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First-principles study of hydronitrogen compounds: Molecular crystalline NH_4N_3 and $N_2H_5N_3$

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ABSTRACT

The structural, elastic, mechanical, electronic properties, formation energy and cohesive energy of orthorhombic NH_4N_3 and monoclinic $N_2H_5N_3$ are studied by the plane-wave method based on the first-principles density functional theory. The calculated results of two compounds are in agreement with the available values. The orthorhombic NH_4N_3 is more energetically stable. The independent elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio of two compounds have been investigated. The electronic band structures, density of states and charge density distributions of orthorhombic NH_4N_3 and monoclinic $N_2H_5N_3$ have been analysed to understand electronic properties and chemical bonding.

1. Introduction

Hydronitrogen compounds (N_nH_m) with hydrogen and nitrogen are potential high energy density materials (HEDMs) with a wide range of applications as energetic materials used in propellants, explosives, weapons and fuels [1–3], hydrogen storage materials based on metal–N–H [4], as well as plasma [5]. A lot of theoretical and experimental works have been devoted to study various phases of hydronitrogen compounds with different stoichiometries, such as N_2H_4 [6], N_nH_n ($n = 2$ [7], 3 [8], 4 [9–14], 5 [15,16], 6 [17,18], 7 [19,20], 8 [21–23]), N_3H_5 [24], and N_3H, N_4H_2 [25] due to that the N atom can form different covalent bonds. However, most of them studied the isomers of hydronitrogen compounds. The crystalline hydronitrogen solids have been reported rarely.

Ammonium azide (NH_4N_3) and hydrazinium azide ($N_2H_5N_3$), with the linear anion N_3^-, have orthorhombic (*Pmna*) and monoclinic ($P112_1/b$) structures, respectively. Using the high pressure ab initio evolutionary structure searches, Hu and Zhang [2] found ammonium azide was stable up to 36 GPa, but the theoretically unobserved phase transition in NH_4N_3 at $P \approx 3$ GPa has been reported by the pressure-dependent Raman spectroscopy studies [11]. Yedukondalu et al. [13] studied the structural, electronic and optical properties of crystalline NH_4N_3 using the density functional theory, indicating that orthorhombic NH_4N_3 was mechanically stable, sensitive along the *b* axis, strong ionic and anisotropy. To the best of our knowledge, no theoretical works have explored monoclinic hydrazinium azide in the literatures. Hence, it is necessary to investigate monoclinic $N_2H_5N_3$ theoretically to take advantage of the properties for HEDM applications. In this paper, we have studied monoclinic $N_2H_5N_3$ compared with orthorhombic NH_4N_3 by the first-principles density functional theory.

2. Computational details

In this paper, the plane-wave ultrasoft pseudopotential method has been used to perform first-principles calculations. The local density approximation (LDA) [26] was applied as the exchange and correlation functional. The H $1s^1$ and N $2s^22p^3$ electrons were treated as valence electrons. The cutoff energy of 500 eV and the Monkhorst–Pack *k* points [27] ($2 \times 4 \times 2$ and $3 \times 1 \times 3$ for NH_4N_3 and $N_2H_5N_3$, respectively) for corresponding Brillouin zone have been used. The set of parameters assures the maximum stress, force and displacement of 0.02 GPa, 0.01 eV/Å and 0.0005 Å, respectively. All results are obtained by the CASTEP code [28].

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3. Results and discussion

3.1. Structural properties

Fig. 1 shows the crystal structures of orthorhombic NH_4N_3 and monoclinic $N_2H_5N_3$. For orthorhombic NH_4N_3 with $a = 8.948(3)$ Å, $b = 3.808(2)$ Å and $c = 8.659(3)$ Å [29], the N1, N2, N3, N4 and N5 atoms occupy the 2*a* (0,0,0), 4*e* (0.1305(5),0,0), 2*b* (0.5,0,0), 4*h* (0.5,0.1098(13),0.1263(5)), 4g (0.25,0.5443(10),0.25), respectively, and the H1 and H2 atoms are located at the 8i (0.2916(9),0.7082(27),0.3355(10)) and (0.3317(9),0.3927(22), 0.2076(9)) positions. For monoclinic $N_2H_5N_3$ with $a = 5.663(2)$ Å, $b = 12.436(3)$ Å, $c = 5.506(2)$ Å and $\gamma = 114.0(1)°$ [30], the N1–N5 and H1–H5 atoms are at the 4e site (0.3431(9),0.0990(4), 0.0238(9)), (0.2104(8),0.3486(3),0.0759(7)), (0.4052(9),0.0750(4), 0.2125(9)), (0.2845(11),0.1235(5),0.8359(10)), (0.9848(8),0.1501 (4),0.4084(8)), (0.2749,0.4335,0.1803), (0.6455,0.138,0.4696), (0.1245,0.1549,0.5054), (0.0913,0.4114,0.799), (0.8507,0.2119, 0.7033), respectively. Our calculated structural parameters are $a = 8.7539$ Å, $b = 3.6363$ Å, $c = 8.3560$ Å for orthorhombic NH_4N_3 and $a = 5.6153$ Å, $b = 11.5194$ Å, $c = 5.4876$ Å, $\gamma = 116.3°$ for monoclinic $N_2H_5N_3$. These lattice constants are all smaller than experimental data [29,30] due to these reasons: (1) LDA calculations underestimate these parameters; (2) the main reason is the neglected nonbonded interactions [13] such as van der Waals interactions and hydrogen bonding [31,32]. This problem can be solved [33] and is not discussed here.

