Materials Chemistry and Physics 148 (2014) 364–370

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Structural, bonding and elastic properties of $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$

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HIGHLIGHTS

- $Sr(NH_2BH_3)_2$ have more dispersion forces over $Mg(NH_2BH_3)_2$ and $Ca(NH_2BH_3)_2$.
- Alkaline-earth metal amidoboranes found to be wide band gap insulators.
- $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$ have strong covalent bonding.
- Alkaline-earth metal amidoboranes are found to be mechanically stable.
- $Ca(NH_2BH_3)_2$ is less plastic than $Mg(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$.

ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form
5 June 2014
Accepted 28 July 2014
Available online 26 August 2014

Keywords:
Ab initio calculations
Compression and shear
Band-structure
Mechanical properties

ABSTRACT

The structural, bonding and elastic properties of alkaline earth metal amidoboranes ($Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$) have been studied using van der Waals (vdW) corrected first principles calculations. Interestingly $Sr(NH_2BH_3)_2$ alone exhibit considerable vdW interactions effect to bind the crystal whereas it is less pronounced in the case of $Mg(NH_2BH_3)_2$ and $Ca(NH_2BH_3)_2$. Later, it is found that these are wide band gap insulators and the band gap values for $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$ are 4.78 eV, 3.87 eV and 3.88 eV, respectively. From the charge density distribution and bond population analysis, we conclude that there exists a strong covalent bond between B–H and N–H atoms. From the calculated elastic constants the alkaline-earth metal amidoboranes are found to be mechanically stable and $Ca(NH_2BH_3)_2$ is found to be less plastic than $Mg(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$.

1. Introduction

Chemical compositional modifications are found to be an effective way in the alteration of dehydrogenation thermodynamics of NH_3BH_3. In particular, replacing one of the hydrogen atoms of N in NH_3BH_3 with metal element leads to the formation of new class of materials, namely metal amidoboranes [1–3]. Due to relatively high hydrogen content and attractive dehydrogenation properties, the newly developed class of materials have received increasing attention as one of the promising candidates for hydrogen storage [4–7]. In the present paper, we deal with the alkaline-earth metal amidoboranes ($Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$)). Alkaline-earth metal amidoboranes have shown improved dehydrogenation properties over NH_3BH_3 [6–9]. In the case of $Ca(NH_2BH_3)_2$, hydrogen desorption starts at ~80 °C and vigorous hydrogen release takes place at ~100 and 140 °C [7,10], whereas in the case of $Sr(NH_2BH_3)_2$ it starts even lower temperatures ~60 °C. In the alkaline-earth metal amidoboranes, calcium amidoborane ($Ca(NH_2BH_3)_2$) has been identified in both liquid [11,12] and solid form [4,6]. CaH_2 and NH_3BH_3 react to form $Ca(NH_2BH_3)_2$ with release of one equivalent of H_2 [6,13]. The crystal structure of $Ca(NH_2BH_3)_2$ has been reported [7,14] as monoclinic with space group *C*2 having two formula units per cell [15,16]. In $Ca(NH_2BH_3)_2$, the Ca^{2+} ions are octahedrally coordinated by $[NH_2BH_3]^-$ groups, in which two Ca–N bonds have an average distance of 2.466 Å. The next compound in the alkaline-earth metal amidoboranes, is Magnesium amidoborane ($Mg(NH_2BH_3)_2$). Several studies [7,14,17,18] are devoted to synthesis of $Mg(NH_2BH_3)_2$ by reacting MgH_2 and NH_3BH_3 in THF (liquid state reaction) or through ball

