Density functional study of electronic structure, elastic and optical properties of MNH$_2$ (M=Li, Na, K, Rb)

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Abstract

We report a systematic first principles density functional study on the electronic structure, elastic and optical properties of nitrogen based solid hydrogen storage materials LiNH$_2$, NaNH$_2$, KNH$_2$, and RbNH$_2$. The ground state structural properties are calculated by using standard density functional theory, and also dispersion corrected density functional theory. We find that van der Waals interactions are dominant in LiNH$_2$ whereas they are relatively weak in other alkali metal amides. The calculated elastic constants show that all the compounds are mechanically stable and LiNH$_2$ is found to be a stiffer material among the alkali metal amides. The melting temperatures are calculated and follow the order RbNH$_2$ < KNH$_2$ < NaNH$_2$ < LiNH$_2$.

The electronic band structure is calculated by using the Tran–Blaha modified Becke–Johnson potential and found that all the compounds are insulators, with a considerable band gap. The [NH$_2$]$^-$ derived states completely dominate in the entire valence band region while the metal atom states occupy the conduction band. The calculated band structure is used to analyze the different interband optical transitions occurring between valence and conduction bands. Our calculations show that these materials have considerable optical anisotropy.

Keywords: electronic structure, elastic properties, optical properties, hydrogen storage materials

(Some figures may appear in colour only in the online journal)
low operating temperatures [5]. Most importantly, alkali metal amides have gained interest because of their potential reversible hydrogen storage applications [6].

The first report on the alkali metal amides KNH₂ and NaNH₂ appeared at the beginning of the 19th century by the authors Gay Lussac and Thenard; later, in 1894, Titherley reported the synthesis of LiNH₂ [7, 8]. These metal amides were traditionally used as reagents in organic synthesis [9, 10]. However, it was only in the year 2002 that Chen et al discovered LiNH₂ as a potential candidate for reversible hydrogen storage and hence paved the way to new insights into the hydrogen storage application of these materials [6]. In general, for any solid state hydrogen storage system the important characteristics are the following: the material should have high volumetric as well as gravimetric hydrogen densities, fast hydriding and dehydriding characteristics, and suitable thermodynamic properties. It is a known fundamental aspect that hydrogen absorption and desorption properties can be well judged through knowledge of the electronic structure and bonding. Moreover, physical aspects such as elastic and optical properties are key to understanding the mechanical stability and optical response of solid state hydrogen storage materials. In addition, these are necessary in determining the thermodynamic properties of these kinds of material [11].

Theoretical calculations based on density functional theory are accurate enough to predict and reproduce the experimentally measured quantities. The electronic structure of LiNH₂ was reported by using first principles plane wave pseudopotential calculations and the authors found that the material has a non-metallic nature [12, 13]. Recently, the electronic structure of LiNH₂ was determined through XAS studies and the results are found to compliment the earlier theoretical reports [14]. Elastic constants of LiNH₂ were reported theoretically by using the density functional theory calculations [15]. The high pressure behaviour of LiNH₂ was reported by using the Raman spectroscopy technique: it was found that the system undergoes a phase transition from an ambient tetragonal α-LiNH₂ structure to a high pressure β-LiNH₂ phase [16]. Pressure-induced structural phase transitions of LiNH₂ were reported from ab initio total energy calculations and evolutionary structure prediction simulations [17, 18]. By using combined synchrotron x-ray diffraction measurements and ab initio density functionals, it was possible to observe a pressure-induced phase transition with a large volume collapse (11%) in LiNH₂ [19]. The high pressure behaviour of NaNH₂ was observed by using Raman and Infrared spectroscopies [20] and also through evolutionary structure simulations [21]. To the best of our knowledge, there are no comparative studies available to explain the structural, electronic, elastic and optical properties of the alkali metal amides LiNH₂, NaNH₂, KNH₂ and RbNH₂. Hence, in this present work we aim to study these properties by performing density functional theory calculations. The rest of the paper is organized as follows: section 2 deals with the computational details and theoretical methods used in the present study. Results and discussion are presented in section 3. Finally in section 4, we end with a brief conclusion of the present study.

