Structural Stability, Electronic Structure and Mechanical Properties of Li–N–H System

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Abstract Ab initio calculations are performed to investigate the ground state properties, structural phase transition, electronic structure and mechanical properties of lithium nitride (Li_3N), lithium imide (Li_2NH) and lithium amide (LiNH_2). The computed ground state properties like equilibrium lattice constant, cell volume, valence electron density, cohesive energy, bulk modulus and its derivatives are in good agreement with available experimental data. The structural phase transitions from α -P6/mmm to β -P6₃/mmc phase at a pressure of 17.5 GPa in Li_3N and cubic (Fm3m) to hexagonal (P6₃/mmc) phase at a pressure of 102 GPa in lithium imide (Li_2NH) are observed. A new high pressure hexagonal (P6₃/mmc) phase is predicted for Li_2NH . Electronic structure reveals that Li_3N and LiNH_2 are semiconductors, whereas Li_2NH is an insulator. The calculated elastic constants indicate that these materials are mechanically stable at ambient condition.

KEY WORDS: Ab initio calculations; Crystal structure; Phase transition; Electronic structure; Mechanical properties

1 Introduction

Lithium nitride is an unusual ionic conductor with several interesting properties and potential applications [1–6]. Li_3N crystallizes in hexagonal structure with the space group P6/mmm (α -phase) [7–12]. The existence of high pressure β -phase was confirmed by experiments, and their

behavior at high pressure was studied [7, 13–15]. Hossain et al. [16] studied the elastic properties of α - and β -phases of Li_3N by means of first principles calculations. The interaction between LiNH_2 and LiH was investigated by Chen et al. [17] and noticed that hydrogen can be reversibly stored in lithium nitride. Lithium imide (Li_2NH) is a potentially important material for hydrogen storage. Safe storage materials for hydrogen are necessary for the manufacture of practical hydrogen-based energy sources. Li_2NH was shown to be able to absorb 6.5 wt% of hydrogen. Ohoyama et al. [18] performed neutron powder diffraction experiments on Li_2NH and proposed a crystal structure with face-centered cubic (fcc) symmetry (space group F4-3m). Magyari-Kope et al. [19] predicted orthorhombic structure (Pnma) as the stable structure for Li_2NH . Noritake et al. [20] performed X-ray powder diffraction experiments and suggested fcc structure (space group Fm-3m) for Li_2NH . Mueller and Ceder [21] proposed layered triclinic (P-1) and orthorhombic (Pbca) phases and concluded that orthorhombic (Pbca) structure is more stable than triclinic (P-1) structure. Tsumuraya et al.

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[22] investigated orthorhombic (Ima2), orthorhombic (Pbca), orthorhombic (Pnma) and layered triclinic (P-1) structures for Li_2NH . Wolverton *et al.* [23] found a low energy orthorhombic Pnma structure for Li_2NH at 0 K. Crivello *et al.* [24] found that the orthorhombic (Pnma) structure is more stable than the cubic (F4-3m) structure at 0 K. Miwa *et al.* [25] investigated hydrogen storage capacity of lithium amide (LiNH_2). Herbst and Hector Jr. [26] performed Li amide/Li imide hydrogen storage reaction and proposed a crystal structure with tetragonal (I4) phase for LiNH_2 . Lin *et al.* [27] investigated the influence of vacancy, impurity vacancy complex in the kinetics of LiNH_2 complex hydrides using the first principles calculations. From the above mentioned literatures, it is observed that there are some contradictions in the structural stability of lithium imide under normal and high pressures. This motivated us to investigate the structural stability, electronic and elastic properties of Li_2NH . To the best of our knowledge, the elastic properties of Li_3N , lithium imide Li_2NH and lithium amide LiNH_2 under normal and high pressures are not yet reported. In this paper, the structural stability, electronic structure and elastic properties are analyzed using the first principles calculations based on density functional theory.

2 Theoretical Framework

The *ab initio* calculations are performed using density functional theory within generalized gradient approximation (GGA) [28, 29] as implemented in the VASP code [30, 31]. The interaction between the ion and electron is described by the projector augmented wave method [32]. Ground state geometries are determined by minimizing stresses and Hellman–Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3} eV/Å. The Kohn–Sham orbitals are expanded using the plane wave energy cutoff of 400 eV [33]. The Brillouin zone integrations are carried out using the Monkhorst–Pack K-point mesh [34] with a grid size of $12 \times 12 \times 12$ for total energy calculation. The electronic configuration of Li, N and H atoms is $\text{Li } 1s^2 2s^1$, $\text{N } 2s^2 2p^3$ and $\text{H } 1s^1$, respectively.

