This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Stabilities and defect-mediated lithium-ion conduction in a ground state cubic Li$_3$N structure

Manh Cuong Nguyen,*$^1$ Khang Hoang,$^2$ Cai-Zhuang Wang,$^1$ and Kai-Ming Ho$^1$

$^1$Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA

$^2$Center for Computationally Assisted Science and Technology, North Dakota State University, Fargo, ND 58108, USA

Abstract

A stable ground state structure with cubic symmetry of Li$_3$N (c-Li$_3$N) is found by ab initio initially symmetric random-generated crystal structure search method. Gibbs free energy, calculated within quasi-harmonic approximation, shows that c-Li$_3$N is the ground state structure for a wide range of temperature. The c-Li$_3$N structure has a negative thermal expansion coefficient at temperatures lower than room temperature, due mainly to two transverse acoustic phonon modes. This c-Li$_3$N phase is a semiconductor with an indirect band gap of 1.90 eV within hybrid density functional calculation. We also investigate the migration and energetics of native point defects in c-Li$_3$N, including lithium and nitrogen vacancies, interstitials, and anti-site defects. Lithium interstitials are found to have a very low migration barrier (~0.12 eV) and the lowest formation energy among all possible defects. The ionic conduction in c-Li$_3$N is thus expected to occur via an interstitial mechanism, in contrast to that in the well-known α-Li$_3$N phase which occurs via a vacancy mechanism.
I. Introduction

Li$_3$N is known for being one of the highest ionic conducting materials.$^1$ The compound receives much attention due to its possible use as a Li-ion battery solid electrolyte, although the decomposition potential is too low for practical applications. Lithium vacancies in the Li$_2$N layer are responsible for the ionic conduction in the material.$^{1-3}$ Li$_3$N is considered as a promising material for hydrogen storage as well.$^4,5$ The compound is also known to be one of the most ionic nitrides as having nitrogen existing in N$^{3–}$ state.$^6,7$

Li$_3$N is well characterized in experiment as possessing a hexagonal structure with layers of Li$_2$N intercalated by Li,$^8,9$ namely P6/mmm $\alpha$-Li$_3$N. Several theoretical studies have been carried out to investigate the electronic, defect, and transport properties of $\alpha$-Li$_3$N.$^2,3,7$ Recent works show that $\alpha$-Li$_3$N possesses imaginary phonon mode associated to the vibration along the c-axis of Li ion in the Li$_2$N plane.$^3,7$ This imaginary phonon mode would transform the $\alpha$-Li$_3$N structure to the so-called P-3m1 $\alpha'$-Li$_3$N structure. This transformation gains a very small energy for $\alpha'$-Li$_3$N, −0.3 meV/atom in our calculation or −0.2 meV/atom in previous calculation.$^3$ The only difference of $\alpha'$-Li$_3$N from $\alpha$-Li$_3$N is that the Li ions in the Li$_2$N plane move out of the plane. The simulated x-ray diffraction patterns of $\alpha$-Li$_3$N and $\alpha'$-Li$_3$N are almost identical and a question on the identification of Li$_3$N structure in experiment might be raised.$^3$ Shen et. al.$^{10}$ very recently performed a systematic search for ambient and high pressure stable phases of Li-N binary by ab initio evolutionary algorithm. They found several new stable high pressure Li-N phases and presented a new high pressure phase diagram for Li-N system. At ambient condition, they found a cubic Li$_3$N structure having formation energy lower than those of $\alpha$-Li$_3$N and $\alpha'$-Li$_3$N structures.

In this work, we find the same low energy structure of Li$_3$N at ambient condition by random-generated crystal structure search method. Physical properties of the new Li$_3$N structure are intensively and comprehensively investigated. The Gibbs free energy of new Li$_3$N and $\alpha$-Li$_3$N structures is calculated by taking into account vibrational entropy and thermal expansion effect within quasi-harmonic approximation. It is interesting that the thermal expansion coefficient of new Li$_3$N is negative at low temperature. The defect and migration calculations show that the lithium interstitial is the dominant native defect and its migration barrier is small, suggesting that
new Li$_3$N could be a candidate for Li-ion conducting materials with interstitial mediated mechanism. The electronic, elastic and mechanical properties of new Li$_3$N are also investigated.

