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Ab initio prediction of high-pressure structural phase transition in BaH_2

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Abstract

We have performed *ab initio* electronic structure calculations to calculate the structural properties and high-pressure phase transition in Barium dihydride (BaH_2). Our results show that BaH_2 crystallizes the orthorhombic phase ($CoSi_2$-type structure) with *Pnma* space group at ambient conditions. A phase transition to the hexagonal (Ni_2In-type structure) with *P*6_3/*mmc* space group is found at pressure around 4 GPa. At the phase transition, the coordination number of hydrogen increases from 9 to 11 and the average bond length of Ba—H increases. The results show a band gap of 2.9 eV for orthorhombic and 1.8 eV for hexagonal phase. In addition, it was also found that more energy is required to desorb hydrogen atom from high-pressure phase as compared to ambient phase.

Keywords: Metal hydrides; Phase transition; High-pressure

1. Introduction

The alkali-earth dihydrides have attracted attention due to their possible use as hydrogen storage materials as well as optical applications. CaH_2, SrH_2, BaH_2, EuH_2, and YbH_2 have the same space group and lattice parameter ratios (c/a; $(a+c)/b$) at ambient conditions [1–3]. They crystallize in the orthorhombic phase (Co_2Si-type) having space group D_{2h}^{16} (*Pnma*) [4]. All of these compounds have the similar dynamical properties at ambient conditions [5].

Up to now, only YbH_2 was known to show a high-pressure first-order structural phase transition from orthorhombic (Co_2Si-type) structure to the hexagonal (Ni_2In-type) structure which has space group D_{2h}^{16} ($P6_3/\mathrm{mmc}$) with the metal atoms in 2(c) positions and the hydrogen atoms in 2(a) and 2(d) positions [6,7]. BaH_2 is one of the compounds which is least studied. Resistivity study under pressure up to 12.5 GPa does not show any significant indication of phase transition in BaH_2 [8]. On the other hand, it was shown that the elastic properties of BaH_2 as compared to CaH_2 are different [9]. High-pressure studies on alkali-earth dihydrides will be also helpful to understand metallization of hydrogen.

In the present paper, we have used *ab initio* calculations to study high pressure structural phase transition as well as bonding properties of BaH_2.

2. Methods of theoretical calculations

Total energies have been calculated using the projected-augmented plane-wave (PAW) as implemented in the Vienna *ab initio* simulation package (VASP). Since it is generally found that the generalized-gradient approximation (GGA) gives better equilibrium structural parameters, we have used GGA for all our calculations. These calculations were performed using the energy cut-off 700 eV with ultrasoft Vanderbilt pseudopotentials in real space; a maximum k-point spacing of 0.01 Å^{-1} was used. A criterion of at least 0.01 meV/atom is placed on the self-consistent convergence of the total energy.

Murnaghan equation of state was used to fit total energy as a function of volume. Equilibrium parameters at zero temperature have been obtained by minimization of the crystal total energy, without including the zero-point energy. The bulk moduli and the equilibrium lattice parameters have been obtained by fitting the equation of state $E(V)$ by the Murnaghan expression:

$$E(V) = E_0 - \frac{B_0 V_0}{B_0' - 1} + \frac{B_0 V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0' - 1}\right] \qquad (1)$$

where B_0 and B_0' are the bulk modulus and its derivative, E_0 is the ground-state total energy and V_0 is the equilibrium volume.

3. Results and discussion

The crystal structures of BaH_2 at ambient condition and under high pressure are determined as orthorhombic phase with

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Table 1
Calculated unit cell parameters, bulk modulus for orthorhombic phase and hexagonal phase at ambient pressure together with the experimental data

Structure		V_0 (Å^3)	c/a	$(a+c)/b$	Bulk modulus (GPa)	B'
Orthorhombic	Cal.	224.61	1.1594	3.5450	31.2	3.2
	Exp. [10]	222.45	1.1569	3.5146		
Hexagonal	Cal.	103.24	1.3480		34.7	3.6

space group *Pnma* and hexagonal phase with space group $P6_3/mmc$, respectively, by our *ab initio* calculations. The calculated equilibrium unit cell parameters, bulk moduli, and pressure derivative for both of structures, as well as referenced experimental data for orthorhombic phase are listed in Table 1. Both phases have low bulk moduli that indicate a very soft and easily compressible compound. The results show a good agreement in computed and experimental data for ambient phase.