3 Results and Discussion

3.1 Ground State Properties of Li_3N , Li_2NH and LiNH_2

The lattice parameters are optimized for Li_3N with hexagonal α - (P6/mmm) and β -phases (P6₃/mmc). For Li_2NH , eight potential structures have been considered. They

include three cubic structures with *space group* Fm-3m, Pm3m, F4-3m, hexagonal structure with *space group* P6₃/mmc, three orthorhombic structures with *space group* Ima₂, Pbca, Pnma and triclinic structure with *space group* P-1. The lattice constants are optimized for LiNH_2 with tetragonal structure (*space group* I-4).

The total energy calculations are carried out for Li_3N , Li_2NH and LiNH_2 with various possible structures for various volumes. The volume corresponding to the minimum energy is the equilibrium volume V_0 . These data are then fitted to the universal second-order Birch–Murnaghan equation of state [35] to determine the bulk modulus B_0 and its first derivative at normal pressure. The cohesive energy (E_{coh}) of a solid is the difference between the total energy per atom of the bulk material at ambient condition and the atomic energies of the atoms belonging to the unit cell of the material. The calculated ground state properties like lattice constants a , b and c (Å), cell volume V_0 (Å³), valence electron density ρ (electrons/Å³), cohesive energy E_{coh} (eV), bulk modulus B_0 (GPa) and its derivatives B'_0 for Li_3N , Li_2NH and LiNH_2 are listed in Tables 1 and 2, respectively, along with the experimental and other available theoretical results [7, 14, 16, 18–22, 25, 27, 36–38]. The optimized lattice parameter for cubic Li_2NH (Fm3m) is found to be $a_0 = 5.045$ Å. This is in good agreement with the experimental value $a_0 = 5.047$ Å [20]. The calculated lattice constants are in good agreement with the experimental results [18–22, 38] and previous theoretical results [7, 14, 16, 25, 27, 36, 37]. The cohesive energies of these materials are observed to be higher than those of the host elements. It is also observed that α - Li_3N , Li_2NH (P6₃/mmc) and LiNH_2 (I-4) are found to be the more stable owing to their highest cohesive energy values. This suggests that these materials can be easily synthesized at ambient condition.

3.2 Structural Phase Transition of Li_3N and Li_2NH

The total energy (E_{tot}) is calculated for hexagonal α - and β -phases of Li_3N and various phases considered for Li_2NH as a function of pressure (P). It is found that Li_3N is more stable in α -phase at normal pressure. On further increasing the pressure, it undergoes a structural phase transition from α - to β -phase, whereas Li_2NH is stable in cubic (Fm-3m) phase at normal pressure and a cubic (Fm-3m) to hexagonal (P6₃/mmc) phase transition is observed under high pressure. The enthalpy (H) is calculated using the formula

$$H = E_{\text{tot}} + PV, \quad (1)$$

where V is the volume of lattice. For Li_3N and Li_2NH , enthalpies as a function of pressure and their plots are given in Fig. 1. A structural phase transition from α - to β -phase is observed at a pressure of 17.5 GPa in Li_3N which is in

Table 1 Calculated lattice parameters a , b and c (Å), equilibrium volume V_0 (Å³), valence electron density ρ (electrons/Å³), cohesive energy E_{coh} (eV), bulk modulus B_0 (GPa) and its derivative B'_0 for Li_3N with P6/mmm and P6₃/mmc space groups

Space group	a	b	c	V_0	ρ	E_{coh}	B_0	B'_0
(P6/mmm)	3.641, 3.600 ^a , 3.6413 ^b , 3.534 ^c , 3.508 ^d , 3.648 ^e		3.846, 3.840 ^a , 3.823 ^b , 3.772 ^c , 3.745 ^d , 3.875 ^e	45.08	0.1774	8.838084	69.17, 63.90 ^a , 58.90 ^c , 61.00 ^d	3.815, 4.000 ^d , 3.800 ^e , 3.700 ^d
(P6 ₃ /mmc)	3.485, 3.558 ^b , 3.445 ^c , 3.418 ^d , 3.552 ^e		6.228, 6.250 ^b , 6.148 ^c , 6.100 ^d , 6.310 ^e	67.30	0.1188	6.756029	86.5, 98.0 ^a , 74.5 ^c , 78.2 ^d	3.421, 4.040 ^a , 3.420 ^c , 3.770 ^d

^a, ^b Ref. [16]; ^c Ref. [7]; ^d Ref. [14]; ^e Ref. [36]

agreement with the Refs. [7, 13–15], and cubic-Fm3m to hexagonal-P6₃/mmc phase transition is predicted at a pressure of 102 GPa in Li_2NH . A new high pressure hexagonal phase with space group P6₃/mmc is observed in Li_2NH .