II. Computational methods

The first-principles density functional theory (DFT) calculations are performed using Vienna *Ab Initio* Simulation Package (VASP) with projector-augmented wave (PAW) pseudopotential method within the generalized-gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE). The energy cutoff is 550 eV and the Monkhorst-Pack’s scheme is used for Brillouin zone sampling. A high-quality k-point grid of $2\pi \times 0.025$ Å$^{-1}$, equivalent to a k-point mesh of $10 \times 10 \times 10$ for the below proposed structure, is used in all calculations. A twice denser k-point mesh is used for accurate density of states calculation. All structures are fully relaxed until the forces acting on each atom smaller than 0.01 eV/Å and pressure smaller than 1 kbar. The phonon frequencies are calculated by finite displacement method, as implemented in the Phonopy code, with forces calculated by VASP. The elastic constants are calculated using strain-stress relationship. The band gap is also calculated with the hybrid functional parameterized by Heyd, Scuseria and Ernzerhof (HSE06). The HSE06 functional has the standard mixing coefficient of 0.25 for the Hartree-Fock exchange energy in the exchange-correlation functional. The crystal structures for the HSE06 calculations are from GGA-PBE calculation. A half dense k-point mesh is used for hybrid functional calculations.

The references for formation energy and free energy calculations are the body-centered cubic Li metal and an N$_2$ molecule at 0 K. The dielectric constant is calculated by density functional perturbation theory. A $3 \times 3 \times 3$ supercell and a $4 \times 4 \times 4$ k-point mesh are used in defect calculations for the below proposed structure of Li$_3$N. In these defect calculations, the atomic coordinates of defected structures are relaxed while the lattice parameters are kept fixed at the calculated bulk values. The defect formation energy is defined as:

\[
E_f (X^q) = E_{tot} (X^q) - E_{tot} (bulk) - \sum_i n_i \mu_i + q(E_v + \mu_e) + \Delta^q,
\]

where $E_{tot}(X^q)$ is the total energy of a supercell containing a defect X in charge state $q$; $E_{tot}(bulk)$ is the total energy of a supercell of the perfect bulk material; $\mu_i$ is the atomic chemical potential of species $i$ (with reference to the bulk Li metal and N$_2$ molecule at 0 K) and $n_i$ is the number of
atom of species $i$ that have been added ($n_i > 0$) or removed ($n_i < 0$) from the supercell of perfect bulk structure to form the defect; $\mu_e$ is the electron chemical potential, i.e., the Fermi level, referenced to the valence-band maximum in the bulk ($E_v$); $\Delta^q$ is the correction term to align the electrostatic potentials of the bulk and defect supercells and to account for the finite cell size effect on the total energy of charged defects. The atomic chemical potentials $\mu_i$ are subject to thermodynamic constraints, such as the condition for the stability of Li$_3$N:

$$3\mu_{Li} + \mu_N = \Delta H_f (\text{Li}_3\text{N}),$$

where $\Delta H_f (\text{Li}_3\text{N})$ is the formation energy of Li$_3$N; $\mu_{Li} = 0$ ($\mu_N = 0$) corresponds to extreme Li-rich (N-rich) conditions. $\Delta^q$ is estimated using the Freysoldt scheme,\textsuperscript{23,24} which requires the value of the static dielectric constant. Our DFT calculation shows that the total static dielectric constant of the cubic Li$_3$N structure described below is $\varepsilon_0 = 6.76$. For comparison, the total static dielectric constant of $\alpha$-Li$_3$N is calculated to be 13.05 (6.96) for $\varepsilon_0^\perp$ ($\varepsilon_0^\parallel$) component. The values for $\alpha$-Li$_3$N are slightly above the upper limit or within the range for $\varepsilon_0^\perp$ and $\varepsilon_0^\parallel$ measured in experiment, which are 10.5 ± 1.5 and 6.0 ± 2.0, respectively.\textsuperscript{25} The electronic contribution to the static dielectric constant of $\alpha$-Li$_3$N is 6.05 (5.63) for $\varepsilon_\infty^\perp$ ($\varepsilon_\infty^\parallel$) in our calculation, in agreement with previous calculation.\textsuperscript{3}