2. Computational details

Density functional calculations are carried out with the plane wave pseudopotential method [22]. Vanderbilt-type ultrasoft pseudopotentials are used for the present calculations [23]. The electronic wave functions are obtained by using density mixing scheme and the structures are relaxed using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method. A local density approximation with a Ceperley–Alder [24] exchange-correlation potential parameterized by Perdew and Zunger [25] (LDA-(CA-PZ)), and also the generalized gradient approximation proposed by Perdew–Burke–Ernzerhof [26] (GGA-PBE), are used to describe the exchange-correlation potential. The pseudo atomic calculations are performed for Li 2s², Na 2s² 2p⁶ 3s¹, K 3s² 3p⁶ 4s¹, Rb 4s² 4p⁶ 5s¹, N 2s² 2p³ and H 1s¹, respectively. The cut-off energy for plane waves is set to 380 eV for LiNH₂, 400 eV for NaNH₂ and 320 eV for KNH₂ and RbNH₂, respectively. Brillouin zone sampling is performed by using the Monkhorst–Pack scheme [27] with a k-point grid of 4 × 4 × 2 for LiNH₂, 4 × 3 × 4 for NaNH₂ and 4 × 4 × 4 for KNH₂ and RbNH₂, respectively. The values of both plane wave cut-off energy and k-point grid are determined by performing total energy calculations to achieve the convergence of 1 meV. For the computation of the electronic band gap, we use the recently developed Tran–Blaha-modified Becke–Johnson potential [28] within the linearized augmented plane wave (LAPW) method, as implemented in the WIEN2k package [29, 30].

It is well known that standard density functional methods are not adequate when treating the weak dispersive interactions present between the molecules of the crystal. To treat vdW interactions efficiently, Grimme recently successfully applied the vdW correction to the exchange-correlation functional of standard density functional theory (GGA-PBE+G06) at a semi-empirical level [31]. According to the semi-empirical dispersion correction approach proposed by Grimme, the total energy of the system can be expressed as

\[ E_{\text{total}} = E_{\text{DFT}} + E_{\text{Dew}} \]  

where

\[ E_{\text{Dew}} = s \sum_{i}^{N} \sum_{j}^{N} f \left( s \left( R_{ij}^6 \right), R_{ij} \right) C_{sij}^{6} \]  

here \( C_{sij} \) is called the dispersion coefficient between any atom pair \( i \) and \( j \) which solely depends upon the material and \( R_{ij} \) is the distance between the atoms \( i \) and \( j \) respectively. In the present calculations, the \( C_{sij} \) values of Li, Na, K and Rb are 1.61 J nm⁶ mol⁻¹, 5.71 J nm⁶ mol⁻¹, 10.80 J nm⁶ mol⁻¹ and 24.67 J nm⁶ mol⁻¹ and the corresponding \( R_{ij}^6 \) values of 0.825 Å for Li, 1.144 Å for Na, 1.485 Å for K and 1.628 Å for Rb have been used. In the case of the N atom, though, we have used \( C_{sij} \) value of 1.23 J nm⁶ mol⁻¹ and \( R_{ij}^6 \) value of 1.397 Å and for H atom the corresponding values are 0.14 J nm⁶ mol⁻¹ and 1.001 Å respectively. Starting from the optimized crystal structure all the related properties have been calculated. The elastic constants were calculated by using the stress-strain method implemented in the CASTEP code.
3. Results and discussions