3.3 Electronic Structure

3.3.1 Li_3N

The energy band structure and total density of states (DOSs) of Li_3N in α -phase is computed, along the symmetry directions G–K–M–G–A–L–H–A at ambient condition. The electronic band structure and DOS of α - Li_3N are given in Fig. 2. It is observed that lithium nitride has four valence bands corresponding to eight valence electrons which comes from $2s^1$ state electron of Li atom and $2s^2 2p^3$ state electrons of N atom. The low lying band, in the energy range from -10 to -12 eV, is mainly due to N- $2s$ state. There is a gap of about ~ 8 eV between the band due to N- $2s$ state and the bottom of the other valence bands. The other valence bands are mainly due to N- $2p$ and Li- s states, indicating a strong covalent interaction between the lithium and nitrogen atoms. Above the Fermi level, empty conduction bands are present with a mixed s and p states of Li and N atoms. At normal pressure, the band gap of Li_3N (1.8 eV) is indirect with top of the valence band in A point and the bottom of the conduction band in G point, which confirms that Li_3N is a wide band gap semiconductor at normal pressure. From the DOS histogram (Fig. 2b), it is found that the peak in the region around -10 eV is due to the s -state electrons of the N atom. The peaks just below the Fermi level are mainly due to the p -state electrons of the nitrogen atom, along with a small contribution from the s -state electrons of the Li atom. The peaks above the Fermi level are due to the s and p states of Li and N atoms. The DOSs also confirms the semiconducting behavior of Li_3N at normal pressure. After 17.5 GPa, β -phase of Li_3N is more stable than α - Li_3N , so high pressure electronic band structure and DOSs are computed for β - Li_3N , and the plots are given in Fig. 3a, b, respectively. It is found that at high pressure, the band gap is increased to 2.3 eV. Thus, at high pressure also, Li_3N is a wide band gap semiconductor.

3.3.2 Li_2NH

The electronic structure of Li_2NH is investigated by computing the band structure and total DOSs in cubic Fm-3m phase, along the symmetry directions L–G–X–W–L–K–G at ambient condition, and the plots are given in Fig. 4. At normal pressure, the valence band minimum is located at the L point. It is observed that eight valence electrons of lithium imide form four valence bands. The band, which is

Table 2 Calculated lattice parameters a , b and c (Å), equilibrium volume V_0 (Å³), valence electron density ρ (electrons/Å³), cohesive energy E_{coh} (eV), bulk modulus B_0 (GPa) and its derivative B'_0 for lithium imide (Li_2NH) and lithium amide (LiNH_2)

Materials	Space group	a	b	c	V_0	ρ	E_{coh}	B_0	B'_0
Li_2NH	F43m	5.649, 5.077 ^a			48.02	0.1665	0.7622	93.01	3.581
	Pnma	7.704, 7.733 ^b	3.75	5.074, 3.60 ^b , 4.872 ^b	42.36	0.1888	3.4819534	68.15	3.116
	P6 ₃ /mmc	3.657		5.884	34.11	0.2345	7.6534	211	3.032
	Fm3m	5.045, 5.047 ^c			32.10	0.2492	6.8820	96.59	3.714
	P-1	4.15, 3.57 ^d	3.57	6.6045, 3.58 ^d , 6.426 ^d	36.42	0.2196	6.7269	78.4	3.441
	Ima2	7.191, 7.118 ^e	10.071	7.0503, 10.072 ^e , 7.088 ^e	44.84 [?]	0.1784	2.27679	91.2	3.160
	pbca	5.12, 5.12 ^f	10.51	5.267, 10.51 ^f , 5.27 ^f	32.79	0.2439	3.3918	59.12	3.947
	Pm3m	3.945			61.40	0.1302	2.4819	112.3	3.017
LiNH_2	I-4	5.0316, 5.032 ^g , 5.017 ^h	5.097 ⁱ	10.069, 10.256 ^g , 10.363 ^h , 10.113 ⁱ	112.74	0.0709	12.0859	77.92	3.569

