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<td>Author(s)</td>
<td>Wu, Shunnian; Dong, Zhili; Boey, Freddy Yin Chiang; Wu, Ping</td>
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Electronic structure and vacancy formation of Li$_3$N

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The electronic structure and vacancy formation of Li$_3$N were studied using first principles methods. We found Li$_3$N exhibits strong ionic character with slight covalent bonding between N and Li. The Li vacancy formation energy decreases with an increase in nitrogen partial pressure, while the N vacancy formation energy increases with increasing nitrogen partial pressure. The Li(2) site vacancy is found to have the lowest formation energy under nitrogen-rich conditions. Formation of V$_{Li}$$_{(2)}^−$ brings about delocalization of valence electrons, and reduces the band gap by 0.2 eV. These results suggest potential ways to enhance vacancy concentration in Li$_3$N for higher ionic conductivity.

Li$_3$N has an exceptionally large Li ionic conductivity due to intrinsic defects and the resulting hopping of Li ions from occupied Li sites into unoccupied ones.$^1$ The nature of the defect plays a critical role in the understanding and application of the material for hydrogen storage and lithium batteries. Li$_3$N can be described as a sequence of Li(1) and Li(2)N layers perpendicular to c in space group P6/mmm (Fig. 1). Early x-ray diffraction and powder neutron diffraction studies reported 1~2% vacancies in Li(2) position at room temperature.$^{1,2}$ The vacancy concentration can go up to 4% at high temperature. Conversely, recent powder neutron diffraction analysis found no Li vacancies in the temperature range of 20–673 K.$^{3}$ This contradiction is attributed to different crystal growing procedures. Clearly, a fundamental understanding of the nature of the vacancy and the impact of Li$_3$N growth environment is necessary to optimize crystal growth conditions for high concentration of vacancy in Li$_3$N.

Although the electronic properties of Li$_3$N have been studied extensively,$^{4,7}$ research on its defect properties is limited. A lattice energy program simulation showed that an interstitial defect cannot form in the structure.$^6$ The energetically favorable vacancy comes from Li(2) removal. Sarnthein et al.$^7$ asserted that Li(2) vacancy must be formed in a charged state based on the band structure. An uncharged Li(2) vacancy would bring about a hole in the valence band and result in an energetically very unfavorable N$^{2−}$ ion. There is, to date, a paucity of data for quantitative comparison of the formation energy of various vacancies. In addition, the effect and role of the crystal growth environment are not established. Therefore, we investigate the formation energies of all major intrinsic vacancies in Li$_3$N under different atmospheric conditions using first-principles calculations. We also attempt to establish the relationship between the fabrication conditions and vacancy formation mechanism.

First-principles calculations were performed using density functional theory and the projector augmented wave method as implemented in VASP.$^{10–12}$

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FIG. 1. Crystal structure of Li$_3$N.
ence potential in the defect supercell with that in the defect-free supercell.\textsuperscript{16,17}

The chemical potential $\mu_i$ depends on crystal growth conditions such as the nitrogen partial pressure. The valid range of $N_2$ partial pressure $P_{N_2}$ is determined by Li$_3$N formation enthalpy $\Delta H_{f}^{Li_3N}$ as

\[
\frac{\Delta H_{f}^{Li_3N}}{kT} \leq \ln P_{N_2} \leq 0 \quad \text{with} \quad \Delta H_{f}^{Li_3N} = 3(\mu_{Li} - \mu_{N}^o) + (\mu_{Li} - \mu_{N}^o),
\]

where $\mu_{Li}$ and $\mu_{N}$ are the chemical potential of Li and N in Li$_3$N, respectively; $\mu_{Li}$ and $\mu_{N}^o$ are the energy of metallic Li and gaseous N$_2$ (per nitrogen atom) in the standard state; $k$ is the Boltzmann constant; and $T$ is the temperature. The Li$_3$N formation enthalpy is calculated to be $-1.59$ eV per Li$_3$N, which is within the typical GGA errors from experimental value of $-1.73$ eV per Li$_3$N.\textsuperscript{18}

The calculated electronic band structure and density of states (DOS) of the defect-free Li$_3$N are shown in Fig. 2. The VBM and conduction band minimum (CBM) are located at A and $\Gamma$, separately, giving an indirect gap consistent with previous experimental and theoretical reports.\textsuperscript{4,6,9} The calculated band gap is 1.1 eV, which is underestimate by 1.1 eV as compared with the measured value.\textsuperscript{19} The band around $-11.5$ eV is dominated by N 2s state with a Li 2s and 2p admixture. The conduction bands are mainly composed of Li 2s and 2p states and the occupied valence bands originate from N 2s and 2p states. The partial overlapping of Li 2s state with N 2p state in the valence band region suggests possible Li(1)–N and Li(2)–N s–p covalent bonds. The different characteristics of $p_x$, $p_y$, and $p_z$ states of N atom indicate the anisotropy of the structure. Employing Bader’s “atoms in molecules” scheme,\textsuperscript{20} we obtained nominal valences of N$^{2-}$, Li(1)$^{+0.82}$, and Li(2)$^{+0.81}$. This further suggests covalent bonding between Li and N. This is consistent with the real-space multiple-scattering (RSFMS) calculations by Fister et al.\textsuperscript{7}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2}
\caption{(Color online) Calculated electronic band structure (a) and DOS for defect-free Li$_3$N (b). The local partial DOS components in (b) are: $s$ black, $p_x$ red, $p_y$ blue, and $p_z$ green. The Fermi level is set to zero energy.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3}
\caption{(Color online) Vacancy formation energies as a function of the Fermi level $e_F$ at nitrogen-rich condition. The inset is a zoomed view of the highlighted rectangle area. The zero energy of $e_F$ corresponds to the valence-band maximum.}
\end{figure}