III. Results and discussion

A. Structural properties

For each unit cell size with 2, 3, 4, 6 and 8 formula units (f.u.) of Li$_3$N, 400 symmetrized structures are generated randomly. Once a space group is randomly selected from 230 available space groups, the lattice parameters in consistent with the chosen symmetry are generated and atoms are placed symmetrically within the unit cell by Wyckoff positions. The generated structures are then fully relaxed to local minima by DFT calculations. Through this random search, we find all the literature known structures of Li$_3$N. They include the known ground state $\alpha$-Li$_3$N structure, recently proposed more stable $\alpha'$-Li$_3$N structure and high pressure structures such as P6$_3$/mmc $\beta$-Li$_3$N and Fm-3m $\gamma$-Li$_3$N. In addition, we find a Pm-3m cubic structure, hereafter called c-Li$_3$N, with formation energy lower than all known structures at ambient
condition. The c-Li$_3$N phase has a formation energy of $-1.621$ eV/f.u., which is 26 or 25 meV/f.u. lower than that of $\alpha$- or $\alpha'$-Li$_3$N, respectively. In our DFT calculation, the formation energy of $\alpha$-Li$_3$N is $-1.595$ eV/f.u., in agreement with previous calculations$^2$ and slightly smaller than the experimental value.$^{26}$ The c-Li$_3$N is the same with new Li$_3$N structure reported recently by Shen et. al.$^{10}$

Figure 1. Crystal structures of (a) c-Li$_3$N and (b) $\alpha$-Li$_3$N with large (green) balls representing Li atoms and small (grey) balls representing N atoms.

We list in Table I the lattice parameters of c-Li$_3$N as well as those of $\alpha$-Li$_3$N and $\alpha'$-Li$_3$N. The calculated values for $\alpha$-Li$_3$N and $\alpha'$-Li$_3$N are in agreement (within 1%) with those from other calculations and experiments.$^{2,3,7,8}$ The c-Li$_3$N structure possesses the Pm-3m symmetry with Li

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Li(1)-N / Li(2)-N (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Li$_3$N</td>
<td>3.874</td>
<td>1.937</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Li$_3$N</td>
<td>3.634</td>
<td>3.869</td>
<td>1.934 / 2.098</td>
</tr>
<tr>
<td>This work</td>
<td>3.640</td>
<td>3.871</td>
<td>1.936 / 2.102</td>
</tr>
<tr>
<td>Ref. 3</td>
<td>3.640</td>
<td>3.871</td>
<td>1.936 / 2.102</td>
</tr>
<tr>
<td>Experimental$^a$</td>
<td>3.648</td>
<td>3.875</td>
<td>1.938 / 2.106</td>
</tr>
<tr>
<td>$\alpha'$-Li$_3$N</td>
<td>3.629</td>
<td>3.871</td>
<td>1.936 / 2.101</td>
</tr>
<tr>
<td>This work</td>
<td>3.635</td>
<td>3.871</td>
<td>1.936 / 2.102</td>
</tr>
<tr>
<td>Ref. 3</td>
<td>3.635</td>
<td>3.871</td>
<td>1.936 / 2.102</td>
</tr>
</tbody>
</table>

$^a$Reference [8].
occupying the 3d Wyckoff position and N occupying the 1a Wyckoff position. Figure 1 shows
the crystal structures of c-Li$_3$N and α-Li$_3$N. In α-Li$_3$N, Li(1) and Li(2) ions have coordination
numbers of 2 and 8, respectively, and N ions are coordinated by 8 Li ions; in c-Li$_3$N, on the other
hand, all Li ions are coordinated by 2 N ions and N ions are coordinated by 6 Li ions. This lower
coordination of both Li and N ions is responsible for an interesting fact that the volume per atom
of c-Li$_3$N is much larger (~30%) than that of α-Li$_3$N. They are 14.54 and 11.06 Å$^3$/atom for c-
Li$_3$N and α-Li$_3$N, respectively. If a negative pressure can be applied on Li$_3$N, the stability of c-
Li$_3$N would be enhanced significantly by the advance of PV term contribution to formation
enthalpy $H = E + PV$, where E is the internal energy, P is pressure and V is volume. In the other
words, this c-Li$_3$N would be synthesized easier with experimental techniques which can employ
negative pressure.