^a Ref. [18]; ^b Ref. [19]; ^c Ref. [20]; ^d Ref. [21]; ^e Ref. [22]; ^f Ref. [25]; ^g Ref. [27]; ^h Ref. [37]; ⁱ Ref. [38]

Fig. 1 The enthalpy as a function of pressure: **a** Li_3N ; **b** Li_2NH **Fig. 2** Electronic structure of Li_3N at normal pressure: **a** band structure; **b** density of states

positioned at the bottom of the valence band, is due to the N-2s state. The remaining three bands appearing just below the Fermi level are due to the s-state electrons of the Li and H atoms and p-state electrons of the N atom, and these valence bands are separated by a wide gap of 8 eV from the bottom most band, indicating the presence of covalent bonding in cubic lithium imide. Near the Fermi level, the band in the energy region 5 eV is due to the large

contribution of hydrogen s-state electron with a small contribution from N-2p-state electrons. Hence, hydrogen can be easily released without excess heating, and Li_2NH can be used as a hydrogen storage material. The empty conduction bands above the Fermi level are due to s and p states of metal and non-metal atoms. At normal pressure, there is no overlapping between the top of the valence band and bottom of the conduction band, which confirms that at

Fig. 3 Electronic structure of Li_3N at high pressure: **a** band structure; **b** density of states

Fig. 4 Electronic structure of Li_2NH at normal pressure: **a** band structure; **b** density of states

ambient pressure cubic, lithium imide is an insulator with an energy gap of 4 eV. The DOSs of cubic lithium imide at normal pressure is divided into three main regions. The peak in the energy region around -9 eV is mainly due to the s -state electrons of the nitrogen atom. In the region below the Fermi level, the peaks are mainly due to the p -state electrons of the nitrogen atom, along with a small contribution from the s -state electrons of the lithium and hydrogen atoms. Finally, the conduction states above the Fermi level are due to the mixed s state of Li and H atoms and p -states N atom. From the DOSs also, it is inferred that lithium imide is an insulator at normal pressure. The

electronic band structure and DOSs for the high pressure stable phase of Li_2NH (hexagonal phase: space group-P63/mmc) are given in Fig. 5a, b, respectively. It is found that at high pressure, the band gap decreases to 3.84 eV in Li_2NH , which confirms the insulating behavior of Li_2NH .

3.3.3 LiNH_2

The computed band structure of LiNH_2 in tetragonal (I-4) phase along the symmetry directions Z–G–X–P–N at ambient condition is given in Fig. 6a. The low lying band at the bottom far from the Fermi level is due to the non-metal

Fig. 5 Electronic structure of Li_2NH at high pressure: **a** band structure; **b** density of states

Fig. 6 Electronic structure of LiNH_2 at normal pressure: **a** band structure; **b** density of states

Fig. 7 Electronic structure of LiNH_2 at high pressure; **a** band structure; **b** density of states

N-2s state. The other bands appearing just below the Fermi level are due to *s*-state electrons of the lithium and hydrogen atom and *p*-state electrons of the nitrogen atom. Since the band formed near the Fermi level is due to the major contribution from hydrogen atom, this material can liberate hydrogen easily and hence used as a hydrogen storage material. These bands are separated from the low lying band by the energy gap of 5 eV, which indicates the presence of covalent bonding in tetragonal lithium amide. The conduction bands above the Fermi level are due to *s* state of Li and H atoms and *p* state of N atom. The energy band gap between the top of the valence band and bottom of the conduction band is observed to be 1.42 eV, which confirms the semiconducting behavior of lithium amide. From the DOSs plot (Fig. 6b), it is seen that the level arising from N-2s state gives rise to a longest peak around -18 eV. The peaks just below the Fermi level are due to the *p*-state electrons of the nitrogen atom along with a small contribution from the *s*-state electrons of the H and Li atoms. Above the Fermi level, the peaks are due to the mixed *s* and *p* states of Li, N and H atoms. The semiconducting behavior of LiNH_2 at normal pressure is also confirmed from the DOSs plot. The band structure and DOSs are computed for various pressures in tetragonal phase, and it is found that at a pressure of 128 GPa, LiNH_2

becomes metal. High pressure band and DOSs plot for tetragonal phase of LiNH_2 are given in Fig. 7. It is found that LiNH_2 exhibits metallic behavior at a pressure of 128 GPa. Thus, a semiconductor to metallic transition is observed at a pressure of 128 GPa in LiNH_2 .

