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Novel lithium-nitrogen compounds at ambient and high pressures

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Using ab initio evolutionary simulations, we predict the existence of five novel stable Li-N compounds at pressures from 0 to 100 GPa (Li_{13}N , Li_5N , Li_3N_2 , LiN_2 , and LiN_5). Structures of these compounds contain isolated N atoms, N_2 dimers, polyacetylene-like N chains and N_5 rings, respectively. The structure of Li_{13}N consists of Li atoms and Li_{12}N icosahedra (with N atom in the center of the Li_{12} icosahedron) – such icosahedra are not described by Wade-Jemmis electron counting rules and are unique. Electronic structure of Li-N compounds is found to dramatically depend on composition and pressure, making this system ideal for studying metal-insulator transitions. For example, the sequence of lowest-enthalpy structures of LiN_3 shows peculiar electronic structure changes with increasing pressure: metal-insulator-metal-insulator. This work also resolves the previous controversies of theory and experiment on Li_2N_2 .

Li-N system contains two well-known compounds: lithium nitride (Li_3N) and lithium azide (LiN_3). Li_3N has potential use as an electrolyte in Li-batteries and a hydrogen storage medium^{1–4}. Extensive experimental and theoretical investigations show that Li_3N undergoes a sequence of phase transitions with increasing pressure. At ambient conditions, X-ray diffraction identified in Li_3N a mixture of two phases: α - Li_3N (P6/mmm) and metastable β - Li_3N (P6₃/mmc); at about 0.5 GPa, α - Li_3N fully transforms to β - Li_3N ; a new phase γ - Li_3N (Fm $\bar{3}$ m) occurs near 40 GPa^{5,6}. Normal ionic materials usually become metallic with increasing pressure, but Li_3N is abnormal since the increasing pressure makes it into a much more strongly ionic state⁷. LiN_3 has been widely used in industry as a nitrogen source, initial explosives and photographic materials⁸. Before 2013, LiN_3 was known in a single phase C2/m, and seemed so simple and well understood. However, several other phases of LiN_3 have been found using evolutionary crystal structure prediction methods coupled with first-principles calculations two years ago. At above 36 GPa, a hexagonal phase (P6/m) of LiN_3 with pseudo-benzene N_6 ring has been predicted by two research groups independently^{9,10}. Some other phases appear as metastable: $\text{P}\bar{1}$ with a polyacetylene-like infinite linear nitrogen chain structure; C2/m and $\text{P}\bar{1}$ with puckered extended 2D decagonal and quasi-2D hexagonal nitrogen layers, respectively¹⁰. Above 375 GPa, Wang *et al.* identified the phase of P2_1 which consists of zigzag N polymeric chains with N_5 ring sharing N-N pairs¹¹. The band structures indicate that there are two metal-insulator transitions in LiN_3 : first from insulator to metal at 36 GPa, and then from metal back to insulator at 375 GPa. Adding the new phases found in this work (see below), the sequence becomes metal-insulator-metal-insulator.

Besides nitrides (with N^{3-} anion) and azides ($[\text{N}_3]^-$), in 2001, Knip *et al.* proved the existence of diazenides $[\text{N}_2]^{2-}$ by synthesizing SrN_2 and BaN_2 under high N_2 pressure^{12,13}. Since then, discovery of new diazenides has been of constant interest. In 2010, alkali diazenides Na_2N_2 and Li_2N_2 (Pmmm) were predicted¹⁴, but then, a different structure of Li_2N_2 (Immm) was obtained under HP/HT conditions

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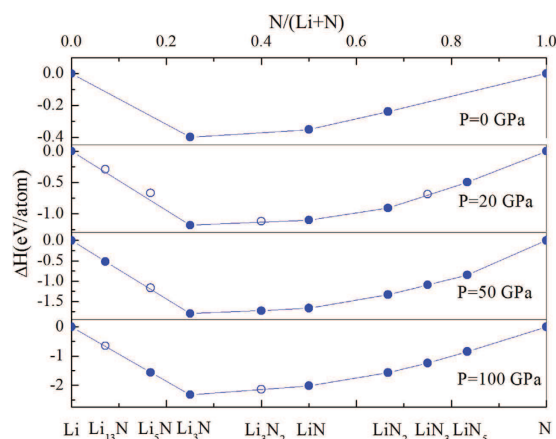


Figure 1. Convex hull diagrams for the Li-N system (showing enthalpies of formation (ΔH) of the compounds from ground-state Li and N) at 0, 20, 50, and 100 GPa.