3.1. Structural properties

In ambient conditions, LiNH$_2$ crystallizes in a tetragonal structure with the space group I-4 (82) ($z = 4$) (shown in figure 1(a)) [32] and NaNH$_2$ crystallizes in an orthorhombic structure with the space group Fddd (70) ($z = 16$) (shown in figure 1(b)) [33]. On the other hand, both KNH$_2$ and RbNH$_2$ crystallize in a monoclinic structure with the space group P2$_1$/m (13) ($z = 2$) (shown in figure 1(c)) [34]. The corresponding reciprocal lattices in the Brillouin zone for LiNH$_2$, NaNH$_2$, and KNH$_2$ (as for RbNH$_2$) are also shown in figures 2(a)–(c) respectively. All the calculations are carried out by adopting the experimental crystal structures as the initial structures and they are relaxed to allow the ionic configurations, cell shape, and volume to change in order to predict the theoretical equilibrium crystal structure within standard density functionals LDA (CA-PZ), GGA (PBE) and with dispersion corrected density functional GGA (PBE+G06). The optimized lattice parameters and internal atomic positions of metal atom M (Li, Na, K, Rb, Cs), nitrogen N and hydrogen H are tabulated in tables 1 and 2 along with experimental data respectively. It can be seen that the calculated GGA (PBE) values are in good agreement with experiment when compared to LDA (CA-PZ) and GGA (PBE+G06) results. This implies that the dispersion interactions do not play a prominent role in these systems as the volume computed with the PBE+G06 function results in large errors compared to the PBE volume, except in the case of LiNH$_2$. Therefore, to calculate the elastic constants, electronic and optical properties we adopted the GGA (PBE) functional.

3.2. Elastic properties

For solid hydrogen storage materials, elastic constants and the related properties are important as they give information regarding the atomic bonding, compressibility characteristics, and phonon properties. Moreover, it was noticed that there is a correlation between the elastic constants and the melting temperature of a solid [35]. Hence, it is necessary to know more about the elastic constants of alkali metal amides MNH$_2$ (where ‘M’ is metal atom) in order to determine their thermodynamic properties, e.g. melting temperature (Tm).

By using Hooke’s law, for small deformations of a crystal, the stress and strain are linearly related by

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}$$

where $\sigma_{ij}$ is the stress tensor, $\epsilon_{kl}$ is the strain tensor and $C_{ijkl}$ is the elastic stiffness tensor. By following Voigt’s notation [36], this equation can be reduced to

$$\sigma_i = C_{x,y} \epsilon_j, \quad \text{with} \quad x = 1-6, \ y = 1-6$$

where $xx, yy, zz, yz, zx, xy$ are replaced by 1, 2, 3, 4, 5, 6, respectively, and therefore $C_{ijkl}$ forms a 6 x 6 matrix. Due to the structural symmetry, the maximum number of independent parameters can be reduced to six for a tetragonal structure, nine for an orthorhombic structure and thirteen for the monoclinic structure.

The calculated elastic constants $C_{ij}$ of MNH$_2$ are displayed in table 3. To the best of our knowledge there are no reports available on the elastic constants of the alkali metal amides, except for LiNH$_2$. The computed elastic constants of LiNH$_2$ in the present work are in good comparison with those of earlier theoretical reports based on GGA calculations [15]. It is useful to know about elastic constants and the mechanical stability of metal amides through the Born stability criteria.
The calculated $C_{ij}$s satisfy the Born stability criteria for tetragonal, orthorhombic and monoclinic crystals [37]. Thus, the tetragonal LiNH$_2$, orthorhombic NaNH$_2$ and monoclinic KNH$_2$ and RbNH$_2$ are mechanically stable systems.

For complex hydrides, the elastic constants $C_{11}$, $C_{22}$, and $C_{33}$ are much important as they give necessary information regarding the atomic bonding characteristics along the a, b, and c-axes respectively. For all the compounds we find that the elastic constants follow the order $C_{11} > C_{22} > C_{33}$ except for LiNH$_2$. For the case of LiNH$_2$, the elastic constants $C_{11}$ and $C_{33}$ are almost identical with $C_{33}$ slightly smaller than $C_{11}$, which might be due to the similar atomic bonding along the (1 0 0) and (0 0 1) planes. Overall, the ordering of the elastic constants suggest that the lattice would be more compressible along the c-direction when compared to other axes. This fact is confirmed by the recent experimental high pressure study of LiNH$_2$ which suggests that the c-axis is more compressible than the a-axis [19]. Therefore the present study of elastic constants would be useful for future high pressure experiments on the other metal amides to assess their compressibility behaviour. By using the elastic constants, we have calculated the melting temperature ($T_m$) of the amides through the formula given by Fine et al [38] $T_m = 354 + 4.5 \left(2C_{11} + C_{33}\right)/3$. Clearly, there is a correlation between the bulk modulus $B$ and the melting temperature $T_m$ of the alkali metal amides. The trend of calculated melting temperature $T_m$ of MNH$_2$ follows, RbNH$_2$($T_m = 464.6$ K) < KNH$_2$($T_m = 481.5$ K) < NaNH$_2$($T_m = 543.8$ K) < LiNH$_2$($T_m = 564.8$ K) same as that of bulk modulus $B$ of MNH$_2$ as it follows the order RbNH$_2$ < KNH$_2$ < NaNH$_2$ < LiNH$_2$.

