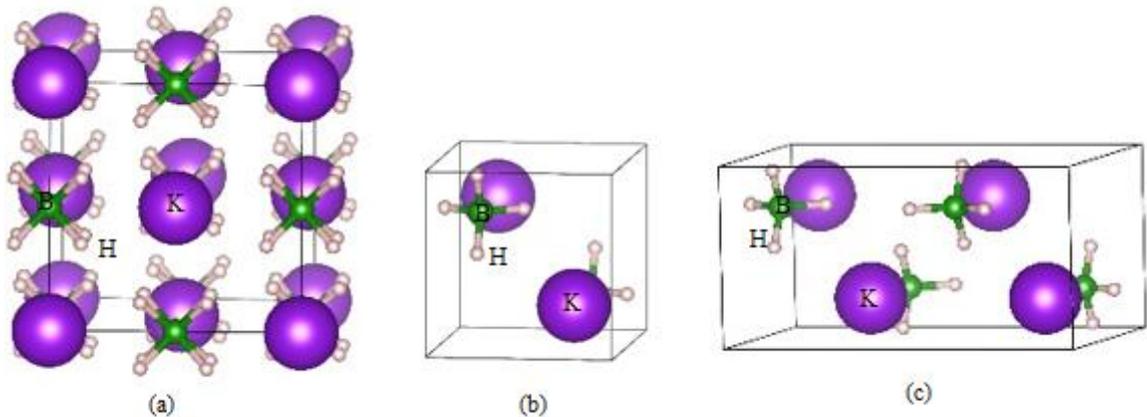


Figure 1. KBH_4 phases, (a) cubic phase $Fm\bar{3}m$, (b) tetragonal phase $P4_2/mn/c$, (c) orthorhombic phase $Pnma$.

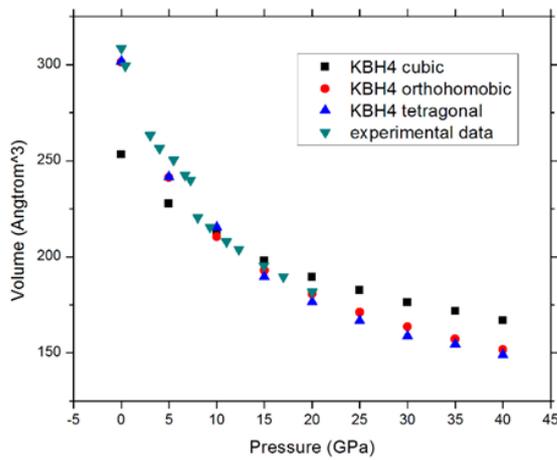


Figure 2. Volume pressure diagram of KBH_4 in pressure range from 0 GPa to 40 GPa.

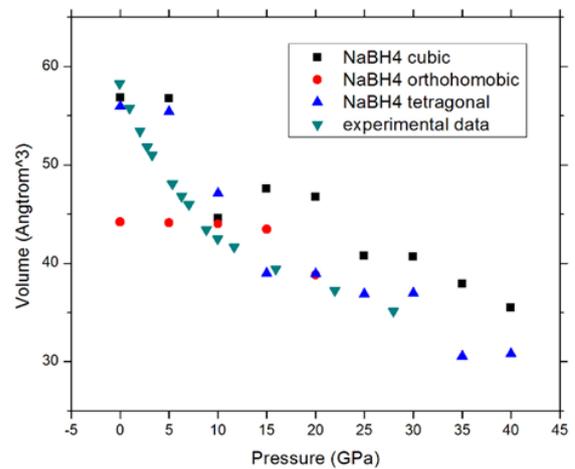


Figure 3. Volume pressure diagram of $NaBH_4$ in pressure range from 0 GPa to 40 GPa.

Similar to KBH_4 , the calculation results of volume of $NaBH_4$ as a function of pressure were also compared to experimental data from Reference [5], and shown in Figure 3. In difference from the case of KBH_4 , the volume of $NaBH_4$ was taken in formula unit. As shown, the results also proved the agreement between theoretical calculation and experiment.

To have further understanding about the effects of hydrostatic pressure on structures, lattice constants and distance between B and H were analyzed. The following tables show calculated data of lattice constants and compared to experiment data in published reports. The tolerance of calculated data about lattice constants is under 5 %, compared with experimental data. This shows an agreement between theory and experiment.