(9 GPa, 750 K) by decomposition of LiN_3 ¹⁵. This discrepancy encourages us to study Li_2N_2 under high pressure in detail.

Nitrogen can form many anionic species, e.g. $[\text{N}_2]^-$, $[\text{N}_2]^{3-}$ and $[\text{N}_5]^-$, which have just been obtained in molecular complexes^{16–19}. We wonder if solid-state compounds with these anions in Li-N system could be synthesized under high pressure. Evolutionary algorithm USPEX has been widely used to predict new ground state structures in various systems without any experimental information, such as B-H, Xe-O, and Na-Cl^{20–22}. The predicted counterintuitive compounds NaCl_3 and Na_3Cl in the Na-Cl system have been confirmed by experiment²². In this work, we have performed extensive structure searches on the Li-N system using variable-composition evolutionary algorithm USPEX, and indeed found many new stable compounds with very diverse and unusual crystal structures.

Results and Discussion

We first studied the phase stability in the Li-N system by calculating the enthalpy of formation (ΔH) of Li-N compounds in the pressure range from 0 to 100 GPa. Stability of compounds is explored by the thermodynamic convex hull construction. If the enthalpy of decomposition of a compound into any other compounds is positive, then the compound is stable, which is depicted on the convex hull. The convex hulls are shown in Fig. 1 at selected pressures: 0, 20, 50, and 100 GPa. The various known phases of solid Li, N_2 , Li_3N , LiN_3 , and Li_2N_2 are reproduced readily in our evolutionary structure searches. Interestingly, five previously unreported compositions of Li-N system: Li_{13}N , Li_5N , Li_3N_2 , LiN_2 , and LiN_5 are found to be on the convex hull under ambient or high pressure in our calculations. The calculated phonon spectra confirmed that all predicted structures are dynamically stable. In total, we have found three new N-rich compounds and two new Li-rich compounds.

Simultaneously with our work (in fact, with submission date after our paper appeared on arxiv.org) Peng *et al.*²³ investigated the Li-N system and found two new stable compounds, LiN_2 and LiN_5 . However, the phase diagram of the Li-N system published by Peng *et al.*²³ missed a number of stable compounds (Li_{13}N , Li_5N , Li_3N_2). The enthalpies of reported phases in ref. 23 are recalculated and compared with our results. Detailed comparisons are shown in Figures S2 and S3 of the Supporting Information. Hence this paper presents a more complete and reliable picture, correcting omissions and presenting more stable crystal structures than those presented before.

We find that: (i) At ambient conditions (0 GPa), besides Li_3N and Li_2N_2 , LiN_2 with space group $\text{P6}_3/\text{mmc}$ is surprisingly stable. These three compositions are always stable in the pressure range from 0 to 100 GPa. (ii) However, the long-known LiN_3 is metastable below 49 GPa, which is in agreement with the known fact that it decomposes into N_2 and Li under external influences (heat, irradiation, etc) at 0 GPa. (iii) At 20 GPa, LiN_5 becomes stable, meanwhile Li_{13}N , Li_3N_2 and LiN_3 lie very close to (or nearly on) the convex hull. At 50 GPa, Li_{13}N , Li_3N_2 and LiN_3 are all stable, and Li_5N lies very close to the convex hull. At 100 GPa, Li_5N is stable, however, Li_{13}N and Li_3N_2 are becoming metastable although they both lie nearly on the convex hull.

The pressure-composition phase diagram of the Li-N system is depicted in Fig. 2. For pure Li, with increasing pressure, the bcc phase ($\text{Im}\bar{3}\text{m}$) transforms into fcc ($\text{Fm}\bar{3}\text{m}$), cI16 ($\text{I}\bar{4}3\text{d}$), Aba2–40, and Pbca phases in sequence, which is in accordance with previous experimental and theoretical data^{24–26}. For pure N, the known $\text{Pa}\bar{3}$, $\text{P2}_1/\text{c}$, P4_12_12 , and I2_13 structures are reproduced in our searches and agree well with other theoretical predictions^{27,28}.

