Novel lithium-nitrogen compounds at ambient and high pressures

Yanqing Shen1,4, Artem R. Oganov1,3,4,5, Guangri Qian4, Jin Zhang4, Huafeng Dong4, Qiang Zhu4 & Zhongxiang Zhou1

Using ab initio evolutionary simulations, we predict the existence of five novel stable Li-N compounds at pressures from 0 to 100 GPa (Li13N, Li5N, Li3N2, LiN2, and LiN5). Structures of these compounds contain isolated N atoms, N2 dimers, polyacetylene-like N chains and N5 rings, respectively. The structure of Li13N consists of Li atoms and Li12N icosahedra (with N atom in the center of the Li12 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 LiN3 shows peculiar electronic structure changes with increasing pressure: metal-insulator-metal-insulator. This work also resolves the previous controversies of theory and experiment on Li2N2.

Li-N system contains two well-known compounds: lithium nitride (Li3N) and lithium azide (LiN3). Li3N has potential use as an electrolyte in Li-batteries and a hydrogen storage medium1-4. Extensive experimental and theoretical investigations show that Li3N undergoes a sequence of phase transitions with increasing pressure. At ambient conditions, X-ray diffraction identified in Li3N a mixture of two phases: α-Li3N (P6/mmm) and metastable β-Li3N (P63/mmc); at about 0.5 GPa, α-Li3N fully transforms to β-Li3N; a new phase γ-Li3N (Fm3m) occurs near 40 GPa5-6. Normal ionic materials usually become metallic with increasing pressure, but Li3N is abnormal since the increasing pressure makes it into a much more strongly ionic state7. LiN3 has been widely used in industry as a nitrogen source, initial explosives and photographic materials8. Before 2013, LiN3 was known in a single phase C2/m, and seemed so simple and well understood. However, several other phases of LiN3 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 LiN3 with pseudo-benzene N6 ring has been predicted by two research groups independently9,10. Some other phases appear as metastable: P1 with a polyacetylene-like infinite linear nitrogen chain structure; C2/m and P1 with puckered extended 2D decagonal and quasi-2D hexagonal nitrogen layers, respectively10. Above 375 GPa, Wang et al. identified the phase of P21 which consists of zigzag N polymeric chains with N5 ring sharing N-N pairs11. The band structures indicate that there are two metal-insulator transitions in LiN3: 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 N3− anion) and azides ([N3]−), in 2001, Kniep et al. proved the existence of diazenides [N2]2− by synthesizing SrN2 and BaN2 under high N2 pressure12,13. Since then, discovery of new diazenides has been of constant interest. In 2010, alkali diazenides Na2N2 and Li2N2 (Pmmm) were predicted14, but then, a different structure of Li2N2 (I4mm) was obtained under HP/HT conditions.
(9 GPa, 750 K) by decomposition of LiN$_3$\textsuperscript{15}. This discrepancy encourages us to study Li$_2$N$_2$ under high pressure in detail.

Nitrogen can form many anionic species, e.g. [N$_2$]$^-$, [N$_2$]$_3$$^-$ and [N$_5$]$^-$, which have just been obtained in molecular complexes\textsuperscript{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\textsuperscript{20–22}. The predicted counterintuitive compounds NaCl$_3$ and Na$_3$Cl in the Na-Cl system have been confirmed by experiment\textsuperscript{22}. 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 ($\Delta$H) 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$_3$N, LiN$_3$, and Li$_2$N$_2$ are reproduced readily in our evolutionary structure searches. Interestingly, five previously unreported compositions of Li-N system: Li$_{13}$N, Li$_5$N, Li$_3$N$_2$, 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.\textsuperscript{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.\textsuperscript{23} missed a number of stable compounds (Li$_{13}$N, Li$_5$N, Li$_3$N$_2$). 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$_3$N and Li$_2$N$_2$, LiN$_2$ with space group P6/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$_2$ becomes stable, meanwhile Li$_{13}$N, Li$_5$N$_2$ and Li$_3$N$_2$ lie very close to (or nearly on) the convex hull. At 50 GPa, Li$_{13}$N, Li$_5$N$_2$ and Li$_3$N$_2$ are all stable, and Li$_2$N lies very close to the convex hull. At 100 GPa, Li$_3$N is stable, however, Li$_{13}$N and Li$_5$N$_2$ 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 (Im$\bar{3}$m) transforms into fcc (Fm$\bar{3}$m), cI16 (I$\bar{4}$3d), Aba2–40, and Pbca phases in sequence, which is in accordance with previous experimental and theoretical data\textsuperscript{24–26}. For pure N, the known Pa$\bar{3}$, P2$_1$/c, P4$_{1}$2$_1$2$_1$, and I2$_3$ structures are reproduced in our searches and agree well with other theoretical predictions\textsuperscript{27,28}.