Table 1. Compare calculated results about lattice constant with experiment data of NaBH₄.

NaBH ₄	Calculated results	Experiment
Cubic	6.1039 Å (at 0 GPa)	6.150 Å [2] (at 0 GPa)
Tetragonal	4.2585 Å (at 5 GPa) 6.1096 Å	4.086 Å [2] (at 6.3 GPa) 5.597 Å [2]
Orthorhombic	7.2698 Å (at 10 GPa) 4.1130 Å 5.5902 Å	7.389 Å [2] (at 8.9 GPa) 4.166 Å [2] 5.633 Å [2]

Table 2. Compare calculated results about lattice constant with experiment data of KBH₄.

KBH ₄	Calculated results	Experiment
Cubic	6.3266 Å (at 0 GPa)	6.6897 Å [9] (at 0.5 GPa)
Tetragonal	4.4124 Å (at 5 GPa) 6.2046 Å	4.4754 Å [9] (at 4 GPa) 6.363 Å [9]
Orthorhombic	7.1466 Å (at 20 GPa) 4.6059 Å 5.4893 Å	6.976 Å [9] (at 20 GPa) 4.933 Å [9] 5.111 Å [9]

The calculated distance between B and H atoms in tetrahedral is about 1.1 - 1.4 Å. When pressure is increasing, BH₄ tetrahedron was deformed. The symmetry of BH₄ decreases when the compounds are stressed under high pressure. The B-H distance in NaBH₄ cubic phase is 1.4668 Å at 0 GPa compared with experiment is 1.19 Å at 200 K [10], in orthorhombic phase is 1.2063 Å at 10 GPa compared with experiment is 1.17 Å at 11.2 GPa [7]; in KBH₄ cubic phase is 1.4494 Å at 0 GPa compared with experiment is 1.09 Å at 293 K [11].

The distance between M-B atoms in NaBH₄ are as followings: for cubic structure, it is 3.05198 Å at 0 GPa compared with 3.065 Å obtained experimentally at 200 K [12], for tetragonal one - it is 3.0548 Å at 5 GPa compared with 2.976-3.091 Å in experiment at 180 K [12], for orthorhombic phase, it is 2.7974 Å at 10 GPa compared with 2.763 - 2.849 Å in experiment at 11.2 GPa [12]. For KBH₄: in cubic structure, it is 3.1633 Å at 0 GPa compared with 3.364 Å in experiment [13].

At high pressure, the symmetry of the structures decreased from highest symmetry phase, which is cubic, to tetragonal and to orthorhombic ones. Changes of structures under pressure is mostly in M-B distance. B-H distance doesn't change much.

The enthalpy values of phases were calculated to get a general view about change of energy of structures. Enthalpy was Calculated by the following fomula :

$$H = E + PV$$

with H is enthalpy, E is total energy, P is pressure, V is volume of structures, then enthalpy values were divided by the number of atom use in program. Results show enthalpy of KBH_4 is lower than enthalpy of $NaBH_4$ ~ 75 eV/atom with similar structures.

With KBH_4 , we cannot observe phase transition between cubic phase and tetragonal phase. The same conclusion is shown in a previous report [14], also as between tetragonal phase and orthorhombic phase. Enthalpy diagram of KBH_4 is shown in Figure 4.

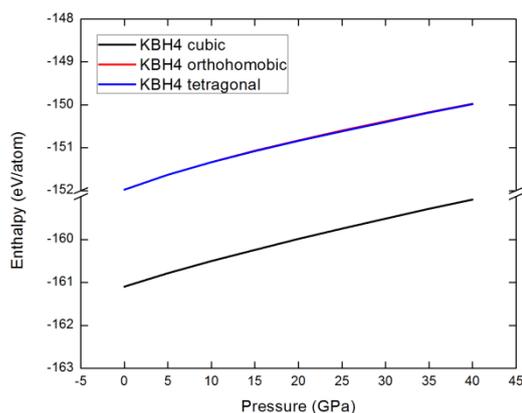


Figure 4. Diagram of enthalpy as a function of pressure of KBH_4 in pressure range from 0 GPa to 40 GPa.

