# Structural, Electronic and Elastic Properties of LiXN (X = Be, Mg): A First Principles Study

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**Abstract**— The structural, electronic and elastic properties of LiXN (X = Be, Mg) are investigated by first principles calculation based on density functional theory using Vienna ab-initio simulation package. Electronic structure reveals that these alloys exhibit semiconducting behavior and α – phase is the most stable phase. The calculated elastic constants indicate that these materials are mechanically stable at ambient condition.

**Keywords:** Electronic structure; Elastic properties; Ab-inito calculations

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## 1 INTRODUCTION

HYDROGEN has been identified as one of the most promising clean fuel for the future. Perhaps the greater technical barrier to its implementation is hydrogen storage. For on-board vehicular hydrogen storage, advanced metal hydrides that are light weight, low cost and high in hydrogen density are necessary [1,2]. Complex hydrides such as amides [3-8], Magnesium based hydrides [9-12] and mixed complex hydrides [13-16] have been reported to have good hydrogen storage capabilities. Recently, in a comprehensive study of destabilization reactions, Alpati *et al.* predicted that a 1:1 mixture of lithium amide and magnesium hydride, LiMgN, could release 8.2 wt % of $H_2$ [17, 18]. The band structure modification of diamond and zinc blende semiconductors has been tested theoretically and widely by insertion of small atoms such as H and He at their tetrahedral interstitial sites, which has been proposed as filled tetrahedral semiconductor [19, 20], such as $LiB^{II}C^V$ ($B^{II}$ = Zn, Mg; $C^V$ = N, P, As). Recently, Kuriyama *et al.* [21] have synthesized a new filled tetrahedral semiconductor LiMgN by direct reaction between $N_2$ and LiMg alloy at around $800^0$C for 8h and determined the energy band gap value as 3.2 eV. Bailey *et al.* performed further studies, by means of PND, reporting that LiMgN under goes a structural transition at temperature above 673 K resulting in the formation of a cubic anti – fluorite structure (space group Fm – 3m) [22].

In this paper, structural stability, electronic structure and elastic properties of LiXN (X = Be, Mg) under ambient condition are analyzed by performing total energy calculation

with zincblende structure using first principles calculation based on density functional theory as implemented in Vienna ab – initio simulation package.

## 2 COMPUTATIONAL DETAILS

The total energy calculations are performed in the frame work of density functional theory using the generalized gradient approximation (GGA-PBE) [23-25] as implemented in the VASP code [26-28]. 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. Birllouin zone integration is performed with a Gaussian broadening of 0.1 eV during all relaxations. The cut-off energy for plane waves in our calculation is 600 eV. The electronic configuration of Li, Be, Mg and N atoms are $1s^1$, $2s^1$ (Z=2), $1s^2$, $2s^2$ (Z=4), [Ne] $3s^2$, (Z=12) and $1s^2$, $2s^2$, $2p^3$ (Z=7). The valence electron configurations are Li $1s^1$, $2s^1$, Be $1s^2$, $2s^2$, Mg $3s^2$ and N $2s^2$, $2p^3$ atoms. Birllouin-zone integrations are performed on the Monkhorst-Pack K-point mesh [29] with a grid size of 11x11x11 for structural optimization and total energy calculation. Iterative procedure is stopped when the change in total energy between successive ionic relaxation steps is less than 1 meV/cell. The unit cell structure of the various phases of LiXN (X = Be, Mg) are given in Fig. 1.