In order to study the structural stability of the orthorhombic phase, we have investigated total energies of both phases as a function of volume. The results are shown in Fig. 1. Both structures are optimized for several volumes and fitted to the Murnaghan equation of state. The energy curves of two structures cross while volume decreased. A first-order phase transition from orthorhombic to hexagonal phase takes place around 4 GPa with a volume collapse of 3%.

For understanding Ba–H bonding and hydrogen environments in the lattice under high pressure, the symmetry of the crystal structures with symmetry are investigated in detail. In orthorhombic phase with space group *Pnma*, all of Barium and Hydrogen atoms occupy 4*c* site, and there are two non-equilibrium hydrogen atoms in the lattice. Ba–H coordination environment for two kinds of hydrogen atoms is different. Hydrogen atoms named H1 coordinates to four Barium and H2 coordinates to five Barium atoms in three different Ba–H bond lengths, respectively. In additional, Barium binds to nine hydrogen atoms as shown in Fig. 2. Nine hydrogen atoms link to 14 triangle around Barium atom.

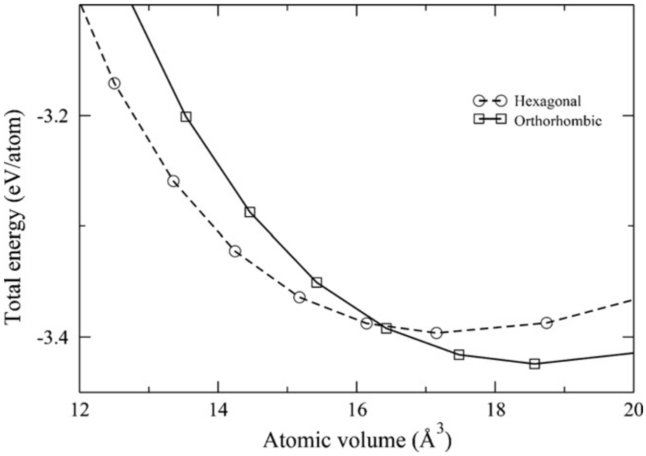
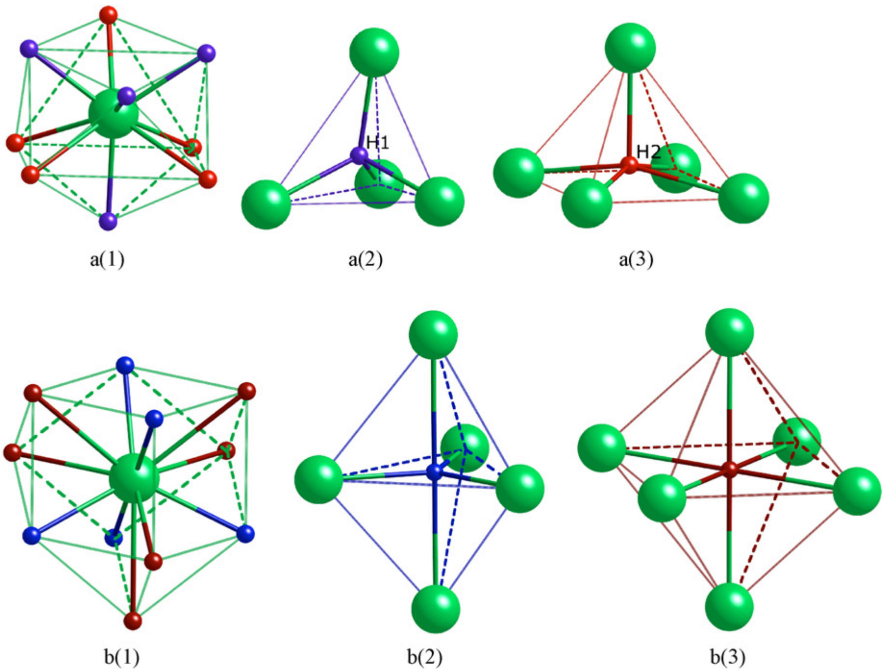


Fig. 1. Total energy as a function of volume for orthorhombic and hexagonal phases.



a(1) a(2) a(3)

b(1) b(2) b(3)

