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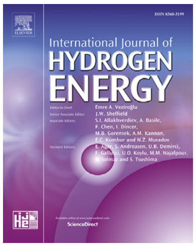

Vibrational and thermodynamic properties of $LiBH_4$ polymorphs from first-principles calculations

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ABSTRACT

The study of phonons describes the thermodynamic properties behavior of compounds with small atoms because phonons have an important influence on its properties. Lithium borohydride, $LiBH_4$, is one of the suitable materials for hydrogen storage solid state. Although the transformations of Lithium borohydride $LiBH_4$ were repeatedly studied by experiments and fundamental side, these transformations are still under discussion. In the present work, the mode vibrational analysis of orthorhombic and hexagonal $LiBH_4$ structures were considered with ab initio lattice-dynamics based on the quasi-harmonic approximation approach as implemented in Phonopy code. The results show that the orthorhombic structure is thermodynamically stable, while the hexagonal structure is unstable owing to the presence of negative mode frequency. The thermal expansion behavior and various thermodynamic properties stability like heat capacity, entropy and Helmholtz energy were also studied and the obtained results are in good agreement with experiments. This shows a deep connection between stability and strength and helps researchers to estimate accurately the thermodynamic performance of $LiBH_4$ materials.

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Introduction

Lithium borohydride is known as a considerable potential candidate for solid hydrogen storage state, owing to its competence to store 18 wt% of hydrogen, which is substantially larger than the DOE roadmap value for 2015 [1]. Nevertheless, the phase transition mechanisms of $LiBH_4$ have not fully understood. Consequently, it is important to explain in detail the thermodynamic properties behavior of $LiBH_4$ according to temperature. Therefore, basic research studied the crystal structure of $LiBH_4$ at several temperatures and pressures and the complex phase transition scheme was analyzed [2,3]. At ambient conditions, lithium borohydride crystallized in the orthorhombic structure (Pnma, 62) and go through a first-order phase transition on heating at 381 K to a hexagonal high-temperature phase ($P6_3mc$, 186). At ambient temperature, a phase transition into a high-pressure phase (Ama2) is observed around 0.6 GPa and a second transition at

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18 GPainduce to a cubic phase (Fm-3m) [4]. The melting of the compound appears at around 550 K. All reported experimental structural studies of $LiBH_4$ have mentioned a tragic increase in hydrogen thermal displacements by almost 2 orders of degree from 4 to 400 K. This was attributed to dynamical disorder in the hexagonal high-temperature phase [5,6]. Buchter et al. [7] reported that for the energies smaller than ~ 15 meV, the phonon density of states of $LiBH_4$ in the low-temperature phase depends quadratically on the phonon energy although for the high temperature phase a continuous dependency is examined, affirming a high lattice anharmonicity in the high-temperature phase. First-principles calculations were very acknowledged to augur structures properties of $LiBH_4$ polymorphs. Despite the fact that, most calculations were realized for the ground state at the zero temperature, a recent advance in computational technique enables us to determine the entire phonon dispersion of solids. Thus, can compute specific heats, vibrational entropy, furthermore many thermodynamic quantities according of temperature. The present study purpose of clarifying the origin of phase transition in $LiBH_4$ by first principles lattice dynamics calculations. Also, the thermodynamics properties of the $LiBH_4$ were be calculated in order to compare the phase transition temperature between orthorhombic and hexagonal structure. In section computational method, the details and methods to perform our calculation are given. Section result and discussion is devoted to the presentation, the discussion and the comparison of numerical results. In the last section, the conclusion is given.

Computational method

The first-principles calculations within the density functional theory (DFT) [8] were performed using the Quantum Espresso program [9]. The generalized gradient approximation (GGA) [11] in the form of the Perdew-Burke-Ernzerhof (PBE) functional [10] was used to solve the Kohn-Shame equation. The structures were optimized by a full relaxation of the ion positions as well as the volume of the unit cell, the electronic ground-state steps were allowed to converge to an accuracy of 10^{-8} Ry. During each of the electronic steps, a plane-wave energy cutoff of 50 Ry was used for all calculations. The Brillouin zones of the unit cells are represented by Monkhorst-Pack special k-point scheme with 8 x 10 x 8 for orthorhombic LiBH4 (o-$LiBH_4$) and 10 x 10 x 8 for hexagonal $LiBH_4$ (h-$LiBH_4$) grid meshes. Computational settings such as plane wave cutoff energy, the number of k-points, and convergence criteria were carefully chosen for high numerical accuracy. Once the converged structures for the both orthorhombic and hexagonal structure were obtained, in order to access the stability of materials, the vibrational density of states (VDOS) was calculated using the software PHONOPY [12]. The VDOS is evaluated using a finite displacement method based on the Parlinski-Li-Kawazoe method. Displacements of 0.02 Å were used for the calculation of the force constants in the displacement method [13]. A larger displacement was used to avoid possible numerical inaccuracies in the system. A complete force constant matrix was obtained, and the phonon frequencies (ω) were then calculated by diagonalization of the dynamical matrix, over the electronic density of states. The Helmholtz energy was thus obtained by combining them with the 0 K total energy calculated within (Plane-Wave Self-Consistent Field method).

Result and discussion

Crystalline structures and optimizations

Using first principles calculations, two $LiBH_4$ phases (o-$LiBH_4$ and h-$LiBH_4$) were built by using crystallographic data in Ref. [14], then, their cell parameters and atomic positions were optimized. As a result, the corresponding total energies as function of the unit cell volume are obtained and plotted in Fig. 1. The relaxed lattice constants and atom positions of $LiBH_4$ phases along with the experimental data are summarized in Table 1. The optimized lattice parameters of both structures are in good agreement with previous theoretical and experimental results [14–16].

Furthermore, the bond length between two different atoms is also calculated and the results are listed in Table 2. This

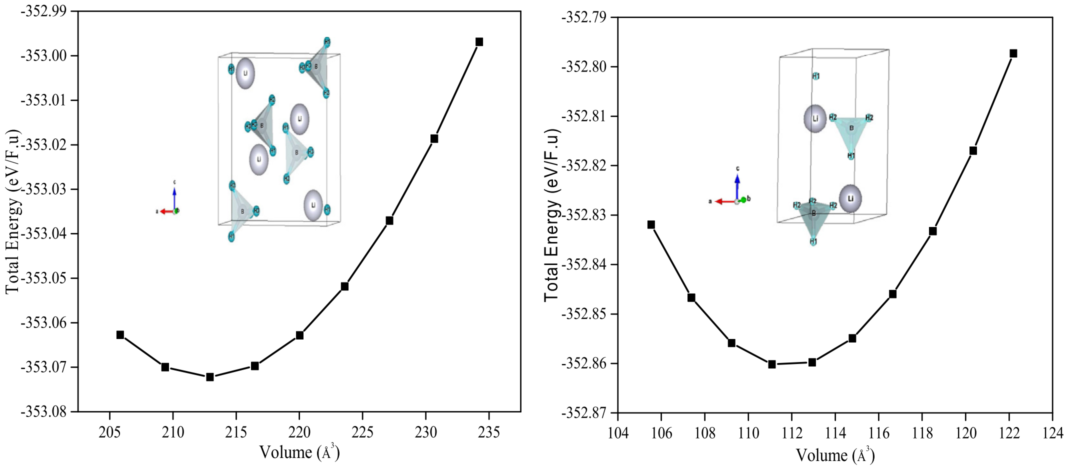

Fig. 1 – Total energy versus primitive unit cell volume of o-$LiBH_4$ (left) and h-$LiBH_4$ (right).

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