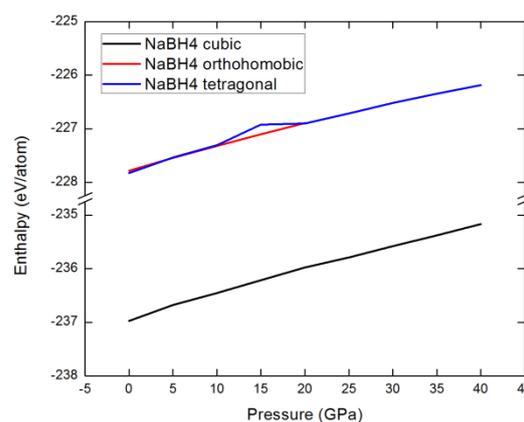


Figure 5. Diagram of enthalpy as a function of pressure of $NaBH_4$ in pressure range from 0 GPa to 40 GPa.

Similar to KBH_4 case, we do not observe phase transition between cubic phase and tetragonal phase in $NaBH_4$ structures. However, phase transition between tetragonal phase and orthorhombic phase can be observed. At 10 GPa, we can see the difference between two enthalpy lines of tetragonal phase and orthorhombic phase clearly. This completely matches with experiment reported before. The enthalpy diagram of $NaBH_4$ is shown in Figure 5.

We can see some differences between sodium and potassium in four figures above. In both theoretical calculation and experiment, sodium compound always shows different behaviors from potassium and other alkali metals. The very similar structures and phase relations of $NaBH_4$ and KBH_4 at atmospheric pressure suggest that the behaviors at high pressure should also be similar but it is not the case. It should be noted that the cubic to tetragonal transformation in $NaBH_4$ gives thermal conductivity measurements rise to large anomalies, involving a step change by 25 percent [4]. In theoretical calculation, Lee *et al.*, have made an attempt to calculate the slope of this phase line using DFT, but the theoretical slope exceeds what found experimentally by a large factor [4]. Experimental values of vibrations by Raman measurement are: 1.83 for sodium compound, 1.79 for potassium, rubidium and cesium compound [15]. In experiments with activation energy, $NaBH_4$ also shows large anomalies than those with KBH_4 [16]. So, the difference of $NaBH_4$ structure behavior likely may be explained due to the relatively distinguished proportion of ion mass/size in the chain of alkali elements. This factor likely leads to the difference of interaction between ($Na^{+\delta}$, $K^{+\delta}$) ions and $BH_4^{-\delta}$ tetrahedrals (*e.g.*, charge distribution, interact distance, *etc.*) in $NaBH_4$ and KBH_4 compounds, and therefore, their different behaviors.

4. CONCLUSIONS

The effects of pressure on MBH₄ (M = Na, K) structures was studied by using density functional theory (DFT) in a range of pressure from 0 GPa to 40 GPa at 0 K. Volume of structures in phases were calculated and matched with experimental data. Analysis of lattice cell data indicates that at high pressure, symmetry degree of the investigated structures decreases. Although the enthalpy diagram of structures reflects only the phase transition between tetragonal and orthorhombic phases of NaBH₄, it can contribute an evidence for the phase transition of the studied structures. Further research is needed to better address this issue.

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TÓM TẮT

ẢNH HƯỞNG CỦA ÁP SUẤT THỦY TĨNH LÊN CẤU TRÚC MBH₄ (M = K, Na)

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Trong những thập niên gần đây, một lượng lớn nghiên cứu đã được thực hiện trên các cấu trúc borohydride kim loại với vai trò vật liệu tiên tiến lưu trữ hydro nhằm sử dụng trên các phương tiện di động. Chúng tôi trình bày nghiên cứu biến đổi cấu trúc của các hợp chất mang tầm quan trọng về công nghệ lưu trữ Hydro MBH₄ (M = K, Na) dưới ảnh hưởng của áp suất cao. Trong nghiên cứu này, chúng tôi khảo sát borohydride kim loại MBH₄ bị nén dưới áp suất từ 0 đến 40 GPa, sử dụng chương trình mô phỏng Abinit trên cơ sở lý thuyết hàm mật độ và sử dụng phép xấp xỉ gradient tổng quát. Các phân tích cấu trúc đã chỉ rõ các biến đổi pha được nhận thấy trong khoảng áp suất khảo sát, với các biểu hiện qua tương tác giữa các ion kim loại và BH₄⁻, và tương tác trong tứ diện BH₄, sự thay đổi thể tích, khoảng cách các ion B-H, chênh lệch enthalpy.

Từ khóa: lý thuyết hàm mật độ, KBH₄, NaBH₄, áp suất, pha.