## 3 Results and discussion

### 3.1 Structural stabilities and ground state properites

The structural stability of LiXN (X = Be, Mg) are analyzed by calculating the total energy using VASP code. The calculated total energy as a function of reduced volume for α, β and γ phases of LiXN (X = Be, Mg) are plotted in Fig. 2. From Fig. 2, it is clear that the α – phase is more stable than β and γ – phases. The calculated ground state properties like cell volume $V_0$ (Å³), lattice constant a (Å), valance electron density ϱ (electrons/ Å³), Bulk modulus $B_0$ (Gpa) and its derivative $B_0'$, Band gap $E_g$ (eV), the band gap volume $a_v$ and pressure deformation potentials $a_P$ of LiXN (X = Be, Mg) are listed in

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Table 1. The lattice constants and Bulk modulus of LiBeN and LiMgN are in good agreement with the experimentally measured values and other theoretical results [30-33].
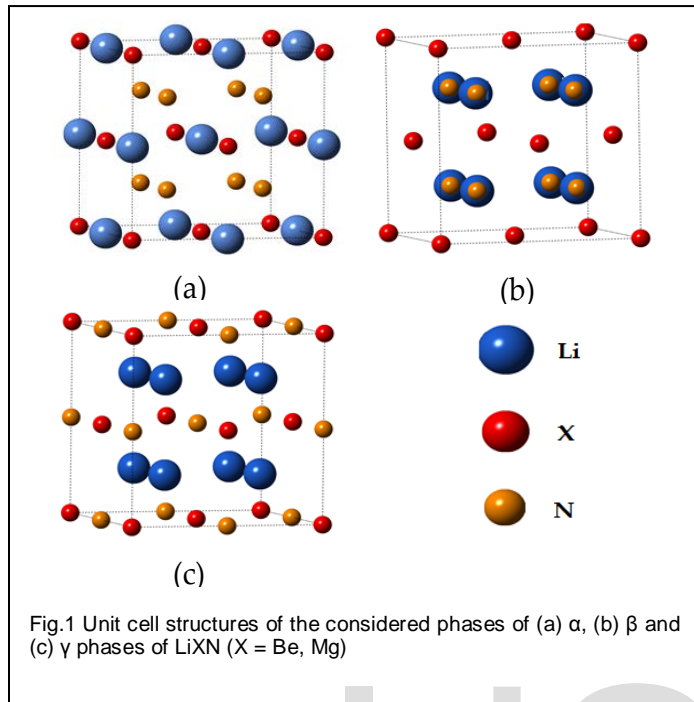


Fig.1 Unit cell structures of the considered phases of (a) α, (b) β and (c) γ phases of LiXN (X = Be, Mg)

## 3.2 Electronic Structure

The electronic density of states (DOS) and band structure of LiXN (X = Be, Mg) alloys are shown in Fig 3. It is seen that the N -2p states are localized between 0 eV and 4 eV with mixing of some Mg 3s and Li s states. The high peak due to 2s state electron of N atom lies at the energy range of -10 eV.
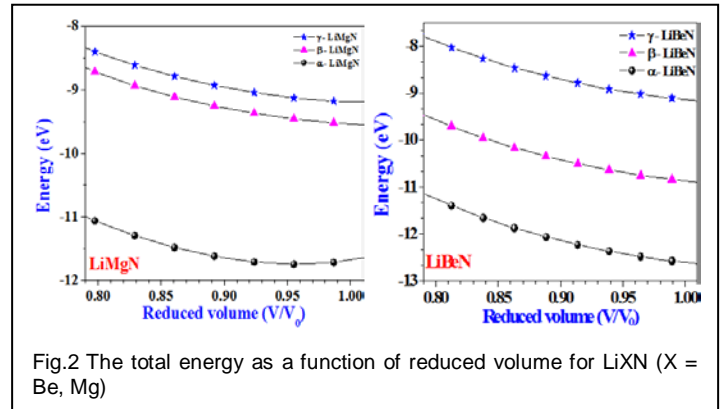