For Li_3N there is a peculiar situation: the experimentally known at ambient conditions $\text{P6}/\text{mmm}$ structure is predicted to be stable only at pressures above 0.2 GPa – at lower pressures, at the GGA level

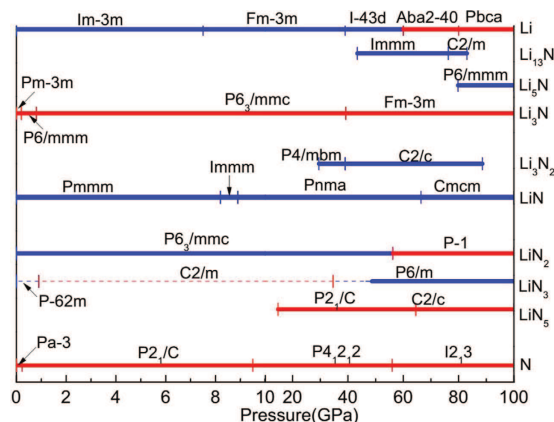


Figure 2. Pressure-composition phase diagram of the Li-N system from 0 to 100 GPa. The stable phases are shown in bold lines and the metastable phases of LiN_3 are depicted in thin dash lines. Blue and red colors represent the metallic and insulating phases, respectively.

of theory, the $\text{Pm}\bar{3}\text{m}$ structure is more stable (at 0 GPa, by 22 meV/formula unit). This small upward shift of phase transition pressures is typical of the GGA, but one wonders whether $\text{Pm}\bar{3}\text{m}$ structure could be stabilized by impurities, temperature etc. The subsequent phases of Li_3N in our calculations are all in agreement with the previous works^{5–7}.

LiN_3 is a thermodynamically stable compound (on the convex hull) only above 49 GPa, but it is well known also at ambient conditions as a metastable material. We found $\text{P}\bar{6}2\text{m}$ to have the lowest enthalpy in the pressure range 0–0.9 GPa, followed by $\text{C}2/\text{m}$ and $\text{P}6/\text{m}$ phases on increasing pressure. $\text{C}2/\text{m}$ is the phase known experimentally at ambient conditions.

For LiN (actually Li_2N_2), the obtained structure at 0 GPa is Pmmm , which is consistent with the previous theoretical result¹⁴. At 8.2 GPa, Pmmm phase of LiN transforms into the Immm structure, indicating that the experimental result obtained at around 9 GPa is also perfectly correct¹⁵. At 8.9 GPa, the Immm structure will lose its stability and the Pnma phase becomes stable in the pressure range from 8.9 to 66.4 GPa. Then the Cmcm phase is stable up to 100 GPa.

Phase transformations of five new compositions of Li-N system are as follows: (i) For Li_{13}N , the Immm structure is predicted to be stable from 43 to 76 GPa, following which the $\text{C}2/\text{m}$ structure is stable up to 83 GPa. In fact, Immm and $\text{C}2/\text{m}$ phases have nearly identical enthalpies (within 0.2 meV/atom), suggesting that Li_{13}N can exist as a mixture of Immm and $\text{C}2/\text{m}$ phases in the whole range of stability of this compound. (ii) Li_5N has a single stable phase $\text{P}6/\text{mmm}$ from 80 to at least 100 GPa. (iii) From 30 to 89 GPa, Li_3N_2 has two stable phases $\text{P}4/\text{mbm}$ and $\text{C}2/\text{c}$. The pressure-induced structural transition from $\text{P}4/\text{mbm}$ to $\text{C}2/\text{c}$ occurs at about 39 GPa. (iv) Besides the $\text{P}6_3/\text{mmc}$ structure, LiN_2 has another phase $\text{P}\bar{1}$, stable above 56 GPa, (v) For LiN_5 , the $\text{P}2_1/\text{C}$ structure becomes stable at 15 GPa and then transforms into the $\text{C}2/\text{c}$ phase at the pressure of 65 GPa. The $\text{C}2/\text{c}$ structure is stable at least up to 100 GPa.