The calculated elastic constants allow us to obtain the polycrystalline mechanical properties such as bulk moduli and shear moduli via Voigt–Reuss–Hill approach [39]. The calculated polycrystalline elastic properties of MNH$_2$ are presented in table 3. We find that the polycrystalline bulk moduli $B_H$ of the amides are much smaller than typical metal and intermetallic compounds, which indicates that all MNH$_2$ are highly compressible materials. Further, the bulk modulus value decreases with increase in size of the metal atom, implies higher hardness for LiNH$_2$. It is interesting to note that the bulk modulus can be directly correlated with the inverse of the density of the materials. From table 1, the density of the metal amides increases from LiNH$_2$ to RbNH$_2$ which is inverse to the bulk modulus of the compounds as given in table 3. This kind of behaviour was earlier observed in the case of scheelite type AWO$_4$ (A = Ca, Sr, Ba, Pb) compounds [40]. Shear moduli $G_H$ represent the strength of the interatomic bonds with respect to the shear deformation, which influences the mobility of dislocations in the solids. The calculated shear modulus of LiNH$_2$ is greater.
than that of the other metal amides. These results on the bulk moduli and shear moduli of MNH$_2$ follow the trend that was observed in the case of alkali borohydrides [41]. The calculated B$_d$ and G$_H$ are used to analyze the ductile-brittle nature of the metal amides through Pugh’s criterion [42], according to which the critical value of B$_d$/G$_H$ ratio that separates the ductile and brittle material is 1.75. If B$_d$/G$_H$ > 1.75, the material behaves in a ductile manner, otherwise the material is brittle. For MNH$_2$ (A=Li, K, Rb), the B/G values are less than 1.75 indicating that these complex amides are brittle in nature. However, the B$_d$/G$_H$ value for NaNH$_2$ is greater than 1.75 indicating that the material is ductile. Young’s modulus (E) provides a measure of the stiffness of the solid and if the magnitude of E is large, then the material can be regarded as stiffer material. Among the four alkali metal amides, LiNH$_2$ is the stiffest material because of its high value of E. However, when compared to other complex hydrides such as LiBH$_4$ (E = 103.68 GPa), LiNH$_2$ has less stiffness.

3.3. Electronic structure

The electronic band structures of alkali metal amides MNH$_2$ are calculated by using GGA (PBE) and TB-mBJ functionals. The reason to choose two different functionals is because, in general the energy band gap calculated with standard density functionals such as GGA (PBE) is underestimated by 30–40% compared to experiment [43, 44]. To achieve accurate band gaps that are in good accord with experiment we adopt a TB-mBJ functional, which is a recently developed semi-local functional adjudged the best replacement for computationally expensive GW calculations when predicting band gaps. Figures 3(a)–(d) show the computed band structures of LiNH$_2$, NaNH$_2$, KNH$_2$ and RhNH$_2$ along the high symmetry directions in the irreducible Brillouin zone when using the TB-mBJ functional. The overall band structure profiles are quite different from each other due to their different crystal geometries. The calculated band structure of LiNH$_2$ shows a band gap of 3.34 eV (PBE) with a maximum valence band at the A-point and the minimum conduction band at the Γ-point, indicating that the compound is an indirect band gap semiconductor. The value of the band gap calculated with PBE is in good accord with earlier theoretical reports using GGA (3.2 eV) [12]. In the case of orthohombic NaNH$_2$, the calculated band structure shows a gap of 2.09 eV (PBE) between Γ-Γ and reveals that the material is a direct gap semiconductor. Both KNH$_2$ and RhNH$_2$ are also found to be indirect gap semiconductors with a gap of 2.07 eV (PBE) and 1.81 eV (PBE) between Z and Γ respectively. However, these calculated band gaps with PBE functional are within the limitation of DFT [28]. The calculated band gaps with TB-mBJ functional are 4.95 eV for LiNH$_2$, 3.55 eV for NaNH$_2$, 3.87 eV for KNH$_2$ and 3.60 eV for RhNH$_2$. Clearly, the band gaps calculated by the TB-mBJ functional are improved to a larger extent compared to the PBE band gap values. To the best of our knowledge there are no experimental data available on the band gaps of the materials. We expect that the present study will be of use for future experimental studies.