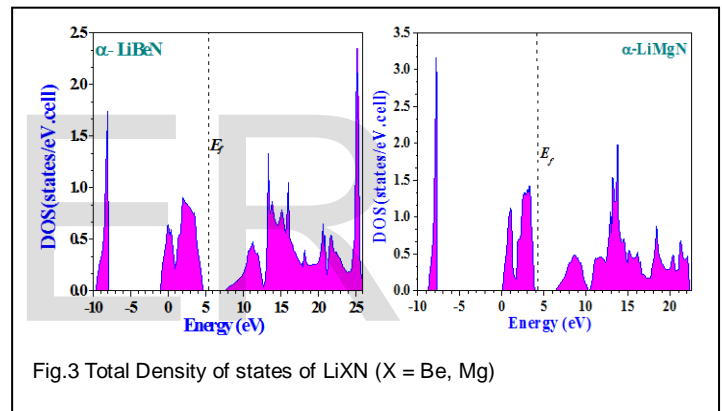Fig.2 The total energy as a function of reduced volume for LiXN (X = Be, Mg)



Fig.3 Total Density of states of LiXN (X = Be, Mg)

## 3.3 Elastic properties

Elastic constants are the measure of the resistance of a crystal to an externally applied stress. For small strains Hooke's law is valid and the crystal energy E is a quadratic function of strain [34]. Thus, to obtain the total minimum energy for calculating the elastic constants to second order, a crystal is strained and all the internal parameters are relaxed. Consider a symmetric 3 x 3 non-rotating strain tensor ε which has matrix elements $E_{ij}$ (i, j = 1, 2 and 3) defined by Eq.1.

$$\varepsilon = \begin{pmatrix} e_1 & \dfrac{e_6}{2} & \dfrac{e_5}{2} \\ \dfrac{e_6}{2} & e_2 & \dfrac{e_4}{2} \\ \dfrac{e_5}{2} & \dfrac{e_6}{2} & e_3 \end{pmatrix} \tag{1}$$

such a strain transforms the three lattice vectors to $a_k'$

$$a_k' = (1 + \varepsilon)\, a_k \tag{2}$$

where I is defined by its elements, $I_{ij}$ =1 for i = j and 0 for i ≠ j and K = 1,2 and 3; K' = 1, 2 and 3. Each lattice vector $a_k$ or $a_k'$ is a 3x1 matrix. The change in total energy due to the above strain (1) is

### TABLE 1
### GROUND STATE PROPERTIES

|  | LiBeN | | | LiMgN | | |
|---|---|---|---|---|---|---|
|  | α | β | γ | α | β | γ |
| $V_0$ | 20.72 | 20.44 | 21.19 | 31.05 | 31.65 | 29.43 |
| a | 4.3599 | 4.3402 | 4.3929 | 4.9891 | 5.0211 | 4.9012 |
|  | 4.366[f] | 4.338[f] | 4.398[f] | 4.970[c] | 5.067[e] | 4.866[e] |
|  |  |  |  |  |  | 4.593[d] |
|  |  |  |  |  |  | 4.955[e] |
| $E_f$ | 5.5805 | 5.9140 | 5.6850 | 4.4722 | 4.5558 |  |
| 5.5967 |  |  |  |  |  |  |
| ϱ | 0.386 | 0.391 | 0.378 | 0.258 | 0.253 | 0.272 |
| $B_0$ | 159, | 147 | 131 | 102 | 89 | 84 |
|  | 153.6[f] | 143.9[f] | 125.4[f] | 99[e] | 77[e] | 97[e] |
| $B_0'$ | 3.834 | 3.832 | 3.837 | 3.878 | 3.879 | 3.873 |
|  | 3.8[f] | 3.9[f] | 3.8[f] |  |  |  |
| $E_g$ | 5.57 | 6.33 | 4.23 | 3.09 | 3.15 | 2.94 |
|  | 5.05[f] | 6.49[f] |  | 3.2[c] | 2.40[c] | 2.39[c] |
|  | 5.71[f] | 7.00[f] |  | 2.46[c] |  |  |
|  |  |  |  | 3.3[e] |  |  |
| $a_v$ | -9.69 | -9.42 | -12.91 | -6.63 | -8.34 | -8.27 |
|  |  |  |  | -5.64[c] |  |  |
| $a_P$ | 6.10 | 6.41 | 9.85 | 6.50 | 9.37 | 9.84 |
|  |  |  |  | 5.70[c] |  |  |