Fig. 2. The bonding and coordination environments of Ba–H in BaH_2 lattice of orthorhombic and hexagonal phases. The green color atoms indicate Barium; the blue color atoms indicate hydrogen H1 of orthorhombic and hydrogen 2d of hexagonal phase in (a) and (b), respectively; the red color atoms indicate hydrogen H2 of orthorhombic and hydrogen 2a of hexagonal phase in (a) and (b), respectively. (a) Orthorhombic phase of BaH_2, Barium binds to four H1 atoms in blue color and five H2 atoms in red color b(1); hydrogen H1 binds to four Barium atoms and forms tetrahedral b(2); hydrogen H2 binds to five Barium atoms and forms octahedral b(3). (b) Hexagonal phase of BaH_2, Barium binds to five hydrogen atoms at site 2d in blue color and six hydrogen atoms at site 2a in red color b(1); hydrogen at site 2d binds to five Barium atoms and forms hexahedral b(2); hydrogen at site 2a binds to six Barium atoms and forms octahedral b(3).

Table 2
Bond length of orthorhombic and hexagonal phases

Bond length (Å)	Orth. (*Pnma*) (at 5 GPa)	Coor.	Hex. ($P6_3/mmc$) (at 6 GPa)	Coor.
Ba—H_1	2.4808–2.5310	4	2.4724–2.8263	3 + 2
Average Ba—H_1	2.5205		2.6140	
Ba—H_2	2.7005–2.8848	5	2.8477–2.8477	6
Average Ba—H_2	2.8053		2.8477	

Different from the ambient phase, the high-pressure phase in hexagonal $P6_3/mmc$ structure appears more homogenous. In high pressure phase, there are two kinds of hydrogen atoms and three different Ba–H bond lengths in the lattice, as shown in Fig. 2. Hydrogen named H1 coordinate to five Barium atoms with two different Ba–H bond length and form a hexahedron. Hydrogen H2 coordinates to six Barium atoms and form a regular octahedron. Metal Barium bindes with 11 hydrogen and form a dodecahedron with six rhombus and six isosceles triangle. The edge of rhombus linked by hydrogen H1 and hydrogen H2 reveals the shortest distance between hydrogen atoms.

We have computed the bond length Ba–H for both phases at high pressure and shown the results in Table 2. The results show that the Ba–H bond length of orthorhombic lattice at 5 GPa are shorter than hexagonal lattice at 6 GPa. This indicates that the average bond length increases when structure change from orthorhombic to hexagonal phase due to increase in coordination number. Two tetrahedron centered by hydrogen atom around four Barium atoms linked together to form a hexahedron at high pressure phase transition, and the shortest distance between hydrogen and hydrogen increases.

For understanding the energy band structure under high pressure, the local density of state for orthorhombic and hexagonal phase are calculated as shown in Fig. 3. Our electronic structure calculations show a band gap of 2.9 eV for orthorhombic phase where as the hexagonal phase shows a band gap of 1.8 eV.

The local densities of state show that the valence band of orthorhombic phase is mainly constituted by Barium d electrons. The conduction band is mainly formed by hydrogen s electrons, Barium d and p electrons. The hydrogen atoms in hexagonal lattice are more delocalized comparing to the atoms in the ambient pressure phase.

For understanding the effect of hydrogen vacancy on structural stabilities for ambient phase and high-pressure phase, the total energy of defect lattice with hydrogen vacancy are calculated. The chemical formula is chosen as $Ba_{32}H_{63}$ for ambient phase and $Ba_{36}H_{71}$ for high-pressure phase. The chemical equation of hydrogen desorption is obtained as:

$$Ba_{32}H_{64} \rightarrow \left(\tfrac{1}{2}H_2 + Ba_{32}H_{63}\right) \qquad (2)$$

for ambient phase and

$$Ba_{36}H_{72} \rightarrow \left(\tfrac{1}{2}H_2 + Ba_{36}H_{71}\right) \qquad (3)$$

for high-pressure phase, respectively.