The representative structures of above-mentioned Li-N compounds under ambient conditions and high pressure are presented in Fig. 3. We first analyze the structures of Li_3N and LiN_3 , and remind that the lengths of nitrogen-nitrogen bonds are 1.10 Å for the triple N–N bond, 1.25 Å for the double N=N bond, and 1.45 Å for the single N–N bond. (i) For Li_3N , the calculated lattice parameters of $\text{P}6/\text{mmm}$, $\text{P}6_3/\text{mmc}$ and $\text{Fm}\bar{3}\text{m}$ are in agreement with experimental data within 0.5%. The $\text{Pm}\bar{3}\text{m}$ structure is very simple, an anti- ReO_3 -type structure made of corner-sharing NLi_6 octahedra (Fig. 3a). Interestingly, across the phase transitions, the number of Li atoms surrounding each N atom increases from 6 for $\text{Pm}\bar{3}\text{m}$ to 8 for $\text{P}6/\text{mmm}$, 11 for $\text{P}6_3/\text{mmc}$ and 14 for $\text{Fm}\bar{3}\text{m}$. (ii) for LiN_3 at ambient conditions, $\text{C}2/\text{m}$ structure consists of Li^+ cations and linear azide anions $[\text{N}_3]^-$ ¹⁰. As illustrated in Fig. 3b, unlike the $\text{C}2/\text{m}$ structure, $\text{P}\bar{6}2\text{m}$ phase does have $[\text{N}_3]^-$ anions, but instead its unit cell contains two Li atoms and three N_2 groups with the N–N distance of 1.151 Å at 0 GPa, smaller than that in the azide-ion $[\text{N}_3]^-$ (1.184 Å), but larger than that in the gas-phase N_2 molecule (1.10 Å) and indicating a bond order between 2 and 3.

The Pmmm structure of Li_2N_2 consists of face-sharing Li_8 parallelepipeds (Fig. 3c). The N_2 groups sit in the center of parallelepipeds, which can be viewed that there are six Li atoms connecting to each N atom of N_2 molecule and each of four Li atoms connects to both N atoms. The N–N bond length is 1.263 Å at 0 GPa, slightly larger than that of Na_2N_2 (1.24 Å)¹⁴ and indicating a double N=N bond and ideal charge of the N_2 group equal to -2 , which matches perfectly the formula Li_2N_2 . Our calculated lattice constants of Immm structure (Fig. 3d) are in good agreement with experimental results¹⁵. The predicted N–N bond length is 1.271 Å, slightly smaller than the experiment. Figure 3e presents the Pnma structure of Li_2N_2 at 10 GPa. Its unit cell contains four N_2^{2-} groups and eight Li^+ ions. The N–N bond length is 1.269 Å.