The calculated total and partial density of states of the metal amides MNH$_2$ (M=Li, Na, K, Rb) are shown in figures 4(a)–(d) respectively. The states near by the Fermi level are mainly dominated by the ‘p’-states of N atom with a small admixture of ‘s’-states of metal atom. The lower valence bands that are situated at about −5 to −6 eV are derived from the combination of ‘s’-states of H atom and ‘p’-states of N atom. Because of the strong hybridization between the states of H and N, the bands in the valence region are dispersive in nature. In the conduction band the states are entirely from the ‘s’ and ‘p’ - states of metal atom. Overall, it is noticeable that for all the compounds the valence band states are mostly dominated by the states of [NH$_3$]$^+$ anion units. A similar feature has also been observed in the other complex metal hydrides with a positive cation and anion complex where the hydrogen atom attached covalently with the other group element [3]. A similar phenomenon was also observed in the case of alkali metal azides with azide anion units [45, 46] which are analogous to alkali metal amides with a positive cation and a negative anion.

3.4. Optical properties

Metal hydrides have received tremendous interest from researchers in recent years due to their potential applications as optical devices. It is thus necessary to know the important optical properties of the metal amide systems [47]. For the metal hydrides LiH, NaH, MgH$_2$, LiAlH$_4$, NaAlH$_4$, and MgAlH$_4$ optical properties such as the complex-dielectric function were reported by using first principles calculations [48]. The optical properties of the boron-based complex metal hydride NH$_3$BH$_3$ and its metal derivative Ca(NH$_3$BH$_3$)$_2$ were studied by using a plane wave pseudopotential method.
of the real and imaginary parts of the dielectric function \( \varepsilon(\omega) \) of alkali metal amides.

In general the optical properties of matter can be described by means of the complex dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \), where \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) describes the dispersive and absorptive parts of the dielectric function. Normally there are two contributions to \( \varepsilon(\omega) \), namely intraband and interband transitions. The contribution from intraband transitions is important only in the case of metals. The interband transitions can further be split into direct and indirect transitions. The indirect interband transitions involve scattering of phonons. But indirect transitions give only a small contribution to \( \varepsilon(\omega) \) in comparison to direct transitions, so we neglected the former in our calculations. The direct interband contribution to the absorptive or imaginary part \( \varepsilon_2(\omega) \) of the dielectric function \( \varepsilon(\omega) \) in the random phase approximation without allowance for local field effects can be calculated by summing all the possible transitions from the occupied and unoccupied states with a fixed k-vector over the Brillouin zone and is given as [51]

\[
\varepsilon_2(\omega) = \frac{V e^2}{2\pi \hbar n_0^2} \int d^3k \sum |\langle \psi_C | p | \psi_r \rangle|^2 \delta(E_C - E_r - \hbar \omega) \tag{5}
\]

where \( \psi_C \) and \( \psi_r \) are the wave functions in the conduction and valence bands, \( p \) is the momentum operator, \( \omega \) is the photon frequency, and \( \hbar \) is the reduced Planck constant. The real part \( \varepsilon_1(\omega) \) of the dielectric function can be evaluated from \( \varepsilon_2(\omega) \) by using the Kramer–Kronig relations.

