High pressure study on structural and vibrational properties of NH$_3$BH$_3$

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Abstract. The structural and vibrational properties of potential hydrogen storage compound NH$_3$BH$_3$ have been studied through density functional theory at ambient as well as high pressures up to 10 GPa. The calculated lattice parameters at ambient pressure are in good agreement with experiments. The compressibility of NH$_3$BH$_3$ along the crystallographic $a$-axis is almost constant when compared to $b$- and $c$-axes, which is an indication of anisotropic compressibility. The zone center vibrational frequencies of NH$_3$BH$_3$ at ambient and 10 GPa pressures are calculated. The $A_2$ and $B_1$ symmetry modes are independent of pressure, whereas the $A_1$ symmetry modes increases and $B_2$ symmetry modes decreases with pressure.

1. Introduction

High pressure studies of many hydrogen storage compounds exhibit phase transitions, and the resultant high pressure phases exhibit superior hydrogen storage properties. Therefore it is important to understand the structural and dynamical behavior of these compounds under pressure [1]. Ammonia borane (NH$_3$BH$_3$) is one of the promising candidates for onboard hydrogen fuel cells. It has remarkable high gravimetric and volumetric hydrogen density and it releases H$_2$ at moderate temperatures [2]. The hydrogen can be released by thermolysis, starting at temperatures 80°C, but at high temperatures the process tends to release volatile gases such as borazine [3]. NH$_3$BH$_3$ related compounds or complexes containing alkali or other metals have been found to have significantly improved hydrogen release properties and rehydrogenation [3, 4]. The high pressure behavior and properties of NH$_3$BH$_3$ have been studied earlier [5, 6]. These studies are basically motivated by the anomalous lattice stability of NH$_3$BH$_3$. At room temperature, in contrast to the very similar compounds like diborane, B$_2$H$_6$ (liquid up to 4GPa [7]) and ethane, C$_2$H$_6$ (gas), NH$_3$BH$_3$ forms in solid phase. This stability in NH$_3$BH$_3$ is due to the existence of dihydrogen bonds between NH$_3$BH$_3$ molecules [8]. The crystalline phases of NH$_3$BH$_3$ are found to be orthorhombic (Pmn21) at 16K and tetragonal (I4mm) at 225K [9]. Upon pressure, NH$_3$BH$_3$ undergo to orthorhombic (Cmc2$_1$) phase at 1.22 GPa and further pressures it undergoes to triclinic (P1) phase at 8 GPa [10]. Recent studies suggest that the Cmc2$_1$ phase can be obtained from low temperature Pmn2$_1$ phase upon pressure [1]. In the present work we report the pressure studies of structure and
vibrational properties of low temperature orthorhombic (Pmn2_1) phase of NH_3BH_3 up to 10 GPa.

2. Computational details

The first principles calculations were carried out on NH_3BH_3 compound using density functional theory as implemented in the Cambridge Sequential Total Energy Package (CASTEP) [11]. The electron-ion interaction can be seen as the electrons are interacting with the rigid ions. Valence electrons experience the core as screened by the core electrons. The pseudopotential is an effective potential constructed to replace the atomic all-electron potential such that core states are eliminated and the valence electrons are described by pseudo-wave functions. For NH_3BH_3, the basis orbitals used as valence states are N: 2s^2, 2p^3, B: 2s^2, 2p^1 and H: 1s^1. We have used Vanderbilt-type ultrasoft Pseudo Potentials [12] for the electron–nuclei interactions together with the local density approximation (LDA) of Ceperley and Alder [13] parameterized by Perdew and Zunger (CA-PZ) [14] for exchange - correlation functionals for electron–electron interactions. A plane wave basis set with an energy cut-off of 520 eV has been used. For the Brillouin zone sampling, a 7 x 7 x 7 Monkhorst–Pack mesh [15] has been used, in which the forces on the atoms are converged to less than 0.0005 eV/Å. The maximum ionic displacement is within 0.005Å and the total stress tensor is reduced to the order of 0.02 GPa.

3. Results and Discussion

3.1. Structural properties at ambient pressure

The optimized crystal structure of low-temperature orthorhombic phase of NH_3BH_3 contains three formula units in which each pair of B and N atoms are surrounded by three H atoms i.e., N is connected to one H1 and two H2, whereas B is connected to two H3 and one H4 [2].