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http://dx.doi.org/10.1016/j.matchemphys.2014.07.056
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milling (solid state reaction). These studies suggest that $Mg(NH_2BH_3)_2$ complexes with ligands is possible to synthesis [18]. Later, Luo et al. [19], successfully synthesized $Mg(NH_2BH_3)_2$ by the post milled 2 NH_2BH_3/MgH_2 and 2 NH_2BH_3/Mg samples with slow solid-phase reaction. The successful synthesis of $Mg(NH_2BH_3)_2$ by Luo et al. further requires experimental confirmation to determine a specific structure. A theoretical model [18] for $Mg(NH_2BH_3)_2$ has been proposed with a similar crystal structure as $Ca(NH_2BH_3)_2$, in which $[NH_2BH_3]^-$ groups coordinate tetrahedrally to Mg^{2+} and establish two Mg–N bonds and two Mg … BH_3 coordinates, these predictions are supported by recent studies [20]. The proposed monoclinic structure of $Mg(NH_2BH_3)_2$ like other alkaline-earth metal amodoboranes may leads to instability in the structure due to the condensed charge borne on Mg^{2+} cation may not be effectively compensated with the large $[NH_2BH_3]^-$. Strontium amidoborane ($Sr(NH_2BH_3)_2$) is another compound in the class of alkaline-earth metal amidoborane which is recently synthesized by Zhang et al. [8], and it crystallizes into a similar structure as $Ca(NH_2BH_3)_2$. The molecular structure and crystal geometries of alkaline-earth metal amidoboranes are entirely different from that of ammonia borane. So, one has to investigate and understand the structure and bonding nature where the intermolecular forces are involved, and thereby bringing basic insights on physical and chemical properties of these materials for further technical applications. We aimed in this paper to explore the structural, electronic and mechanical properties of $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$ along with $Mg(NH_2BH_3)_2$ model structure. The rest of the paper is organized as follows, in Section 2 we discuss computational details. Results are presented in Section 3 and Section 4 deals with the conclusions.

2. Computational details

The first principles calculations were carried out by using the plane wave pseudopotential method based on density functional theory as implemented in the CAmbridge Series of Total Energy Package (CASTEP) [21,22]. For $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$, the basis orbitals used as valence states for Mg: $2p^6$, $3s^2$, Ca: $3s^2$, $3p^6$, $4s^2$, Sr: $4s^2$, $4p^6$ $5s^2$ H: $1s^1$, B: $2s^2$,$2p^1$, and N: $2s^2$, $2p^3$. We have used ultrasoft pseudopotentials introduced by Vanderbilt [23] together with local density approximation (LDA) of Ceperley and Alder [24] parameterized by Perdew and Zunger (CA-PZ) [25] and also generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [26,27]. A plane wave basis set with energy cut-off of 500 eV has been applied for $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$. The vdW forces were taken into account through the semiempirical methods proposed by the Grimme (G06) [28], and by Tkatchenko and Scheffler (TS) [29] using ultrasoft pseudopotentials. For the Brillouin zone sampling, the $4 \times 5 \times 5$, $5 \times 6 \times 5$ and $5 \times 6 \times 5$ Monkhorst–Pack [30] mesh has been used for $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$, respectively, in which the forces on the atoms are converged to less than 0.0005 eV $Å^{-1}$. The maximum ionic displacement is within 0.005 Å and the total stress tensor is reduced to the order of 0.02 GPa.

3. Results and discussion

3.1. Structural properties

Table 1
The optimized structural parameters of $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$ along with experimental data.

Property	LDA	GGA	G06	TS	Expt
$Mg(NH_2BH_3)_2$					
a(Å)	8.439	8.449	8.481	8.614	8.5722[a]
b(Å)	5.561	5.927	5.629	5.675	5.6048[a]
c(Å)	4.835	5.923	5.017	5.014	5.6216[a]
	85.18	84.43	84.73	83.80	85.84[a]
$V(Å^3)$	226.18	295.31	238.55	243.73	269.38[a]
$Ca(NH_2BH_3)_2$					
a(Å)	8.813	9.263	8.922	9.058	9.100(2)[b]
b(Å)	4.047	4.424	4.140	4.235	4.371(1)[b]
c(Å)	6.173	6.628	6.293	6.301	6.441(2)[b]
β^0	91.61	93.13	91.26	94.21	93.19(2)[b]
$V(Å^3)$	220.08	271.20	232.38	241.05	255.80[b]
$Sr(NH_2BH_3)_2$					
a(Å)	7.505	8.284	7.927	7.665	8.166[c]
b(Å)	4.756	5.120	4.848	4.903	5.096[c]
c(Å)	7.180	7.945	6.645	7.097	6.725[c]
β^0	92.83	92.51	87.26	89.78	94.39[c]
$V(Å^3)$	256.04	336.72	255.15	266.79	279.11[c]