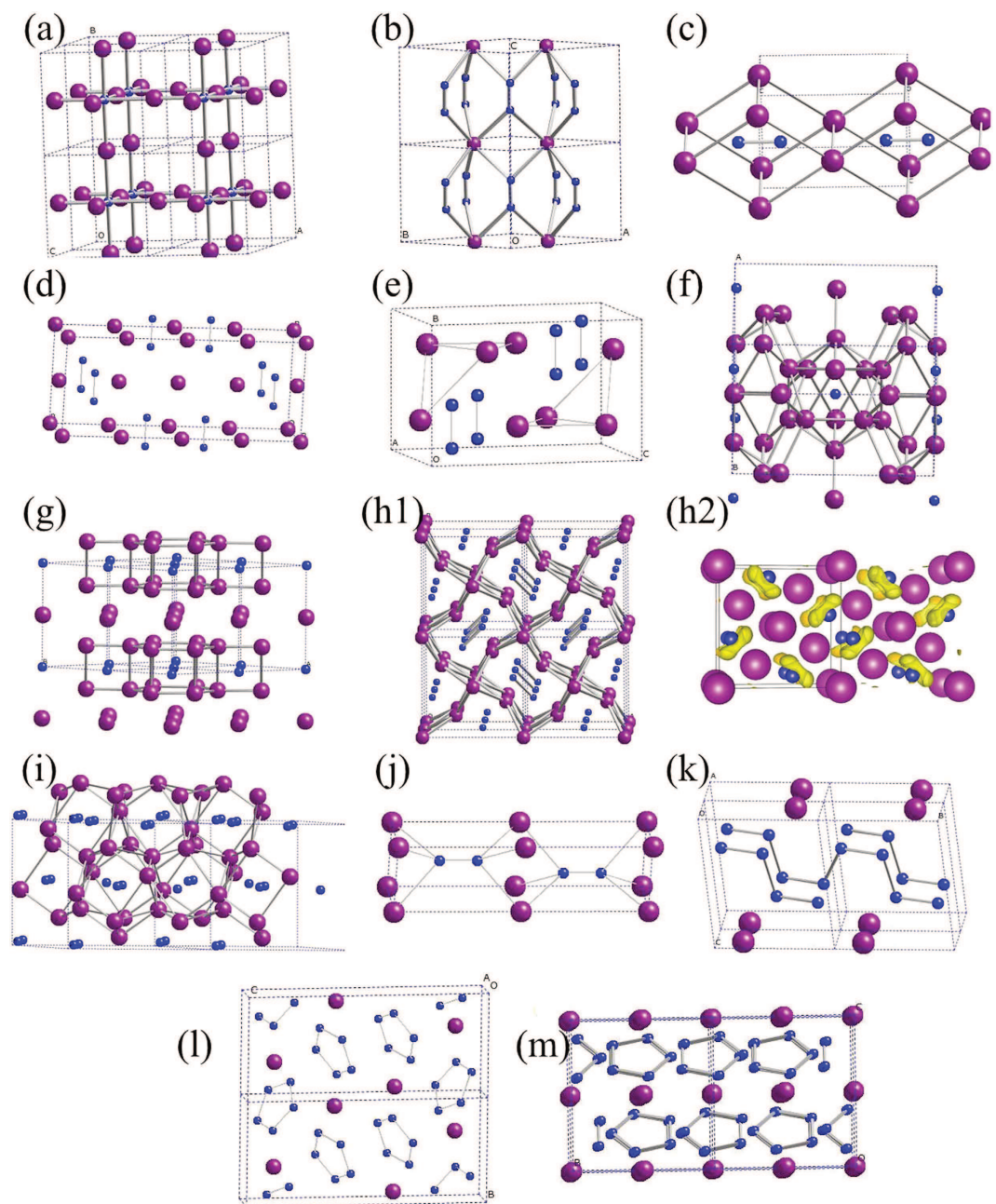


Figure 3. Crystal structures of Li-N compounds. (a) $Pm\bar{3}m$ - Li_3N at 0 GPa, (b) $P\bar{6}2m$ - LiN_3 at 0 GPa, (c) $Pmmm$ - Li_2N_2 at 0 GPa, (d) $Immm$ - Li_2N_2 at 10 GPa, (e) $Pnma$ - Li_2N_2 at 10 GPa, (f) $Immm$ - $Li_{13}N$ at 50 GPa, (g) $P6/mmm$ - Li_5N at 90 GPa, (h1) $P4/mbm$ - Li_3N_2 at 30 GPa, (h2) ELF isosurfaces (ELF = 0.85) of (h1), (i) $C2/c$ - Li_3N_2 at 40 GPa, (j) $P6_3/mmc$ - LiN_2 at 0 GPa, (k) $P\bar{1}$ - LiN_2 at 60 GPa, (l) $P2_1/c$ - LiN_5 at 50 GPa, (m) $C2/c$ - LiN_5 at 80 GPa.

For $Li_{13}N$, $Immm$ and $C2/m$ phases have similar structures. The $Immm$ structure of $Li_{13}N$ at 50 GPa is shown in Fig. 3f. This structure is an interesting example of Li-N compounds which can be viewed as a combination of a single Li atom and a slightly distorted $Li_{12}N$ icosahedral group (with N atom inside the Li_{12} icosahedron). A similar $Li_{12}Cs$ icosahedron is present in the $Pnna$ structure of Li_3Cs compound²⁹, where neighboring icosahedra share Li-Li edges. However, the $Li_{12}N$ icosahedra are isolated and do not share Li atoms with each other in our $Li_{13}N$ compound. The Li-N bond lengths in the $Li_{12}N$ icosahedron are 1.934, 1.951 and 2.011 Å, i.e. nearly identical, and Li-Li distances are also nearly identical, ranging from 2.026 to 2.113 Å (maximum difference 4.3%, to compare with 22.3% in Li_3Cs ²⁹).