![Figure 1a](image-url) **Figure 1a.** The isothermal equation of states (EOS) for NH_3BH_3.

![Figure 1b](image-url) **Figure 1b.** Lattice constants of NH_3BH_3 as a function of pressure.
The calculated structural parameters and fractional coordinates are in good agreement with the other theoretical studies [2] and also compared well with experimental data [9]. The ground-state properties such as equilibrium lattice parameters, atomic positions, bond angles, and bond lengths are in agreement with the experiments with error ±10%, and they agree well with other theoretical calculations. This error is due to the inherent limitation of LDA for the exchange and correlation functional. The optimized structure for ambient pressure is found to agree well with the experiments. The external pressure was gradually increased by an increment of 1 GPa in each time. From the hydrostatic compression simulations, the isothermal equation of state (EOS) was obtained and is shown in Figure 1(a) as a function of the volume compression ratio, V/V₀, where V and V₀ are the compressed and uncompressed volumes, respectively. The volume compression of NH₃BH₃ is found to be linear with pressure. The crystallographic directions a-, b-, and c-axis are reported in Figure 1(b) as a function of pressure. The crystallographic directions b- and c-axis exhibit a relatively smooth monotonic behaviour with pressure, but the crystallographic direction a, is almost constant. It is very hard to compress NH₃BH₃ along the crystallographic direction a-axis. This is an indication of anisotropic compressibility. These results are in accord with the earlier studies [2], indicating that NH₃BH₃ is a soft material towards the compression.

3.2. Vibrational properties at ambient and high pressures

We have also performed the density functional perturbation calculations to find the zone centre vibrational frequencies of NH₃BH₃ for ambient and 10 GPa pressures. The harmonic vibrational frequencies of the compound were computed from the matrix of Cartesian second derivatives (i.e. Hessian matrix). The Hessian elements were computed by displacing each atom, and finding a gradient vector thus building up a complete second derivative matrix. The infrared intensities are obtained from the atomic polar tensor, which is a second derivative of the total energy with respect to the Cartesian coordinates and dipole moments.

![Figure 2. IR spectrum of NH₃BH₃ at ambient and 10 GPa pressures](image)
The intensity of each mode can be evaluated as a square of all transition moments of the mode and expressed in terms of the atomic polar tensor matrix and eigenvectors of the mass-weighted Hessian. Figure 2 shows the infrared absorbance as a function of frequency. The zone centre vibrational frequencies are shown in Table 1. The group symmetry decomposition into irreducible representations of the Pmn2₁ space group of NH₃BH₃ yields sums A₁+B₁+B₂ for three acoustic modes and 13A₁+10A₂+9B₁+13B₂ for 45 optical modes for ambient and 10 GPa pressures. Except A₂ symmetry modes, all other modes are found to be Raman active. At ambient pressure, the lowest frequencies of A₁, A₂, B₁ and B₂ are found to be 98.9 cm⁻¹, 95 cm⁻¹, 245.6 cm⁻¹ and 155.4 cm⁻¹, respectively. Whereas at 10 GPa, the lowest frequencies of A₁, A₂, B₁ and B₂ are found to be 169.5 cm⁻¹, 95.8 cm⁻¹, 279.8 cm⁻¹ and 97.4 cm⁻¹, respectively. The A₂ and B₁ symmetry modes are independent of pressure, whereas the A₁ symmetry modes increases and B₂ symmetry modes decreases with pressure. Higher bond orders results in higher frequencies i.e higher the frequency, stronger are the bonds. The

