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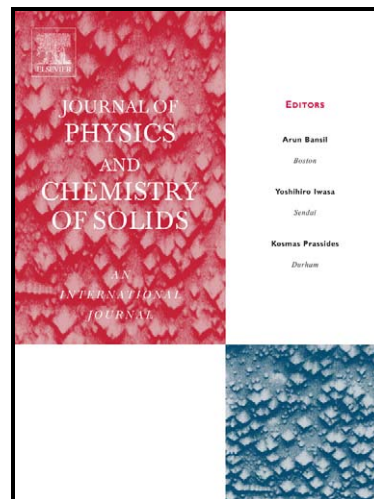
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High pressure and temperature study of hydrogen storage material BH_3NH_3 from *ab initio* calculations

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(Dated: March 9, 2010)

Abstract

We report on BH_3NH_3 , which is material that is considered promising to use as hydrogen storage, using density functional theory with generalized gradient approximation (GGA). We study the phase transition of BH_3NH_3 at high pressure and temperature. Our observed phase transition of BH_3NH_3 from body-centered tetragonal to orthorhombic at $\approx 220^\circ\text{K}$ supports the recent and earlier studies. We observe the phase transformation of BH_3NH_3 at ≈ 11.5 GPa, which is in good agreement with experimental value. Specifically, we predict the phase transition at ≈ 11.5 GPa to be orthorhombic to body-centered tetragonal on the basis of our first principles calculations.

PACS numbers: 33.15.Fm, 61.50.Ah, 61.66.Fn, 84.60.-h

Keywords: hydrogen storage, phase transition, high pressure

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I. INTRODUCTION

Hydrogen has been studied as environment friendly and efficient energy carrier in the search of alternative energy sources [1, 2]. The reliable storage system is the key issue in the use of hydrogen as an alternate energy source. Nowadays, researchers have paid their attention on a solid state hydrogen storage material BH_3NH_3 , because of its high volumetric and gravimetric properties (19.6 wt%) [3–8], which exceeds the target (9 wt%) for hydrogen storage systems, set by U.S. Department of Energy [9, 10]. At moderate temperatures, hydrogen released irreversibly through thermolysis [4, 7, 11] and dehydrogenation with the use of transition metal [12, 13] or acid [14, 15] catalysis, from BH_3NH_3 . The thermal decomposition of BH_3NH_3 consists of three steps and the process completes with the release of all hydrogen atoms at 500°C . The acidic catalyzed dehydrogenation requires a solvent, which reduces the gravimetric density. The release of hydrogen causes in polymerization to $(\text{NH}_2\text{BH}_3)_n$ and then to $(\text{NHBH})_n$ [3–7]. The rapid polymerization creates a difficulty for rehydrogenation. The released hydrogen is also contaminated with unwanted trace quantities of borazine and aminoborane [3–7]. In recent years, significant research efforts have been carried out to the efficient release of hydrogen from BH_3NH_3 by lowering the decomposition temperature and improving the discharge rate of hydrogen using the nanoscaffolds [16], ionic liquids [11] and acid [14, 15] or transition metal [12, 13] catalysts.

It is important to understand the geometric and electronic properties, which are responsible for the reactivity, inter and intramolecular interactions and stability, for the improvement of hydrogen absorption and desorption kinetics in ammonia borane. Therefore, the determination of accurate crystal structure of ammonia borane is necessary. High pressure studies are more helpful to understand the structural properties of hydrogen storage materials and can play an important role to improve the design of such materials [17]. Recently, Lin *et al.* [18] have reported three phase transitions of ammonia borane up to 22 GPa on the basis of Raman spectroscopy. They [18] have observed the two new transitions of ammonia borane at approximately 5 and 12 GPa. Very recently, Hess *et al.* [19] have reported the structural evolution of ammonia borane from 15 to 340°K on the basis of neutron powder diffraction and molecular simulations. In this paper, we focus on the high pressure and temperature studies of the structural properties of ammonia borane on the basis of density functional theory calculations. We predict the orthorhombic to body-centered tetragonal

phase transformation of ammonia borane at high pressure. Furthermore, we observe the temperature dependent phase transition of ammonia borane from body-centered tetragonal to orthorhombic structure on the basis of *ab initio* molecular dynamics calculations, which is in good agreement with the recent and earlier studies.

II. STRUCTURAL AND COMPUTATIONAL DETAILS

Ammonia borane has body-centered tetragonal structure and crystallized in the $I4mm$ space group No. 107 at ambient conditions, with the unit cell having two formula units [21, 22]. At 16°K, BH_3NH_3 has been reported to have an orthorhombic structure and crystallized in the $Pmn2_1$ space group No. 31, having two molecules in the unit cell [23]. We have performed all the calculations with the use of projector-augmented wave (PAW) method [24] as implemented in the Vienna *Ab initio* Simulation Package (VASP) code [25, 26]. We have used generalized gradient approximation (GGA) [27]. The chemically “active” electrons in the PAW calculations were N: $2s^22p^3$; B: $2s^22p^1$; H: $1s^1$. A $5 \times 5 \times 5$ k -points mesh generated by the Monkhorst-Pack method [28] was found sufficient to achieve convergence. All the structures had its total energy converged upto an accuracy of 0.005 eV. The kinetic energy cutoff of 520 eV was found sufficient for the plane wave basis.