For Li$_3$N there is a peculiar situation: the experimentally known at ambient conditions P6/mmm structure is predicted to be stable only at pressures above 0.2 GPa – at lower pressures, at the GGA level
of theory, the Pm3m 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 Pm3m structure could be stabilized by impurities, temperature etc. The subsequent phases of Li3N in our calculations are all in agreement with the previous works5–7.

LiN3 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 P62m to have the lowest enthalpy in the pressure range 0–0.9 GPa, followed by C2/m and P6/m phases on increasing pressure. C2/m is the phase known experimentally at ambient conditions.

For LiN (actually Li2N2), 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 I4mm structure, indicating that the experimental result obtained at around 9 GPa is also perfectly correct15. At 8.9 GPa, the I4mm 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 Li3N, the Immm structure is predicted to be stable from 43 to 76 GPa, following which the C2/m structure is stable up to 83 GPa. In fact, Immm and C2/m phases have nearly identical enthalpies (within 0.2 meV/atom), suggesting that Li3N can exist as a mixture of Immm and C2/m phases in the whole range of stability of this compound. (ii) Li2N has a single stable phase P6/mmm from 80 to at least 100 GPa. (iii) From 30 to 89 GPa, Li3N2 has two stable phases P4/mmb and C2/c. The pressure-induced structural transition from P4/mmb to C2/c occurs at about 39 GPa. (iv) Besides the P6/mmmc structure, LiN5 has another phase P1, stable above 56 GPa. (v) For LiN5, the P21/c structure becomes stable at 15 GPa and then transforms into the C2/c phase at the pressure of 65 GPa. The C2/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 Li3N and LiN3, 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 Li3N, the calculated lattice parameters of P6/mmm, P6/mmmc and Fm3m are in agreement with experimental data within 0.5%. The Pm3m structure is very simple, an anti-ReO3-type structure made of corner-sharing NLi6 octahedra (Fig. 3a). Interestingly, across the phase transitions, the number of Li atoms surrounding each N atom increases from 6 for Pm3m to 8 for P6/mmm, 11 for P6/mmmc and 14 for Fm3m. (ii) For LiN3 at ambient conditions, C2/m structure consists of Li+ cations and linear azide anions [N3]−10. As illustrated in Fig. 3b, unlike the C2/m structure, P62m phase does have [N3]− anions, but instead its unit cell contains two Li atoms and three N2 groups with the N-N distance of 1.151 Å at 0 GPa, smaller than that in the azide-ion [N3]− (1.184 Å), but larger than that in the gas-phase N2 molecule (1.10 Å) and indicating a bond order between 2 and 3. The Pmmm structure of Li2N2 consists of face-sharing Li8 parallelepipeds (Fig. 3c). The N2 groups sit in the center of parallelepipeds, which can be viewed that there are six Li atoms connecting to each N atom of N2 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 Na2N2 (1.24 Å)14 and indicating a double N–N bond and ideal charge of the N2 group equal to −2, which matches perfectly the formula Li2N2. Our calculated lattice constants of I4mm 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 Li3N2 at 10 GPa. Its unit cell contains four N2−+− groups and eight Li+ ions. The N-N bond length is 1.269 Å.
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$_3$Cs compound\textsuperscript{29}, 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$_3$Cs\textsuperscript{29}).