3.4 Mechanical Properties

In order to calculate the elastic constants of a structure, a small strain is applied onto the structure, and its stress is determined. The energy of a strained system [39, 40] can be expressed in terms of the elastic constants C_{ij} as

$$E(V, \varepsilon_i) = E(V_0, 0) + V_0 \sum_{i=1}^6 \sigma_i \varepsilon_i + \frac{V_0}{2} \left(\sum_{i,j=1}^6 C_{ij} \varepsilon_i \varepsilon_j \right) + O(\{\varepsilon_i^3\}), \dots, \quad (2)$$

where V_0 is the volume of the unstrained lattice, E_0 is the total minimum energy at this unstrained volume of the crystal, and V is the volume of the lattice due to strain tensor. The elasticity tensor has three independent components (C_{11} , C_{12} , C_{44}) for cubic crystals, five independent components (C_{11} , C_{12} , C_{44} , C_{13} and C_{33}) for hexagonal crystals and six independent components (C_{11} , C_{33} , C_{44} , C_{66} , C_{12} and C_{13}) for tetragonal crystals. A proper choice

Table 3 Calculated elastic constants C_{ij} (GPa), Vogit–Reuss–Hill bulk modulus B (GPa), shear modulus G (GPa) and Young's modulus E (GPa), Poisson's ratio ν and B/G ratio for Li_3N with P6/mmm and P6₃/mmc space groups under different pressure P (GPa)

Space group	P	C_{11}	C_{12}	C_{44}	C_{13}	C_{33}	B	G	E	ν	B/G
P6/ mmm	0	177, 165.7 ^a , 114 ^b , 122.8 ^c	28.95, 22.7 ^a , 38 ^b , 24.6 ^c	16.27, 18.1 ^a , 17.0 ^b , 16.6 ^c	10.01, 8.3 ^a , 4.5 ^b , 5.4 ^c	216, 180 ^a , 118 ^b , 129.5 ^c	74.14	63.7	162.08	0.1868	1.163
	17.5	224	32	18.9	11.6	225	86.98	73.89	172.75	0.1899	1.177
P6 ₃ / mmc	20	237	39	46.76	19.01	268	99.54	89.64	206.83	0.1737	1.110
	50	332	51	59	21.6	365	135.26	115.3	269.36	0.1890	1.173

^a Ref. [16]; ^b Ref. [9]; ^c Ref. [46]**Table 4** Calculated elastic constants C_{ij} (GPa), Vogit–Reuss–Hill bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν and B/G ratio for Li_2NH and LiNH_2 under different pressure P (GPa)

Materials	P	C_{11}	C_{12}	C_{44}	C_{13}	C_{33}	C_{66}	B	G	E	ν	B/G
Fm3m Li_2NH	0	179	62	90				101	75.73	181.7	0.2222	1.33
	13	239	69	116				126	102.41	241.74	0.2017	1.230
	62	320	111	120				181	113.54	281.72	0.2633	1.594
	102	484	142	149				256	157.44	391.97	0.2675	1.626
P6 ₃ /mmc Li_2NH	106	545	81.2	214	136	763		279.2	234.19	549.06	0.1933	1.192
	244	761	218	264	210	976		417.0	278.99	684.35	0.2492	1.494
I-4 LiNH_2	0	118.2	101	18.38	44.82	41.86	42.34	79.29	29.14	77.87	0.3557	2.721

of the set of strains $\{e_i, i = 1, 2, \dots, 6\}$ in Eq. (5) leads to a parabolic relationship between $\Delta E/V_0$ ($\Delta E \equiv E - E_0$) and the chosen strain. For each lattice structure of Li_3N , lithium imide (Li_2NH) and lithium amide (LiNH_2), the lattice was strained by 0, ± 1 , and $\pm 2\%$ to obtain their total minimum energies E (V). These energies and strains were fitted with the corresponding parabolic equations of $\Delta E/V_0$ to yield the required second-order elastic constants [41]. While computing these energies, all atoms are allowed to relax with the cell shape and volume fixed by the choice of strains $\{e_i\}$. From the calculated C_{ij} values, the bulk modulus and shear modulus for the cubic, hexagonal and tetragonal crystals are determined using the Voigt–Reuss–Hill averaging scheme [42–44].