**B. Thermodynamic, dynamic and mechanical stabilities**

We calculate the phonon spectrum of c-Li$_3$N to investigate its dynamical stability. Figure 2
shows the phonon spectra of c-Li$_3$N and α-Li$_3$N along the high symmetry points of the c-Li$_3$N
and α-Li$_3$N Brillouin zones. The α-Li$_3$N structure shows a negative phonon frequency around the
Γ point, which is consistent with previous calculations and implies a dynamical instability of α-
Li$_3$N as pointed out in previous works.$^{3,7}$ In contrast, c-Li$_3$N does not possess any negative phonon frequency, indicating that this structure is dynamically stable. This result is consistent
with previous work.$^{10}$

![Phonon spectra of (a) c-Li$_3$N and (b) α-Li$_3$N structures.](image)

Table II shows the calculated elastic constants and moduli of c-Li$_3$N. The elastic constants are
calculated based on strain-stress relationships and the bulk, shear and Young moduli are
calculated from elastic constants using the Voigt-Reuss-Hill approximation.\(^{27}\) We find that the elastic constants of c-Li\(_3\)N satisfy the following Born stability criteria\(^{28}\):

\[
C_{11} - C_{12} > 0, \quad C_{11} + 2C_{12} > 0, \quad C_{44} > 0.
\]

The c-Li\(_3\)N structure is thus mechanically as well as dynamically stable. We note that in our calculations the elastic constants of both α- and α’-Li\(_3\)N satisfy the corresponding Born stability criteria for the hexagonal crystal.

Table II. The elastic constants (C\(_{ij}\)), bulk (B), shear (G) and Young (Y) moduli in the unit of GPa for c-Li\(_3\)N structure.

<table>
<thead>
<tr>
<th>C(_{11})</th>
<th>C(_{12})</th>
<th>C(_{33})</th>
<th>C(_{44})</th>
<th>B</th>
<th>G</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>112.4</td>
<td>5.6</td>
<td>112.4</td>
<td>13.7</td>
<td>41.2</td>
<td>24.5</td>
<td>61.3</td>
</tr>
</tbody>
</table>

We also perform Gibbs free energy calculation for c-Li\(_3\)N and α’-Li\(_3\)N within the quasi-harmonic approximation to investigate the change of structures and their relative stabilities with temperature. Because α-Li\(_3\)N is not dynamically stable, at least in our calculations and those reported in the literature, we use α’-Li\(_3\)N in the Gibbs free energy calculation in the place of α-Li\(_3\)N. The α-Li\(_3\)N and α’-Li\(_3\)N structures are almost identical as mentioned above so we assume that the thermal properties of α-Li\(_3\)N and α’-Li\(_3\)N are very similar. Phonon frequencies of c-Li\(_3\)N and α’-Li\(_3\)N at different scaled volumes, from 96% to 112% of the equilibrium volume with 26 equally spacing sampling volume points, are calculated to get the Helmholtz free energies as a function of unit cell volume. The temperature effect is taken into account via vibrational (phonon) entropy. The Vinet equation of state then is used to fit the Helmholtz energy curve at each temperature. The Gibbs free energy is obtained from Helmholtz free energy by a Legendre transform. Figure 3(a) shows the calculated Gibbs free energies of c-Li\(_3\)N and α’-Li\(_3\)N. It is clear that c-Li\(_3\)N is always more stable than α’-Li\(_3\)N in the whole range of temperature under consideration, from 0 to 600 K. This result, together with the above discussed thermodynamic and dynamical stabilities, show that c-Li\(_3\)N is indeed the ground state structure of Li\(_3\)N in a wide range of temperature. However, all experiments up to now have observed α-Li\(_3\)N as the stable structure of Li\(_3\)N at ambient condition. There could be a kinetic barrier blocking the formation of c-Li\(_3\)N, making α-Li\(_3\)N more favorable within the experimental synthesis techniques having been
used so far to synthesize Li$_3$N. On the other hand, experiment showed that $\alpha$-Li$_3$N contains close to 3% of Li vacancy, mostly at the Li(2) site, at room temperature. Previous calculation also show that the formation energy of Li(2) vacancies is low. These observation and calculation results imply that off-stoichiometry could be another driving force in favor the formation of $\alpha$-Li$_3$N instead of c-Li$_3$N at ambient condition although c-Li$_3$N is more thermodynamically stable.

![Figure 3](image)

Figure 3. (a) Gibbs free energies and (b) thermal expansion coefficients of c-Li$_3$N and $\alpha'$-Li$_3$N structures as a function of temperature.