[a]Reference [30], [c] Reference [21], [d] Reference [31], [e]Reference [32],
[f]Reference [33].

$$\Delta E = \left(1 - \frac{V}{V_0}\right)P(V_0) + \frac{1}{2}\left(\sum_1^6 \sum_1^6 C_{ij}e_i e_j\right) + O\left(\{e_i^3\}\right) \qquad (3)$$

where $V_0$ is the volume of the unstrained lattice, $E_0$ is the total minimum energy at this unstrained volume of the crystal, $P(V_0)$ is the pressure of the unstrained lattice, and V is the new volume of the lattice due to strain in Eq. (1). The elasticity tensor has three independent components ($C_{11}$, $C_{12}$, $C_{44}$) for cubic crystals. A proper choice of the set of strains $\{e_i, i = 1, 2,..., 6\}$, in Eq.(3) leads to a parabolic relationship between $\Delta E/V_0$ ($\Delta E \equiv E - E_0$) and the chosen strain. From the calculated $C_{ij}$ results, the bulk modulus and shear modulus for the cubic crystal is calculated using the Voigt-Reuss- Hill (VRH) averaging scheme [35-37] and averaged compressibility in the form $\beta = 1/B$. The strain energy $1/2 C_{ij}e_i e_j$ of a given crystal in Eq. (3) must always be positive for all possible values of the set $\{e_i\}$; otherwise the crystal would be mechanically unstable. The calculated elastic constants $C_{ij}$ (GPa), Young's modulus Y (GPa), Shear modulus G (GPa), Poisson's ratio ($\nu$), elastic anaisotropy factor A, B/G ratio, G/B ratio, Hardness parameter H, averaged compressibility $\beta$ and Lame's constants $\mu$, $\lambda$

TABLE 2
ELASTIC PROPERTIES

| | LiBeN | | | LiMgN | | |
|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | $\alpha$ | $\beta$ | $\gamma$ |
| $C_{11}$ | 290.91 | 172.87 | 152.37 | 242.04 | 171.43 | 118.12 |
| $C_{12}$ | 92.99 | 133.82 | 120.70 | 31.42 | 47.86 | 66.54 |
| $C_{44}$ | 88.45 | 19.08 | 69.87 | 84.56 | 40.28 | 21.54 |
| Y | 245.87 | 56.11 | 45.68 | 235.04 | 276.83 | 70.86 |
| G | 98.96 | 19.53 | 15.84 | 105.31 | 61.79 | 25.78 |
| $\nu$ | 0.2422 | 0.4363 | 0.4420 | 0.1149 | 0.2182 | 0.3624 |
| A | 0.8937 | 0.9772 | 4.4123 | 0.6184 | 0.3674 | 0.2833 |
| B/G | 1.607 | 7.527 | 1.875 | 0.969 | 1.440 | 3.258 |
| G/B | 0.622 | 0.130 | 0.533 | 1.022 | 0.694 | 0.307 |
| H | 17 | 0.83 | 0.62 | 27.06 | 21.35 | 2.15 |
| $\beta$ | 0.006 | 0.007 | 0.008 | 0.009 | 0.011 | 0.012 |
| $\mu$ | 122 | 28 | 22 | 131 | 169 | 48 |
| $\lambda$ | 92.98 | 133.78 | 120.71 | 15.73 | 43.99 | 33.91 |