The $P6/mmm$ phase of Li_5N has a layered structure, made of alternating layers of stoichiometry Li_4N (here, N atoms are sandwiched between two Li-graphene sheets) and Li, see Fig. 3g. Such unusual layered structures with alternation of “metallic” and “non-metallic” layers have been previously reported by some

of us for the Na-Cl system (e.g., Na₃Cl, also confirmed experimentally²²) and for the K-Cl system³⁰. Bader analysis shows that Li₅N at 90 GPa has charge configuration [Li₄N]^{-0.68} Li^{+0.68}, indicating that most of the valence electrons of Li layer transfer to the Li₄N sandwich layer³¹. Interestingly, the Bader charge of Li atom in upper Li-graphene sheet of Li₄N sandwich layer is nearly neutral (+0.1 e) and the charge of Li atom in bottom Li-graphene sheet is +0.74 e.

As observed in Fig. 3h1, the P4/mbm structure of Li₃N₂ consists of a three-dimensional network of Li atoms, which has open channels along z direction. This structure is very similar to the structure of the new compound Mg₃O₂ predicted by some of us recently³², except that in Li₃N₂ there is pairing of N atoms with the N-N distance of 1.353 Å at 30 GPa, indicating bond order between 1 and 2. Just like in P4/mbm-Mg₃O₂, we can clearly see columns of face-sharing body-centered cubes of metal atoms. The electron localization function (ELF) of Li₃N₂ (Fig. 3h2) shows strong charge transfer from Li to N. However, unlike Mg₃O₂ which is an electride, there is no strong interstitial electron location in Li₃N₂. Bader analysis also confirms the above result. The charges of P4/mbm-Li₃N₂ are +0.794 e for one Li atom, +0.809 e for the other two Li atoms, and -1.146 e and -1.266 e for two N atoms, respectively. The C2/c structure has a more complex three-dimensional network of lithium atoms with N₂ groups also sitting in its channels (Fig. 3i), with the N-N distance of 1.391 Å at 40 GPa.

The P6₃/mmc structure of LiN₂ can be described as a NiAs-type structure, where anionic positions are occupied by the N₂ groups (Fig. 3j). At zero pressure, the N-N distance is 1.173 Å, indicating a bond order between 2 and 3. The P $\bar{1}$ phase contains an infinite polyacetylene-like nitrogen chain (Fig. 3k), similar to the metastable phase of LiN₃¹⁰. The N-N distances are 1.316, 1.320 and 1.333 Å at 60 GPa, suggesting bond order between 1 and 2. We can clearly see how pressure destroys molecular groups, favoring extended structures.

As observed in Fig. 3l, the P2₁/c structure of LiN₅ consists of isolated Li atoms and N₅ rings, which up to now were only detected in molecular complexes¹⁹. At 50 GPa, the N-N distances are 1.286, 1.291, 1.299, 1.303 and 1.305 Å, respectively. The higher-pressure C2/c phase also consists of isolated Li atoms and N₅ rings (Fig. 3m). Unlike in P2₁/c, the N₅ ring here is a nearly isosceles pentagon, with N-N distances of 1.277, 1.277, 1.301, 1.301, and 1.281 Å, respectively, at 80 GPa.

To obtain deeper insight into these new Li-N compounds, we calculated their band structures and density of states (DOS) at selected pressures. We found that all stable phases of Li₁₃N, Li₅N and Li₃N₂ are metallic. The Pm $\bar{3}$ m phase of Li₃N is a semiconductor with the DFT band gap of 0.84 eV. All three stable phases of Li₂N₂ are also metallic, in agreement with experiment¹⁵. Interestingly, LiN₂ has a metal-insulator transition: P6₃/mmc is metallic at low pressure, but semiconducting in the high-pressure P $\bar{1}$ phase, with the band gap of 0.13 eV at 60 GPa. Since the newly predicted P $\bar{6}$ 2m phase of LiN₃ is also metallic, combining with previously known phases of LiN₃, we find that the sequence of transitions of LiN₃ under pressure is extremely unusual: from metallic to insulating to metallic to insulating. The P2₁/c and C2/c phases of LiN₅ are wide-gap insulators: e.g., the DFT band gap of the C2/c phase at 80 GPa is 2.19 eV.