\[
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\varepsilon_2(\omega') \omega' d\omega'}{(\omega')^2 - (\omega)^2} \tag{6}
\]

where ‘P’ is the principle value of the integral. Knowledge of both the real and imaginary parts of the dielectric function allows calculation of the important optical properties, such as the refractive index \( n(\omega) \), through the following equation

\[
n(\omega) = \sqrt{1 + \varepsilon_2(\omega)^2 + \varepsilon_1(\omega)^2 + \varepsilon_1(\omega)}^{\frac{1}{2}} \tag{7}
\]

To calculate the optical properties, it is important to use a sufficient number of k-points in the Brillouin zone because...
the matrix element changes more rapidly within the Brillouin zone than the electronic energies themselves. Therefore, one requires more k-points to integrate this property accurately than are needed for an ordinary SCF calculation. Hence, in this study we use a k-point mesh of $8 \times 8 \times 6$, $8 \times 7 \times 8$, $12 \times 12 \times 12$ for LiNH$_2$, NaNH$_2$, and KNH$_2$, RbNH$_2$ respectively for the optical properties calculation. The calculated optical spectra using the PBE functional were shifted...
Figure 5. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ of alkali metal amides LiNH$_2$(a), NaNH$_2$(b), KNH$_2$(c) and RbNH$_2$(d) as a function of photon energy calculated within the PBE functional with a scissors shift at experimental volume.

Figure 6. Refractive index $n(\omega)$ of alkali metal amides LiNH$_2$(a), NaNH$_2$(b), KNH$_2$(c) and RbNH$_2$(d) as a function of photon energy calculated within the PBE functional with a scissors shift at experimental volume.
by the scissors operator with a magnitude of difference of TB-mBJ and PBE band gap values. In figure 5, we show the calculated imaginary part of the ε(ω) as a function of photon energy up to 30 eV. From figure 5, it can be seen that the threshold of ε2(ω) occurring at the band gap value of the material and this corresponds to the interband optical transition between N−‘p’ states occupied at the top of the valence band to the lowest occupied conduction band states of M−‘s’. In all four compounds the highest peak in ε2(ω), occurring at around 10 eV, is due to the optical transition from the occupied H−‘s’ states in the valence band to the unoccupied M−‘p’ states in the conduction band. The calculated dependence of the refractive index of the metal amides on the photon energy is displayed in figure 6. The refractive index along the three polarizations follows that n[1 0 0](0) ≠ n[0 1 0](0) ≠ n[0 0 1](0) for NaNH2, KNH2, RbNH2 and n[1 0 0](0) ≠ n[0 0 1](0) for LiNH2, which implies that the materials are optically anisotropic. For all the compounds the refractive index reaches maximum in the near Ultra-Violet region (5–10 eV). When the refractive index increases with photon energy the compounds show anomalous dispersion and this is found in the visible and near Ultra-Violet region (5–10 eV). When the refractive index increases with photon energy the compounds show anomalous dispersion and this is found in the visible and near Ultra-Violet region (5–10 eV). When the refractive index increases with photon energy the compounds show anomalous dispersion and this is found in the visible and near Ultra-Violet region (5–10 eV). When the refractive index increases with photon energy the compounds show anomalous dispersion and this is found in the visible and near Ultra-Violet region (5–10 eV).

4. Conclusions

In conclusion, we have studied the structural, electronic, elastic and optical properties of alkali metal amides. We find that a GGA functional with PBE parameterization give better results when compared to the LDA functional. Among the alkali metal amides LiNH2 has a larger bulk modulus as the material is stiffer when compared to the other amides. From the calculation of elastic constants, we conclude that the lattice is stiffer along the axes of the metal amides. The melting temperatures Tm were calculated through the elastic constants; it was found that Tm follows the order of the bulk moduli of the compounds. The electronic band structures are calculated by means of the PBE and TB-mBJ functionals; it was found that all the studied materials have a nonconducting nature. The valence region of the band structure is entirely dominated by the states of [NH2]+ complex with p-states of nitrogen atoms at the Fermi level. The optical properties of the amides were calculated and analyzed. Our study shows that the compounds show considerable optical anisotropy in the studied properties.

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