The formation energies of all major intrinsic vacancies in Li(1), Li(2), and N sites calculated with Eq. (1) are shown in Fig. 3 as a function of Fermi level at N-rich condition (i.e., $\mu_N^o=\mu_{N}^o$). The Li(2) site vacancies are located in N-containing layers, while the Li(1) site vacancies lie in the layers between these N-containing layers (Fig. 1). Li(2) site vacancy shows the lowest formation energy, which is consistent with experimental observations.\textsuperscript{2,3} The negative $V_{Li(2)}^-$ vacancy is the most abundant vacancy with the formation energy as low as $-1.5$ eV, indicating that thermal generation of vacancies is important even at low temperature in agreement with experimental report.\textsuperscript{1} The high concentration of Li(2) site vacancy is believed to contribute significantly to the unusually large ionic conductivity of Li$_3$N since it provides pathways for Li ion hopping. An increase in Li vacancy concentration corresponds to high Li ion mobility and thus high ionic conductivity.\textsuperscript{21} The vacancy formation energy in the Li(1) site is about 1.7 eV higher than that in the Li(2) site. Therefore, removal of the lithium between the Li$_2$N layers is a very energetically unfavorable process since the two nearly triply negative nitrogen ions would now be repelled by their own ionic charges and by the effective negative charge of $V_{Li(1)}^-$. The formation energy of neutral nitrogen vacancies is the highest. Even the most stable $V_{N}^{3+}$ vacancy among possible N vacancies has a formation energy that is about 1.0 eV higher than that of $V_{Li(2)}^-$. This indicates that the nitrogen vacancies rarely exist under N-rich conditions.

The vacancy formation energy as a function of nitrogen partial pressure is shown in Fig. 4 for two characteristic Fermi levels, VBM and CBM. Atmospheric nitrogen conditions determine the type and concentration of vacancies in Li$_3$N. When the Fermi energy is set at the VBM, $V_{N}^{3+}$ and $V_{Li(2)}^-$ may form. The difference in formation energy of $V_{N}^{2+}$ and $V_{N}^{3+}$ is only 0.01 eV, and consequently they have similar concentrations. The formation energy of N vacancies increases with an increase in nitrogen partial pressure, while the formation energy of Li vacancies decreases with an increase in nitrogen partial pressure.
Formation of charged vacancies in Li₃N brings about a significant change in band structure. $V_{\text{Li}(2)}$ vacancy splits the peak at about $-11$ eV into two peaks with separation of 0.3 eV. The accompanying highly splitted $p_x$, $p_y$, and $p_z$ states indicate valence electron delocalization, and thus enhance conductivity. The vacancy charge is unevenly distributed among all atoms with the neighboring N atoms allocated the largest portion. This brings about a decrease in the gap between VBM and CBM by $-0.2$ eV. Conversely, the formation of $V_{N}^{3+}$ in the structure expands the gap by 0.2 eV. The $p_z$ state exhibits moderate splitting, indicating valence electron delocalization in Li₂N layers. This increases the anisotropy of conductivity. The alternation of band structure with vacancy implicates additional controlling of Li₃N conductivity via vacancy selection.

In conclusion, first-principles calculations suggest that vacancies in Li(2) sites are responsible for the experimentally observed apparent nonstoichiometry of Li₃N. The vacancy formation energy at Li(2) sites decreases with an increase in nitrogen partial pressure. Since the vacancies in the Li(2) sites are responsible for the conductivity of Li₃N, nitrogen-rich condition is preferred for Li₃N fabrication process to attain high vacancy concentration and thus conductivity. Under extreme conditions, the dominant $V_{\text{Li}(2)}$ vacancy reaches formation energy as low as $-1.50$ eV. Such low formation energy suggests that thermal generation of vacancies plays an important role in controlling vacancy level and therefore conducive mechanism. Formation of $V_{\text{Li}(2)}$ brings about valence electron delocalization and thus enhances the ionic conductivity. These results enhance our understanding of the physics of intrinsic defects and potential measure to control the vacancy in Li₃N and its derivatives.

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References:


FIG. 4. Vacancy formation energies as a function of nitrogen partial pressure at two typical Fermi level VBM (a) and CBM (b).