The P6/mmm phase of Li$_5$N has a layered structure, made of alternating layers of stoichiometry Li$_4$N (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

Figure 3. Crystal structures of Li-N compounds. (a) Pm\textsuperscript{3}m-Li$_3$N at 0 GPa, (b) P\textsuperscript{6}2\textsubscript{1}m-LiN$_3$ at 0 GPa, (c) Pmmm-Li$_2$N$_2$ at 0 GPa, (d) Immm-Li$_2$N$_2$ at 10 GPa, (e) Pnma-Li$_2$N$_2$ at 10 GPa, (f) Immm-Li$_{13}$N at 50 GPa, (g) P\textsuperscript{6}/mnm-Li$_3$N at 90 GPa, (h1) P4/mmm-Li$_{13}$N$_2$ at 30 GPa, (h2) ELF isosurfaces (ELF = 0.85) of (h1), (i) C2/c-Li$_3$N$_2$ at 40 GPa, (j) P\textsuperscript{6}/mmm-Li$_5$N$_2$ at 0 GPa, (k) P\textsuperscript{1}1-LiN$_2$ at 60 GPa, (l) P2\textsubscript{1}/c-LiN$_5$ at 50 GPa, (m) C2/c-LiN$_5$ at 80 GPa.
of us for the Na-Cl system (e.g., Na₆Cl, also confirmed experimentally²²) and for the K-Cl system³⁰. Bader analysis shows that Li₃N at 90 GPa has charge configuration [Li₃N]−⁰.⁰⁸ Li¹−.⁶⁶, indicating that most of the valence electrons of Li layer transfer to the Li₃N sandwich layer³¹. Interestingly, the Bader charge of Li atom in upper Li-graphene sheet of Li₃N 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/mmb 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 recently⁶⁸, except that in Li₃N, 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/mmb-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/mmb-Li₃N₂ are +0.809 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 1.733 Å, indicating a bond order between 2 and 3. The P1 phase contains an infinite polyacetylene-like nitrogen chain (Fig. 3k), similar to the metastable phase of LiN₃.¹⁰ 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 LiN₃ 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 1.287, 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 Pm₃m phase of Li₃N is a semiconductor with the DFT band gap of 0.84 eV. All three stable phases of Li₅N₂ are also metallic, in agreement with experiment¹⁵. Interestingly, LiN₃ has a metal-insulator transition: P6₃/mmc is metallic at low pressure, but semiconducting in the high-pressure phase, with the band gap of 0.13 eV at 60 GPa. Since the newly predicted P6₂m 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 LiN₃ 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 LiN (or Li₅N₂ or LiN₃) at 0 GPa are obviously different. The newly found phases Pm₃m -LiN, Pmmm-Li₅N₂ and P6₂m-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 P1-LiN₂ and P6₃/mmc-LiN₃ 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, P1-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 Li₅N, Li₅N₂ and LiN₃, we found five novel compositions which should be experimentally synthesizable under pressure, including Li₁₃N, Li₅N, Li₅N₂, Li₃N₂, and LiN₃. Notably, the N-N bonding patterns evolve from isolated N ions to N₅ dumbbells, to linear N₅ groups, infinite nitrogen chains, N₅ rings with increasing N content. Interestingly, for the experimentally known compounds Li₅N and LiN₃ at ambient conditions we find new lowest-energy structures (Pm₃m and P6₂m, 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 Li₅N₂. 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.
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. 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 theory. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was employed to treat the exchange-correlation energy, and the all-electron projector augmented wave (PAW) potentials were used to describe the core-valence interactions. The cut-off energy of 650 eV and Monkhorst-Pack k-point meshes for sampling the Brillouin zone with resolution \(2\pi \times 0.04 \text{ Å}^{-1}\) 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 code. Our tests

Figure 4. Electronic structures of selected Li-N compounds. (a–c) PDOSs of \(\text{Li}_3\text{N}, \text{Li}_2\text{N}_2\) and \(\text{LiN}_3\) at 0 GPa. (d–e) Band structures of \(\text{P}_{\text{1}}\)-Li\(_2\text{N}_2\) and \(\text{P6}_3\text{mmc}-\text{LiN}_2\) at two different pressures.
showed that the effect of van der Waals interactions\(^{40,41}\) on stability of lithium nitrides is negligible, which is consistent with other works\(^{23}\).