| Table 1. Calculated Vibrational Frequencies (v) of NH₃BH₃ at Ambient and 10 GPa pressures |
|---|---|---|---|
| Ambient | 10 GPa | Ambient | 10 GPa |
| v (cm⁻¹) | Symmetry | v (cm⁻¹) | Symmetry | v (cm⁻¹) | Symmetry | v (cm⁻¹) | Symmetry |
| 15.65 | B₂ | 5.81 | A₁ | 104.17 | A₁ | 1145.02 | B₂ |
| 19.06 | A₁ | 20.72 | B₂ | 1109.87 | B₂ | 1147.05 | A₁ |
| 27.20 | B₁ | 30.46 | B₁ | 1132.84 | A₁ | 1164.24 | A₁ |
| 95.00 | A₂ | 95.84 | A₂ | 1138.20 | B₂ | 1168.71 | B₂ |
| 98.99 | A₁ | 97.48 | B₂ | 1179.19 | B₁ | 1200.03 | B₁ |
| 155.48 | B₂ | 169.52 | A₁ | 1182.97 | A₂ | 1210.12 | A₂ |
| 218.84 | A₂ | 248.70 | A₂ | 1331.17 | A₁ | 1296.07 | A₁ |
| 227.67 | A₁ | 279.84 | B₁ | 1360.90 | B₂ | 1344.39 | B₂ |
| 245.68 | B₁ | 300.91 | A₁ | 1484.00 | B₁ | 1445.30 | B₁ |
| 248.56 | B₂ | 349.27 | B₂ | 1497.57 | A₂ | 1462.97 | A₂ |
| 274.05 | A₂ | 406.26 | A₂ | 1543.71 | A₁ | 1508.76 | A₁ |
| 296.74 | B₁ | 416.86 | B₁ | 1562.54 | B₂ | 1547.18 | B₂ |
| 395.90 | B₁ | 483.46 | B₁ | 2303.59 | A₁ | 2413.67 | A₁ |
| 416.79 | A₂ | 491.79 | A₂ | 2314.47 | B₂ | 2420.44 | B₂ |
| 720.84 | B₂ | 705.38 | B₂ | 2386.85 | A₁ | 2530.95 | A₁ |
| 729.09 | A₂ | 722.13 | A₁ | 2398.08 | B₂ | 2538.89 | B₂ |
| 736.00 | A₁ | 779.78 | A₂ | 2413.92 | B₁ | 2566.35 | B₁ |
| 739.71 | B₁ | 806.55 | B₁ | 2417.36 | A₂ | 2567.85 | A₂ |
| 877.13 | B₂ | 960.98 | A₁ | 3194.66 | A₁ | 3218.32 | A₁ |
| 877.15 | A₁ | 973.54 | B₂ | 3210.94 | B₂ | 3235.68 | B₂ |
| 1032.49 | A₁ | 1037.60 | A₁ | 3236.21 | A₂ | 3254.24 | A₂ |
| 1050.23 | B₁ | 1047.11 | B₁ | 3236.56 | B₁ | 3255.12 | B₁ |
| 1061.39 | A₂ | 1059.89 | A₂ | 3349.13 | A₁ | 3372.10 | A₁ |
| 1066.96 | B₂ | 1083.77 | B₂ | 3353.12 | B₂ | 3376.25 | B₂ |
frequencies around 2300-2400 cm\(^{-1}\) are shifted to 2400-2500 cm\(^{-1}\) at 10 GPa pressures, the lower frequencies up to 877 cm\(^{-1}\) are shifted to 973 cm\(^{-1}\) at 10 GPa pressures. A blueshift represents decrease in wavelength (increase in frequency); the opposite effect is referred to as redshift [16]. The frequencies around 2300-2400 cm\(^{-1}\) are increased (shifted) to 2400-2500 cm\(^{-1}\) at 10 GPa pressures, the lower frequencies up to 877 cm\(^{-1}\) are increased (shifted) to 973 cm\(^{-1}\) at 10 GPa pressures. This is an indication of blue shift. The blueshift indicates the contraction of bonds under pressure [16]. Rest of the frequencies are unchanged. This is a clear indication that, NH\(_3\)BH\(_3\) under pressure becomes relatively hard material.

4. Conclusions

In summary, the structural and vibrational properties of NH\(_3\)BH\(_3\) under hydrostatic compression up to 10 GPa have been studied using density functional theory. It is observed that NH\(_3\)BH\(_3\) is a soft material towards the compression and it is becoming hard material.

Acknowledgments

Ch BL thanks CAS-RFSMS and K RB thanks DRDO through ACRHEM for the financial support. Ch BL and K RB thank CMSD, University of Hyderabad for computational time.

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