From the Helmholtz free energy calculations, we can extract the temperature dependences of the unit cell volumes of c-Li$_3$N and $\alpha'$-Li$_3$N and hence their thermal expansion coefficients as a function of temperature. For comparison, the thermal expansion coefficient of $\alpha$-Li$_3$N is $3.5 \times 10^{-5}$ K$_{-1}$ at 300 K as observed in experiment by fitting to refined lattice parameters from neutron diffractions at different temperatures. The thermal expansion coefficient of $\alpha'$-Li$_3$N in our calculation is $5.6 \times 10^{-5}$ K$_{-1}$. As mentioned above, $\alpha$-Li$_3$N has negative phonon frequencies therefore $\alpha'$-Li$_3$N is used for comparisons with experimental data. Although the comparison may not be direct, it shows that our calculations are reliable and the results are comparable with experimental observations. Figure 3(b) shows the thermal expansion coefficients of c-Li$_3$N and $\alpha'$-Li$_3$N as a function of temperature. Interestingly, c-Li$_3$N is found to have a negative thermal expansion coefficient at temperature lower than room temperature. The thermal expansion coefficient of $\alpha'$-Li$_3$N is always positive in the whole range of considered temperature. The negativity of thermal expansion coefficient of c-Li$_3$N implies that the newly identified structure could be used as a functional material for controllable thermal expansion composite to tailor the
expansion coefficient to a desired value for using in applications like high precise optical mirrors, fiber optic systems, electronics, low temperature sensing or even in dental fillings.\textsuperscript{30,31} Our mode Grüneisen parameter calculations for different phonon modes show that two transverse acoustic phonon modes have much more negative Grüneisen parameters than other phonon modes. The mode Grüneisen parameters of these two transverse acoustic phonon modes along the $q$-path from $\Gamma$ to $X$ points are negative and can be as low as $-41$. At low temperatures where only acoustic modes are excited, the negativity of mode Grüneisen parameters of these two acoustic modes is mainly responsible for the negative thermal expansion of c-Li$_3$N. The same phenomenon was found in the well-known negative thermal expansion material ZrW$_2$O$_8$, where the transverse vibrations of the Zr-O-W linkage between WO$_4$-tetrahedron and ZrO$_6$-octahedron are responsible for the negative thermal expansion.\textsuperscript{32-34} Huang et al recently generalized the origin of negative thermal expansion of water/ice to suggest that the negative thermal expansion of a material is resulting from the evolvement of the disparity of interactions such as the strong O-H bond and weak O:H non-bond in water/ice.\textsuperscript{34} In the c-Li$_3$N (ZrW$_2$O$_8$) system, the strong Li-N bonding within NLi$_6$-octahedron (W-O bonding within WO$_4$-tetrahedron and Zr-O bonding within ZrO$_6$-octahedron) and the rotational vibration of the octahedron (tetrahedron and octahedron) induced by the transverse vibration of the bridging Li (O) atom play very much the roles of strong O-H bond and weak O:H non-bond in the generalized model for negative thermal expansion.\textsuperscript{34}

Before considering the electronic properties, let us consider the bonding character of c-Li$_3$N. We perform Bader charge analysis\textsuperscript{35} for both $\alpha$-Li$_3$N and c-Li$_3$N. The charges associated with Li (N) ions are +0.83 $|e|$ ($-2.49 |e|$) in both $\alpha$-Li$_3$N and c-Li$_3$N, compared to the formal charges of +1 $|e|$ ($-3 |e|$), showing that the bonding in c-Li$_3$N is strongly ionic as in $\alpha$-Li$_3$N.\textsuperscript{6}

C. Electronic properties
Figure 4. Electronic (a) band structure and (b, c) projected density of states (states/eV/unit cell) of c-Li$_3$N. The zero of energy is set to the highest occupied state.

Figure 4 shows the electronic band structure along the lines connecting high symmetric $k$-points of the Brillouin zone and the projected density of states of c-Li$_3$N. The c-Li$_3$N structure is indirect semiconducting with the valence-band maximum (VBM) at the R point and the conduction-band minimum (CBM) at the Γ point. The band gap is 0.85 eV from our GGA calculation. However, it is well known that GGA underestimates the band gap of semiconductors and insulators. So we perform HSE06 hybrid functional calculation\textsuperscript{16} for c-Li$_3$N structure obtained from GGA calculation to get a better description of the energy band gap. Our HSE06 calculation shows that the band gap of c-Li$_3$N is 1.90 eV. For comparison, the HSE06 band gap of α-Li$_3$N is 2.07 eV in our calculation, in good agreement with the experimental value of 2.18 eV.\textsuperscript{36} As can be seen in Fig. 4, the N 2$s$ band lies very deep below the Fermi level, which is similar to the N 2$s$ band in α-Li$_3$N.\textsuperscript{2} There is a small hybridization between Li 1$s$ and 2$s$ orbitals with N 2$s$ orbitals at this energy level. The contribution of N to the occupied states near the VBM is almost solely from the N 2$p$ orbitals. The contribution from Li 2$s$ orbital to occupied states near the VBM is small in comparison to that from N 2$p$ orbitals. The unoccupied states near CBM are mainly from N 2$p$ orbital. These results are consistent with previous work.\textsuperscript{10}