[a] Ref. [18].
[b] Ref. [7].
[c] Ref. [8].

The crystal structures of $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$ have been optimized using various methods. The optimized structural parameters using LDA and GGA within G06 and TS are compared along with experimental data in Table 1. The atomic positions are given in supporting information. In optimized structures, each formula unit contains one alkaline-earth metal atom, two pairs of B and N atoms, where B is connected to H1, H2 and H3, and N is connected to H3 and H4. Two NH_2BH_3 ligands are connected through metal (Mg, Ca and Sr) atoms. The unit cell volume obtained by LDA is underestimated by 16% for $Mg(NH_2BH_3)_2$, 13% for $Ca(NH_2BH_3)_2$ and 8% for $Sr(NH_2BH_3)_2$. The same is overestimated by 9.6% for $Mg(NH_2BH_3)_2$, 6% for $Ca(NH_2BH_3)_2$ and 20% for $Sr(NH_2BH_3)_2$ using GGA. In order to study the role of vdW interactions in $Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$ we have also carried out the calculations including vdW forces. The unit cell volume calculated by the dispersion correction methods underestimated by G06 it is 11% for $Mg(NH_2BH_3)_2$, 9% for $Ca(NH_2BH_3)_2$ and 8% for $Sr(NH_2BH_3)_2$. And by TS is 9.5% for $Mg(NH_2BH_3)_2$, 5.7% for $Ca(NH_2BH_3)_2$, 4% for $Sr(NH_2BH_3)_2$. Interestingly, $Sr(NH_2BH_3)_2$ shows a considerable vdW interaction corrections in reproducing the experimental cell volume. Whereas $Mg(NH_2BH_3)_2$ and $Ca(NH_2BH_3)_2$ the correction brought through vdW interactions on the structural properties is found to be too strong. From the present calculations, we conclude that GGA is better choice for $Mg(NH_2BH_3)_2$ and $Ca(NH_2BH_3)_2$, while it is TS for $Sr(NH_2BH_3)_2$. Hence, further all calculations of $Mg(NH_2BH_3)_2$ and $Ca(NH_2BH_3)_2$ are done within the GGA and for $Sr(NH_2BH_3)_2$ are within the TS functionals. The uncertainty in the percentage of the volume from their experiments in these compounds is due to the different potentials, as we noted that from compound to compound and interaction to interactions, the suitability of the functional varies. So, it is always preferred to check which functional is suitable for the each compound. In our previous studies we found that the parent compound ammonia borane (NH_3BH_3) [31] has a various vdW interactions and these are playing a major role in binding the crystal, so when it comes to its derivatives i.e., alkali metal amidoboranes ($LiNH_2BH_3$, $LiNH_3$ BH_4 and $NaNH_2BH_3$) these vdW interactions are found to be completely absent [32]. This cannot be taken directly to the alkaline-earth metal amidoboranes ($Mg(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2$ and $Sr(NH_2BH_3)_2$), since because the size of alkali metals are small compared to the alkaline-rath metals. Moreover, the alkaline-earth metal amidoboranes are soft towards the dispersion correction unlike their counterpart alkali metal amidoboranes. As the atomic size is increase from Mg to Ca to Sr, there will be relatively large separation between the NH_2BH_3 ligands in $Sr(NH_2BH_3)_2$ than