Some electronic structures are shown in Fig. 4. As is seen from Fig. 4(a–c), the PDOSs of two different phases of Li₃N (or Li₂N₂ or LiN₃) at 0 GPa are obviously different. The newly found phases Pm $\bar{3}$ m-Li₃N, Pmmm-Li₂N₂ and P $\bar{6}$ 2m-LiN₃ have one character in common: the states near the Fermi level come mostly from Li-s and N-p orbitals. Figure 4(d–e) show the band structures of P $\bar{1}$ -LiN₂ and P6₃/mmc-LiN₂ at different pressures, respectively. The band structures at different pressures for the same phase are similar. When pressure increases, the band structure is more dispersive and the bandwidths also increase: both the conduction and valence bands broaden, and conduction band tends to shift upwards in energy. These changes can lead to both metallization and demetallization: for example, P $\bar{1}$ -LiN₂ is metallic at 0 GPa, whereas it becomes semiconductor with the gap of 0.13 eV at 60 GPa.

Conclusions

A number of new Li-N compounds have been predicted using *ab initio* evolutionary structure search. Other than the well-known compositions Li₃N, Li₂N₂ and LiN₃, we found five novel compositions which should be experimentally synthesizable under pressure, including Li₁₃N, Li₅N, Li₃N₂, LiN₂, and LiN₅. Notably, the N-N bonding patterns evolve from isolated N ions to N₂ dumbbells, to linear N₃ groups, infinite nitrogen chains, N₅ rings with increasing N content. Interestingly, for the experimentally known compounds Li₃N and LiN₃ at ambient conditions we find new lowest-energy structures (Pm $\bar{3}$ m and P $\bar{6}$ 2m, respectively): these are stable (at the GGA level of theory) in very narrow pressure ranges near 0 GPa. While this is most likely an artefact of the GGA (known to slightly overstabilize open structures and shift phase transition pressures upwards), these phases may be stabilized by doping, temperature, etc. We also resolve previous discrepancy on stable phases of Li₂N₂. In conclusion, this paper presents a more complete and reliable picture, correcting omissions and presenting more stable crystal structures than those presented before. Our work provides the basis for the future experimental investigations of the Li-N system.