D. Defects and Lithium-ion conduction
The Li vacancy at the Li(2) position is identified responsible for the charge carriers in high ionic conducting $\alpha$-Li$_3$N. Previous defect calculations also show that lithium vacancies at the Li(2) site in $\alpha$-Li$_3$N have the lowest formation energy under N-rich condition. In the present work, we calculate the formation energies of native defects in the newly identified c-Li$_3$N structure. Figure 5 shows the calculated formation energies of lithium and nitrogen vacancies ($V_{Li}$ and $V_{N}$), interstitials (Li$_i$ and N$_i$), and anti-site defects (Li$_N$ and N$_Li$) in different charge states. We find that the positively charged lithium interstitial Li$_i^+$ is the defect with the lowest formation energy in the entire range of the Fermi-level values, under both the Li-rich and N-rich conditions, indicating that it is the dominant native defect in c-Li$_3$N. This interstitial is most stable at a position 0.49 Å off the center and on the diagonal line of a cubic unit cell surface, which has local environment quite similar to that of Li(2) in $\alpha$-Li$_3$N [see Fig. 1(b)]. Since Li$_i^+$ has a low formation energy and hence can occur with a high concentration, more lithium can be incorporated into c-Li$_3$N, making it a high-capacity lithium storage medium. Besides, given that Li$_i^+$ is a shallow donor, see Fig. 5, this defect can lead to n-type conductivity. The positively charged nitrogen vacancy $V_{N}^+$ also has a low formation energy under the extreme Li-rich condition. The formation energy of $V_{Li}^0$ is about 2.3 eV under the extreme N-rich condition, comparable to that of the lithium vacancy at the Li(1) site in $\alpha$-Li$_3$N reported by Wu et al.
Finally, we find a metastable structure for the lithium Frenkel pair, \((\text{Li}_i^+, V_{\text{Li}}^-)\), that has a formation energy of 1.64 eV and a binding energy of 1.39 eV; the distance between the two components of the pair is 2.09 Å.

![Diagram of migration path and barrier for Li$_i^+$](image)

Figure 6. Migration path and barrier for Li$_i^+$. Red to black balls represent the Li$_i^+$ along the migration path.

Lithium migration in c-Li$_3$N is investigated using the climbing-image nudged elastic-band method (NEB).$^{37}$ The NEB calculations are performed with a same 3×3×3 supercell with that of defect calculations. Figure 6 shows a schematic picture of the migration path (within a single unit cell only) and the calculated migration barrier of Li$_i^+$. The migration barrier is about 0.12 eV for Li$_i^+$. For comparison, the migration barrier of $V_{\text{Li}}^-$ is calculated to be 0.46 eV. Given the much lower formation energy and migration barrier associated with Li$_i^+$, it is expected that the ionic conduction in c-Li$_3$N proceeds via the interstitial mechanism. This is in contrast to α-Li$_3$N where ionic conduction occurs through a vacancy mechanism.$^1$

IV. Conclusions

In summary, we have identified a cubic ground state structure of Li$_3$N, namely c-Li$_3$N. The Gibbs free energy of c-Li$_3$N is always lower than that of α’-Li$_3$N in the considered temperature range from 0 to 600 K. The c-Li$_3$N structure is also dynamically and mechanically stable against thermal vibration and mechanical distortion. Its thermal expansion coefficient is negative at low temperatures and the negativity of mode Grüneisen parameters of two transverse acoustic modes is mainly responsible for this negative thermal expansion. The cubic phase is semiconducting
with an indirect energy band gap of 1.90 eV. Amongst possible native defects, the lithium interstitial is dominant in c-Li$_3$N and its migration barrier is small, implying that the ionic conduction in c-Li$_3$N is interstitial mediated.

Acknowledgements

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division, including computing time at the National Energy Research Scientific Computing Center (NERSC). The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358. K. H. was supported by the U.S. Department of Energy Grant No. DE-SC0001717.

*Email: mcnguyen@ameslab.gov

References