for LiXN (X = Be, Mg) alloys are given in Table 2.
For a stable cubic structure, the three independent elastic constants $C_{ij}$ ($C_{11}$, $C_{12}$, and $C_{44}$) should satisfy the Born-Huang criteria [37].
$C_{44} > 0$, $C_{11} > |C_{12}|$, $C_{11} + 2 C_{12} > 0$
Clearly, the calculated elastic constants for LiBeN and LiMgN are satisfying Born-Huang criteria, suggesting that they are mechanically stable. At normal pressure LiXN (X = Be, Mg) are mechanically stable due to positive $C_{44}$.
One of the most important parameters for estimating mechanical properties of compounds is elastic anaisotropy of crystal. It has an important implication in engineering science since it is highly correlated with the possibility to induce microcracks in materials [38]. The elastic anaisotropy behaviour of a crystal

can be measured by the Zener ratio

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \qquad (4)$$

The value of A = 1, represents completely elastic isotropy, while values smaller or larger than 1 measures the degree of elastic anisotropy. From the table 3, it is seen that LiBeN and LiMgN are elastically anisotropic at ambient condition.

The Young's modulus (Y) and Lame constants ($\lambda$, $\mu$) are often measured for polycrystalline materials when investigating their hardness. Physically, the first Lame constant ($\lambda$) represents the compressibility of the material, while the second Lame constant ($\mu$) reflects its shear stiffness. These quantities are calculated using the following relations:

$$Y = \frac{9BG}{3B + G} \qquad (5)$$

$$\lambda = \frac{\nu E}{(1 + \nu)(1 - 2\nu)} \qquad (6)$$

$$\mu = \frac{E}{2(1 + \nu)} \qquad (7)$$

Bulk modulus ($B_0$) and shear modulus (G) can measure the resistance of a material to volume and shape change respectively. The results in Table. 2, indicate that these alloys have seemed to be 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. From Table.3, it is seen that $\alpha$ – phase of LiBeN and $\beta$- phase of LiMgN are stiffer than the other considerd phases. Poisson's ratio is associated with the volume change during uniaxial deformation, which is expressed as

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \qquad (8)$$

During elastic deformation no volume change occurs, If $\nu = 0.5$, the material is incompressible. The low $\nu$ value means that a large volume change is associated with its deformation. In addition, Poisson's ratio provides more information about the characteristics of the bonding forces than any of the other elastic constants. Among these alloys, the Poisson's ratio of $\alpha$ – LiXN is lower than $\gamma$ – LiXN (X = Be, Mg). The ratio of bulk modulus to shear modulus is used to estimate the brittle or ductile behaviour of materials. A high B/G value is associated with ductility, while a low B/G value corresponds to brittle nature. The critical value which separates ductile and brittle materials is about 1.75. From Table 3, it is found that $\alpha$ – LiXN (X = Be, Mg) are brittle. Moreover, for covalent and ionic materials the typical relations between bulk and shear moduli are $G \approx 1.1B$ and $G \approx 0.8B$, respectively [39]. Since the present values are near to 0.8, this result strongly supports the ionic contribution to inter atomic bonding.

The investigation of the stiffness can be completed by providing the microhardness parameter [40], given by the following relation:

$$H = \frac{1 - 2\nu}{6(1 + \nu)} \qquad (9)$$

The calculated H values are 27.06 Gpa, 21.35 Gpa, 2.15 Gpa for $\alpha - LiMgN$, $\beta - LiMgN$ and $\gamma - LiMgN$ and 17 Gpa, 0.83 Gpa and 0.62 Gpa for $\alpha - LiBeN$, $\beta - LiBeN$ and $\gamma - LiBeN$. This indicates that both LiMgN and LiBeN are hard materials at ambient condition.

## 4 CONCLUSION

In conclusion, first principles calculations have been performed using Vienna ab-initio simulation package to investigate the electronic and mechanical properties of LiXN (X = Be, Mg) with possible structures. The calculated ground state properties are in good agreement with the available results. Our results suggest that $\alpha$-phase is the most stable phase at ambient condition. Electronic structure reveals that these materials exhibit semiconducting behavior. The calculated elastic constants obey the necessary mechanical stability condition suggesting that these alloys are mechanically stable at ambient condition

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