The Born–Huang elastic stability criteria [45] for the cubic crystals are

$$C_{44} > 0, C_{11} > |C_{12}|, C_{11} + 2C_{12} > 0, \quad (3)$$

for hexagonal phase

$$C_{44} > 0, C_{11} > C_{12}, (C_{11} + 2C_{12})C_{33} > 2C_{13}^2, \quad (4)$$

and for tetragonal phase

$$\begin{aligned} C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, (C_{11} - 2C_{12}) > 0, \\ (C_{11} + C_{33} - 2C_{13}) > 0, [2(C_{11} + 2C_{12}) + C_{33} + 4C_{13}] > 0. \end{aligned} \quad (5)$$

The mechanical properties for Li_3N , Li_2NH and LiNH_2 with considered structures are presented in Tables 3 and 4 along with the available data [9, 16, 46]. Clearly, the calculated elastic constants for Li_3N and Li_2NH under normal and high pressure and LiNH_2 at normal pressure satisfy Born–Huang criteria, suggesting that they are mechanically stable. Bulk modulus (B_0) and shear modulus (G) can measure the resistance of a material to volume and shape change, respectively. The results in Tables 3 and 4 indicate that Li_3N , Li_2NH and LiNH_2 have seemed more inclined to resist with volume change than shape change. Young's modulus is often used to provide a measure of stiffness of a solid, i.e., larger the value of Young's modulus, stiffer is the material. It is found that Li_2NH is the stiffest among the considered materials. In addition, Poisson's ratio provides more information about the characteristics of the bonding forces than any of the other elastic constants. The ratio of bulk modulus to shear modulus is used to estimate the brittle or ductile behavior of materials. A high B/G ratio is associated with ductility, while a low B/G ratio corresponds to brittle nature. The critical value which separates ductile and brittle materials is about 1.75. The calculated values of B/G ratio predict that the Li_3N , Li_2NH and LiNH_2 are brittle in nature.

The variations of elastic moduli with pressure for Li_3N and Li_2NH are shown in Figs. 8 and 9. It is observed that

Fig. 8 Pressure dependence of elastic moduli of Li_3N

Fig. 9 Pressure dependence of elastic moduli of Li_2NH

all the elastic constants increase monotonically with pressure. There is a dip in the variation of elastic moduli at the transition pressure. The elastic constants C_{11} and C_{33} show a drastic increase with pressure, whereas other constants show moderate increase.

3.5 Hydrogen Storage in Li_3N , Li_2NH and LiNH_2

Hydrogen fuel, which can be readily produced from renewable energy sources, contains at least three times larger chemical energy per mass 142 MJ/kg than any chemical fuel, thus making a hydrogen fuel cell an attractive alternative to the internal combustion engine for transportation [47]. Elements, especially those in group I–IV and some transition metals, have their hydride and amide/imides forms. The density of H per unit cell of Li_2NH and LiNH_2 is 0.0521 and 0.0262 g/cm³. The storage capacity of Li_2NH and LiNH_2 is 3.49 and 8.77. It is seen that the weight percentage of hydrogen is higher in LiNH_2 compared to Li_2NH .

4 Conclusions

The structural, electronic and mechanical properties of lithium nitride (Li_3N), lithium imide (Li_2NH) and lithium amide (LiNH_2) have been investigated. The results suggest that Li_3N , Li_2NH and LiNH_2 are crystallized in α -phase, cubic (Fm-3m) phase and tetragonal (I-4) phase, respectively, at normal pressure. The pressure-induced structural phase transitions from α -P6₃/mmm to β -P6₃/mmc phase at a pressure of 17.5 GPa in Li_3N and cubic-Fm3m to hexagonal-P6₃/mmc phase transition at a pressure of 102 GPa in Li_2NH are observed. A new high pressure hexagonal-P6₃/mmc phase is predicted for Li_2NH . Electronic structure reveals that both Li_3N and Li_2NH are non-metallic in nature at normal and under high pressure, whereas in LiNH_2 semiconductor to metallic transition is predicted at a pressure of 128 GPa. All the calculated elastic constants obey the Born–Huang criteria, suggesting that they are mechanically stable at normal pressure. It is observed that

pressure has an important influence on elastic constants, Young's modulus, bulk modulus and shear modulus.

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