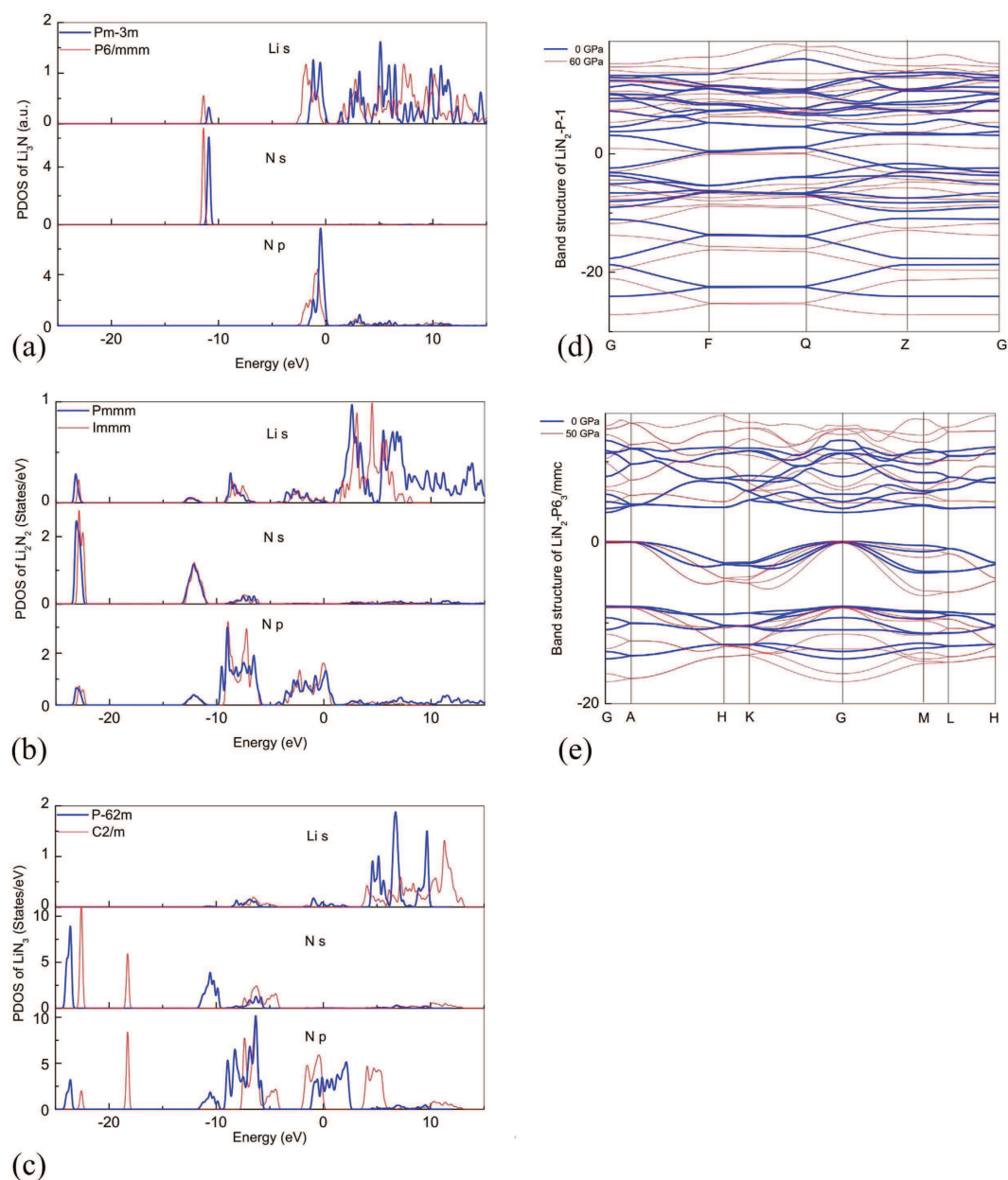


Figure 4. Electronic structures of selected Li-N compounds. (a–c) PDOSs of Li_3N , Li_2N_2 and LiN_3 at 0 GPa. (d–e) Band structures of $\text{P}\bar{1}$ - LiN_2 and $\text{P6}_3/\text{mmc}$ - LiN_2 at two different pressures.

Methods

To search for stable compounds, the Li-N system was first explored using the variable-composition evolutionary technique, as implemented in the USPEX code^{33–35}. Evolutionary crystal structure predictions were performed in the pressure range from 0 to 100 GPa. Initial structures included up to 16 atoms in the unit cell. The first generation of structures was produced randomly. The child structures were obtained applying heredity, transmutation, softmutation, and random symmetric generator, with probabilities of 40, 20, 20 and 20%, respectively. Then we performed detailed fixed-composition evolutionary calculations to explore the most promising compositions.

All structure relaxations and electronic structure calculations were done using the Vienna Ab Initio Simulation Package (VASP) in the framework of density functional theory³⁶. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was employed to treat the exchange-correlation energy³⁷, and the all-electron projector augmented wave (PAW) potentials were used to describe the core-valence interactions³⁸. The cut-off energy of 650 eV and Monkhorst-Pack k-point meshes for sampling the Brillouin zone with resolution $2\pi \times 0.04 \text{ \AA}^{-1}$ ensured that all the enthalpy calculations were well converged to better than 1 meV/atom. To ensure that the structures of predicted compounds in Li-N system are dynamically stable, phonon calculations were carried out using the Phonopy code³⁹. Our tests

showed that the effect of van der Waals interactions^{40,41} on stability of lithium nitrides is negligible, which is consistent with other works²³.

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Author Contributions

A.R.O. designed the project and Y.-Q.S. carried out structure prediction and electronic structure calculations. G.-R.Q. and J.Z. performed phonon calculations. H.-F.D. and Q.Z. computed the electron localization function and Bader charges. Y.-Q.S., A.R.O. and Z.-X.Z. analysed the data and wrote the manuscript.

Additional Information

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