



Structural properties of NaBeH₃ material: *Ab-initio* calculations

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Abstract

Ab-initio calculations from first principle methods were performed to investigate the structural properties of perovskite-type hydride NaBeH₃ material. The pseudopotential plane-wave approach in the framework of density functional theory (DFT) as implemented in the ABINIT code computer was used. The exchange-correlation functional for all elements of our material of interest was described with the local density approximation (LDA). Our results of the equilibrium lattice parameter, the bulk modulus, and the pressure derivative of the bulk modulus of cubic NaBeH₃ semiconducting material were found at around 3.335 Å (3.339 Å), 65.64 GPa and 3.56, respectively. Our data are in good agreement with the available theoretical data of the literature. In addition, the melting point of our material of interest was calculated and found equal to 1217.45 K. To the best of the authors' knowledge, no data is available in the literature on the melting point of NaBeH₃ material.

Keywords: Ab-initio calculations, DFT, local density approximation (LDA), structural properties, perovskite-type hydride.

1. Introduction

Hydrogen is the fuel of the future, which is stored in many ways as a compressed gas, as liquid in suitable containers, or sometimes as solid in metal and complex hydrides [1-3]. Among the most important factors that determine the ability of materials to store hydrogen is the crystal structure and its shape and surface composition [3-5]. One of the complex hydrides used in hydrogen storage is NaBeH₃. Many theoretical studies on perovskite-type hydride NaBeH₃ semiconducting material have been carried out using *ab initio* calculations with many approaches [6-8]. In this study, we focus on cubic perovskite-type NaBeH₃ semiconductor and discuss the method used in the calculation as well as the results obtained from structural properties.

2. Method of calculations

The first-principle calculations were performed by employing pseudopotential plane-waves (PP-PW) approach based on the density functional theory (DFT) [9] as implemented in the ABINIT code [10]. ABINIT code computer is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors. We used the Teter and Pade parameterization [11] for the local density approximation (LDA). Only the outermost electrons of each atom were explicitly considered in the calculation. The effect of the inner electrons and the nucleus was described within a pseudopotential scheme. We used the Trouiller-Martins scheme [12] to generate the norm-conserving nonlocal pseudopotentials, which results in highly transferable and optimally smooth pseudopotentials. A plane-wave basis set was used to solve the Kohn-Sham equations in the pseudopotential implementation of the DFT-LDA. The Brillouin zone integrations were replaced by discrete summations over a special set of *k*-points, using the standard *k*-point technique of Monkhorst and Pack [13] where the *k*-point mesh used is (6 × 6 × 6). The plane wave energy cut-off to expand the wave functions is set to be 60 Hartree.

3. Results and discussions

The structure discussed in this work is cubic perovskite-type NaBeH₃ (space group Pm3m) [5, 8] with a unit cell of 5 atoms (one atom of Na, one atom of Be, and three atoms of H). They are positioned in the following positions: Be (0, 0, 0), Na (1/2, 1/2, 1/2) and H (0, 0, 1/2), respectively. The structure of cubic perovskite-type NaBeH₃ is shown in Figure 1.

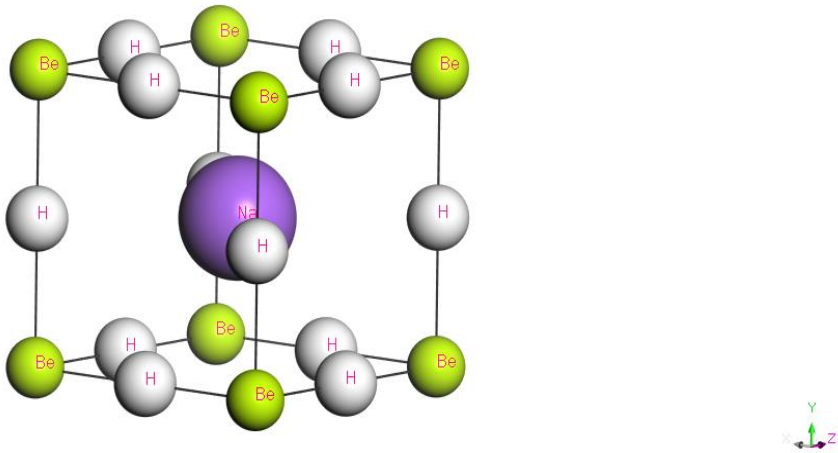


Figure 1. Crystal structure of cubic NaBeH₃ perovskite-type hydride material.

Usually, before starting simulations of different physical properties for a studied material using the Abinit code computer, it is necessary to know the optimal values of two important quantities, i.e., the plane wave kinetic energy cutoff (E_{cut}) and the grid of special k -points (nkpt) [14-16]. The kinetic energy cutoff and the number k -points are two parameters which can have an enormous effect on the quality of the calculation [17]. These two parameters are not known in advance when launching a calculation. Increasing the values of E_{cut} and nkpt considerably affects the value of the total energy, as shown in Figure. 2 (a) and (b).