**References**

1. Boukamp, B. A. & Huggins, R. A. Lithium ion conductivity in lithium nitride. *Phys. Lett. A* **58**, 231–233 (1976).
2. Rabenau, A. Lithium nitride and related materials case study of the use of modern solid state research techniques. *Solid State Ionics* **6**, 277–293 (1982).
3. Chem., P., Xiong, Z., Luo, J., Lin, J. & Tan, K. L. Interaction of hydrogen with metal nitrides and imides. *Nature* **420**, 302–304 (2002).
4. Hu, Y. H. & Ruckenstein, E. Ultrafast reaction between Li\(_2\)N and LiNH\(_2\) to prepare the effective hydrogen storage material Li\(_2\)NH. *Ind. Eng. Chem. Res.* **45**, 4993–4998 (2006).
5. Lazièki, A. et al. New cubic phase of Li\(_2\)N: Stability of the N\(_6^-\) ion to 200 GPa. *Phys. Rev. Lett.* **95**, 165503 (2005).
6. Lazièki, A. et al. Pressure-induced loss of electronic interlayer state and metallization in the ionic solid Li\(_2\)N: Experiment and theory. *Phys. Rev. Lett.* **78**, 15133 (2008).
7. Cui, S., Feng, W., Hu, H., Feng, Z. & Wang, Y. Structural transition of Li\(_2\)N under high pressure: A first-principles study. *Solid State Commun.* **149**, 612–615 (2009).
8. Evans, B. L., Yofe, A. D. & Gray, P. Physics and chemistry of the inorganic azides. *Chem. Rev.* **59**, 515–568 (1959).
9. Zhang, M., Yan, H., Wei, Q., Wang, H. & Wu, Z. Novel high-pressure phase with pseudo-benzene \(\text{N}_9\) molecule of Li\(_3\)N. *Eur. Phys. J. B* **101**, 26004 (2013).
10. Prasad, D. L. V. K., Ashcroft, N. W. & Hoffmann, R. Evolving structural diversity and metallicity in compressed lithium azide. *J. Phys. Chem. C* **117**, 20838–20846 (2013).
11. Wang, X. et al. Polymerization of nitrogen in lithium azide. *J. Chem. Phys.* **139**, 164710 (2013).
12. Aufler, M., Prots, Y. & Kniep, R. SrN\(_3\) and SrN\(_2\): Diazeneides by synthesis under high N\(_2\) pressure. *Angew. Chem. Int. Ed.* **40**, 547–549 (2001).
13. Vajenine, G. et al. Preparation, crystal structure, and properties of barium permitride, BaN\(_2\). *Inorg. Chem.* **40**, 4866–4870 (2001).
14. Zhang, X., Zunger, A. & Trimarchi, G. Structure prediction and targeted synthesis: A new NaN\(_2\) diazenide crystalline structure. *J. Phys. Chem. C* **133**, 194504 (2010).
15. Schneider, S. B., Frankovsky, R. & Schnick, W. High-pressure synthesis and characterization of the alkali diazenide Li\(_2\)N\(_2\). *Angew. Chem. Int. Ed.* **51**, 1873–1875 (2012).
16. Chiesa, M. et al. Reductive activation of the nitrogen molecule at the surface of \("\text{electron-rich}\) MgO and CaO. The N\(_2\) surface chem. Ed radical ion. *J. Phys. Chem. B* **105**, 497–505 (2001).
17. Kaim, W. & Sarkar, B. N\(_2\)\(^{\text{3+}}\): Filling a gap in the N\(_2\)\(^{\text{n+}}\) Series. *Angew. Chem. Int. Ed.* **48**, 9409–9411 (2009).
18. Chirik, P. J. One electron at a time. *Nature Chem.* **1**, 520–522 (2009).
19. Vij, A., Pavlovich, J. G., Wilson, W. W., Vij, V. & Christe, K. O. Experimental detection of the pentaazacyclopentadienide (pentazolate) anion, cyclo-N\(_5\). *Angew. Chem. Int. Ed.* **41**, 3051–3054 (2002).
20. Hu, C.-H. et al. Pressure-induced stabilization and insulator-superconductor transition of BH. *Phys. Rev. Lett.* **110**, 165504 (2013).