III. RESULTS AND DISCUSSION

For high pressure studies of BH_3NH_3 , all calculations were performed at 0°K. Our theoretical investigations were initiated by first determining the equation of state (EOS), using the internal energy of the crystal at different chosen volumes. We have obtained the equilibrium parameters and total energies by relaxing the bct and orthorhombic structures of BH_3NH_3 with respect to fractional atomic coordinates and cell parameters, with the use of, fully self-consistent *ab initio* electronic structure calculations. We have compared the total energies for the relaxed tetragonal and orthorhombic structures by plotting the volume ratio versus total energy and the results are shown in fig. 1. From this it can be easily seen that at ≈ 33 % compression, the body-centered tetragonal structure has become lower in energy, which is an evidence of structural phase transition from orthorhombic to tetragonal structure at this compression. We have fitted the resulting energy versus volume data to an

integrated third-order Birch-Murnaghan equation of state (EOS). The pressure was calculated by taking the volume derivative of the total energy for the both structures. For the further authentication of our results, we have calculated the structural enthalpies for the both structures and plotted it as a function of pressure. The results have been displayed in fig. 2. The calculated phase transition pressure has been found ≈ 11.5 GPa. Our calculated phase transition pressure is in good agreement with experimental value of ≈ 12 GPa [18]. Temperature dependent studies were carried out, using the *ab initio* molecular dynamics simulations for orthorhombic and bct structures of BH_3NH_3 . The 5×10^3 ionic steps with a time step of 1.0 fs were used in our calculations. The simulations were carried out on a series of different temperatures. A schematic of our results is presented in fig.3, and the phase transformation of BH_3NH_3 from body-centered tetragonal $I4mm$ to orthorhombic $Pmn2_1$ at $\approx 220^\circ\text{K}$ can be seen clearly. Our estimated phase transition of ammonia borane at $\approx 220^\circ\text{K}$ is in good agreement with recent and earlier studies, at $\approx 225^\circ\text{K}$ [19, 20].

IV. CONCLUSIONS

In summary, we have presented the structural properties of BH_3NH_3 for the ground state, and high pressure and temperature phase, from our systematic first-principles calculations. We have estimated the structural enthalpies for the bct and orthorhombic structures of BH_3NH_3 . We have observed the phase transition of BH_3NH_3 , at high pressure and temperature, which supports the earlier studies. Our estimated phase transition temperature of BH_3NH_3 from body-centered tetragonal $I4mm$ to orthorhombic $Pmn2_1$ is $\approx 220^\circ\text{K}$, which supports the recent and earlier studies. In particular, we have predicted the phase transformation of BH_3NH_3 to be orthorhombic $Pmn2_1$ to body-centered tetragonal $I4mm$ at ≈ 11.5 GPa. Finally, our work will be helpful to understand the internal structural properties of BH_3NH_3 to make it more promising hydrogen storage material and can play an important role to improve the design of such materials.

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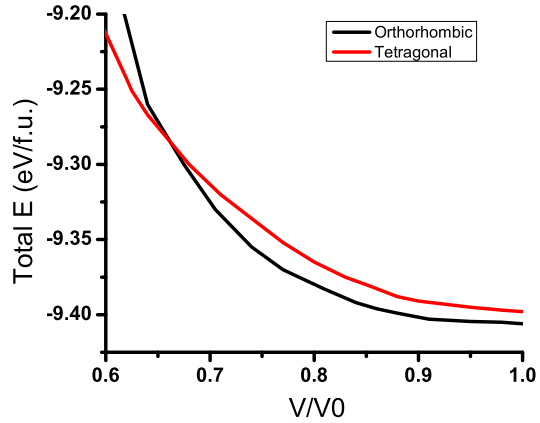


FIG. 1: Computed variations in the total energies with volume compression for the orthorhombic and tetragonal structures of BH_3NH_3 .

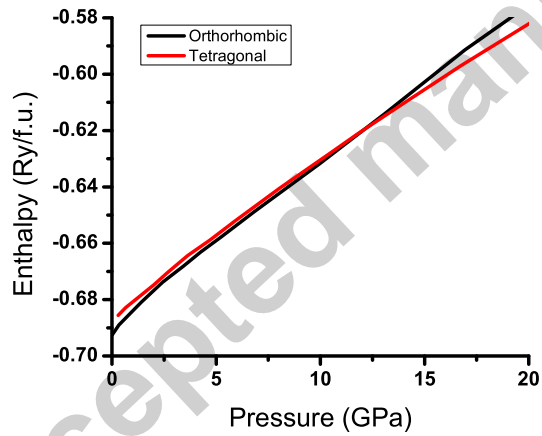


FIG. 2: Phase transition of BH_3NH_3 from orthorhombic to tetragonal structure at ≈ 11.5 GPa, determined by our *ab initio* calculations.

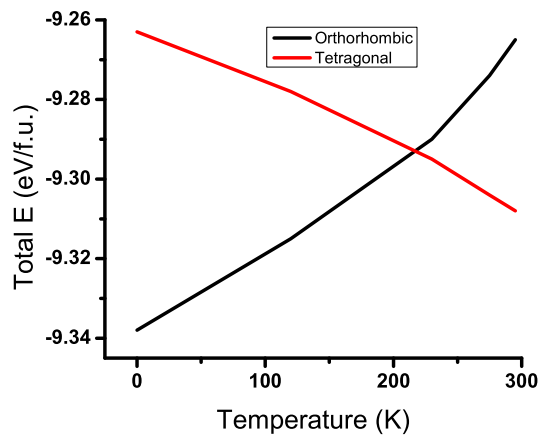


FIG. 3: Phase transition of BH_3NH_3 from tetragonal to orthorhombic structure at 220° K, estimated by our *ab initio* molecular dynamics calculations.