3.2. Formation energy and cohesive energy

The reactive possibility from pure elements to final compounds and the energetical stability of final compounds can be estimated by using the formation energy and the cohesive energy, respectively. The negative values indicate that the reaction is possible and the final compound is stable. The formation energy and cohesive energy of hydronitrogen compounds can be defined as follows:

$$\Delta H = \frac{E_{N_nH_m} - \frac{n}{2}E_{N_2} - \frac{m}{2}E_{H_2}}{n+m} \qquad (1)$$

$$\Delta E = \frac{E_{N_nH_m} - nE_{N_{atom}} - mE_{H_{atom}}}{n+m} \qquad (2)$$

where $E_{N_nH_m}, E_{N_2}, E_{H_2}, E_{N_{atom}}$ and $E_{H_{atom}}$ are total energies of hydronitrogen compounds, N_2, H_2, N and H atoms, respectively. The calculated formation energy and cohesive energy of orthorhombic NH_4N_3 are −0.471 eV/atom and −6.295 eV/atom, and those of monoclinic $N_2H_5N_3$ are −0.399 eV/atom and −6.223 eV/atom, respectively, indicating that the reactions from pure elements to orthorhombic NH_4N_3/monoclinic $N_2H_5N_3$ are favorable and the orthorhombic NH_4N_3/monoclinic $N_2H_5N_3$ are stable at 0 K and 0 GPa. However, there is no available data to compare at those conditions. The standard heat of formation defined as the enthalpy change for a reaction at 1 atm and 298.15 K is positive for ammonium azide and hydrazinium azide [34]. It can be seen that environment conditions are important to reactions. Moreover, we can see that orthorhombic NH_4N_3 is more stable, which is in agreement with available results [34].

3.3. Elastic and mechanical properties

Elastic constants are related to the strength of materials, which are associated with various fundamental solid state phenomena.

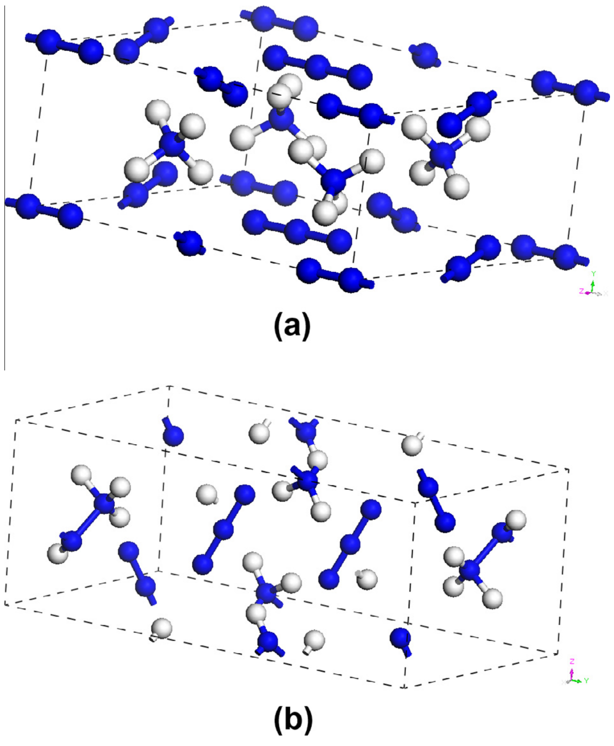

Fig. 1. Crystal structures of (a) orthorhombic NH_4N_3 and (b) monoclinic $N_2H_5N_3$.

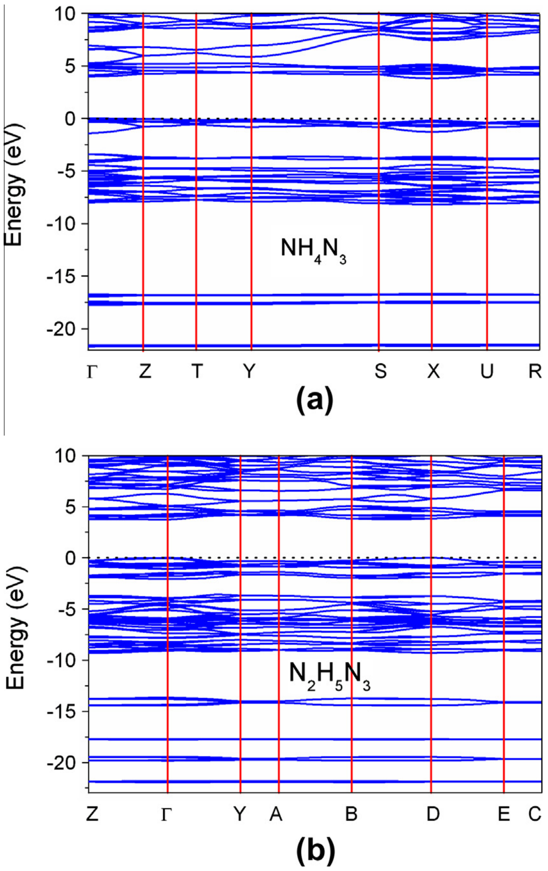

Fig. 2. Electronic band structures of (a) orthorhombic NH_4N_3 and (b) monoclinic $N_2H_5N_3$.