To expand the wave functions, we used a value of 60 Ha (1 Hartree = 27.211396 eV) for E_{cut} , and the Brillouin zone integrations were replaced by discrete summations over a special set of k -points using the standard k -point technique of Monkhorst and Pack with $6 \times 6 \times 6$ meshes. Using the verified values of cutoff energy and k -point mesh, the relative energy converged to better than 10^{-5} Hartree.

After having determined the kinetic energy cut-off and the number of special k -points which gives the best convergence possible of total energy, they are used to calculate total energy for various values of the lattice constant. Energies were calculated for various values of the lattice constant, the different values obtained are then presented as function of the unit cell volume.

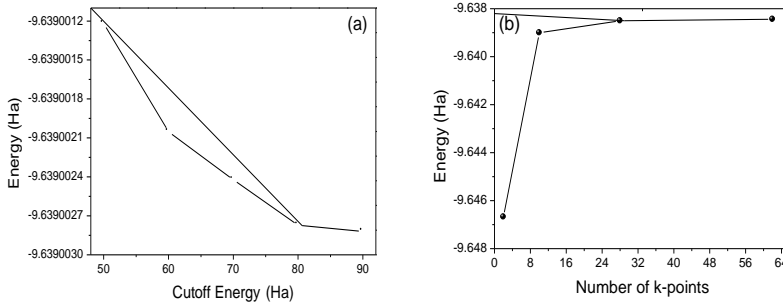


Figure 2. Total energy of cubic structure NaBeH_3 as a function of E_{cut} off (a) and k-points (b).

From the total energy E_{Tot} presented as a function of the lattice volume V , one can deduce the static structural properties such as the equilibrium lattice constant from the volume which gives the minimum energy, the bulk modulus B_0 and its pressure derivatives B_0' by fitting the total energy with so-called Birch Murnaghan's equation which have the following expression: [18, 19]

$$E_{\text{total}}(V) - E_0(V) = \frac{B_0 V}{B'(B'-1)} \left[B \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B'} - 1 \right] \quad (1)$$

where, V_0 is the equilibrium unit-cell volume, while $E(V_0)$ is the corresponding energy.

Figure 3 shows the evolution of the total energy as a function of the unit cell volume of cubic perovskite-type NaBeH_3 . The equilibrium lattice parameter was computed also from the structural optimization, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [20] minimization.

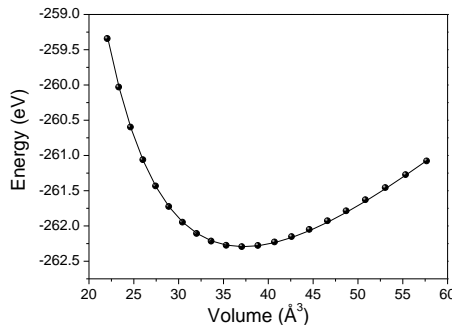


Figure 3. Total energy per formula unit of cubic NaBeH_3 versus volume.

The results of the lattice parameter a_0 obtained from the fit of the Birch Murnaghan equation and from the BFGS technique, that of bulk modulus B_0 , and that of its pressure derivative B'_0 are reported in Table 1, and compared with the available theoretical data [6, 7, 8, 21]. The calculated lattice parameters, bulk modulus and its pressure derivative of cubic NaBeH₃ are in good agreement with the previous studies.

Table 1. Optimized equilibrium structural parameters a (Å) (^a from the relation of Eq. (1), ^b from the BFGS technique), bulk modulus B_0 (GPa), and pressure derivative of bulk modulus (B'_0) for cubic NaBeH₃.

	Our data LDA	Other calculus			
		LSDA	GGA	WC-GGA	PBE-GGA
a (Å)	3.335 ^a , 3.339 ^b	3.281 [8]	3.318 [7], 3.2662 [21]	3.350 [8]	3.352 [6], 3.352 [7]
B_0 (GPa)	65.64 ^a	65.92 [8]	62.7 [7], 62.7 [21]	61.06 [8]	61.55 [7]
B'_0	3.56 ^a		3.5 [21]		

For several materials having a cubic structure, the melting point T_m correlates with the bulk modulus B by an linear empirical formula, which is expresses as follow [22, 23]:

$$T_m = 9.3B + 607 \quad (2)$$

where the melting point T_m is expressed in K, while the bulk modulus B is expressed in GPa.

Using the previous expression, the melting point T_m of NaBeH₃ material was found equal to 1217.45 K. This value is very lower than the values 2264.30 ± 30 K and 1758.05 ± 300 K of T_m reported for BAs and BSb semiconducting material, respectively [24]. Unfortunately, to the best of the authors' knowledge, the melting point T_m of cubic NaBeH₃ material has never been previously reported in the literature.

4. Conclusion

In this study, the equilibrium lattice constant, the bulk modulus, and the pressure derivative of bulk modulus of the cubic NaBeH₃ material were determined using the pseudopotential plane-wave method within the local density approximation (LDA). Our calculated ground state parameters agree well with the other available results of the literature. The melting point of NaBeH₃ material was also predicted, and found at around 1217.45 K. To the best of our knowledge; there is no other theoretical data or experimental values of T_m for NaBeH₃ material to make comparison.

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