We have optimized the atomic position, unit cell shape and equilibrium volume of BaH_2 to get the minimum energy for defect free and the structure with vacancy in hydrogen position. Furthermore, we define the energy difference as:

$$\Delta_E(\text{Pnma}) = E_{\text{total}}(Ba_{32}H_{64}) - \left(\tfrac{1}{2}E_{\text{total}}(H_2) + E_{\text{total}}(Ba_{32}H_{63})\right) \qquad (4)$$

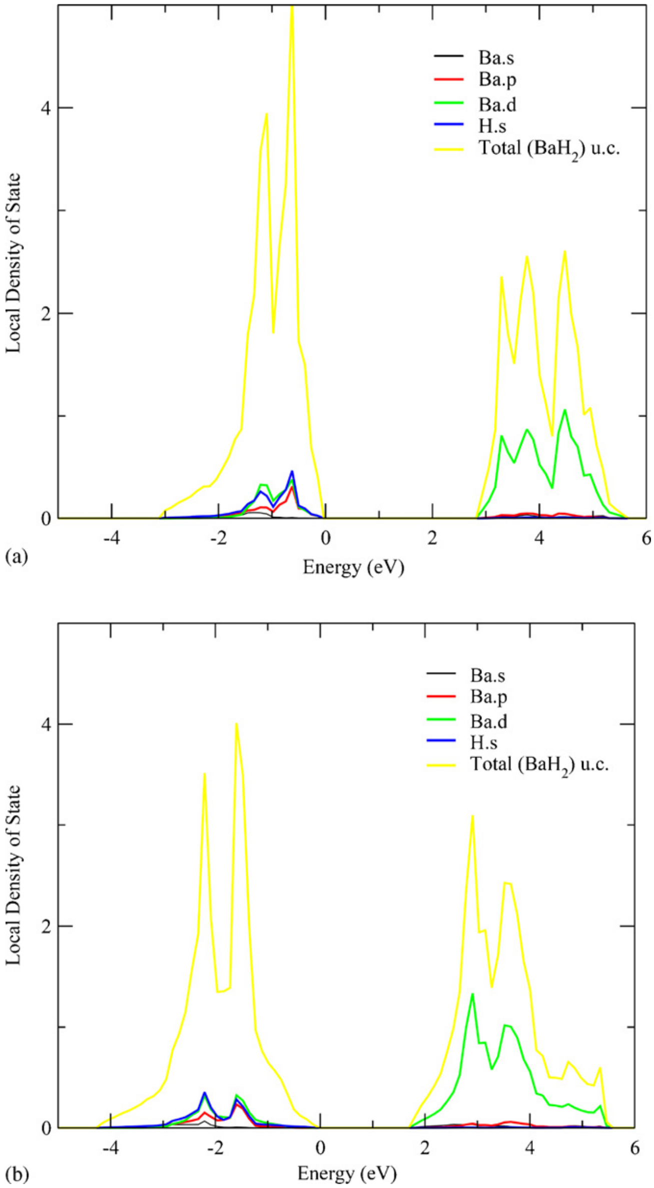


Fig. 3. Density of state near Fermi level on BaH_2 in orthorhombic (a) and hexagonal (b) phase.

for ambient phase, and

$$\Delta_E(\mathrm{P6_3/mmc}) = E_{\mathrm{total}}(\mathrm{Ba_{36}H_{72}}) - \left(\tfrac{1}{2}E_{\mathrm{total}}(\mathrm{H_2}) + E_{\mathrm{total}}(\mathrm{Ba_{36}H_{71}})\right) \quad (5)$$

for high-pressure phase, respectively. E_{total} represents the total energy of the system. Our results showΔ_E(Pnma)greater than zero andΔ_E(P6$_3$/mmc)smaller than zero, this indicates that more energy needed to desorb hydrogen from defect free $\mathrm{BaH_2}$. If we compare the energy difference between ambient phase and high-pressure phase, the results show$|\Delta_E(Pnma)| > |\Delta_E(P6_3mmc)|$. This suggests that the more energy is required to break Ba–H bond in the high-pressure phase than the ambient phase. It also indicates that the Ba–H bonding is stronger in high-pressure phase than ambient phase.

4. Conclusions

We have studied the pressure-induced phase transition in $\mathrm{BaH_2}$ by *ab initio* theory. A first order structural phase transition from orthorhombic to hexagonal phase around 4.0 GPa was observed. At the phase transition coordination number of Barium hydride increased from 9 to 11 and the Ba–H bond length increased. A band gap of 2.9 eV in orthorhombic phase and to 1.8 eV in hexagonal phase has been calculated at ambient conditions.

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