21. Zhu, Q. et al. Stability of xenon oxides at high pressures. *Nature Chem.* **5**, 61–65 (2013).
22. Zhang, W. et al. Unexpected stoichiometrics of stable sodium chlorides. *Science* **342**, 1502–1505 (2013).
23. Peng, F., Yao, Y., Liu, H. & Ma, Y. Crystalline Li\(_3\)N predicted from first-principles as a possible high-energy material. *J. Phys. Chem. Lett.* **6**, 2363–2366 (2015).
24. Hanfland, M., Syassen, K., Christensen, N. E. & Novikov, D. L. New high-pressure phases of lithium. *Nature* **408**, 174–178 (2000).
25. Pickard, C. J. & Needs, R. J. Dense low-coordination phases of lithium. *Phys. Rev. Lett.* **102**, 146401 (2009).
26. Li, J., Wang, Y., Zhu, L. & Ma, Y. Predicted novel high-pressure phases of lithium. *Phys. Rev. Lett.* **106**, 015503 (2011).
27. Pickard, C. J. & Needs, R. J. High-pressure phases of nitrogen. *Phys. Rev. Lett.* **102**, 125702 (2009).
28. Wang, X. et al. Cagelike diamondoid nitrogen at high pressures. *Phys. Rev. Lett.* **109**, 175502 (2012).
29. Botana, J. & Xiao, M.-S. Pressure-stabilized lithium caesides with caesium anions beyond the -1 state. *Nat. Commun.* **5**, 4861 (2014).
30. Zhang, W. & Oganov, A. R. Stability of numerous novel potassium chlorides at high pressure. arXiv:1405.3007 (2014).
31. Bader, R. F. W. Atoms in Molecules: A Quantum Theory (Oxford Univ. Press, Oxford, 1990).
32. Zhu, Q., Oganov, A. R. & Lyakhov, A. O. Novel stable compounds in the Mg-O system under high pressure. *Phys. Chem. Chem. Phys.* **15**, 7696–7700 (2013).
33. Oganov, A. R. & Glass, C. W. Crystal structure prediction using ab initio evolutionary techniques: principles and applications. *J. Chem. Phys.* **124**, 244704 (2006).
34. Oganov, A. R., Lyakhov, A. O. & Valle, M. How evolutionary crystal structure prediction works - and why. *Acc. Chem. Res.* **44**, 227–237 (2011).
35. Lyakhov, A. O., Oganov, A. R., Stokes, H. T. & Zhu, Q. New developments in evolutionary structure prediction algorithm USPEX. *Comput. Phys. Commun.* **184**, 1172–1182 (2013).
36. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
37. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
38. Blochl, P. E. Projector augmented-plane wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
39. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl\(_2\)-type SiO\(_2\) at high pressures. *Phys. Rev. B* **78**, 134106 (2008).
40. Beuk, T., Hafner, J., Lebégue, S. & Angýn, J. G. Improved description of the structure of molecular and layered crystals: Ab initio DFT calculations with van der Waals corrections. *J. Phys. Chem. A* **114**, 11814 (2010).
41. BuKo, T., Lebégue, S., Hafner, J. & Angýn, J. G. Tkatchenko-Scheffler van der Waals correction method with and without self-consistent screening applied to solids. *Phys. Rev. B* **87**, 064110 (2013).

**Acknowledgments**

Y. Shen thanks Dongxu Li, Xiao Dong, Xiangfeng Zhou, Qianku Hu, Shengnan Wang and Haiyang Niu for valuable discussions. The research is supported by National Natural Science Foundation of China (No. 11204053 and No. 11074059) and the China Postdoctoral Science Foundation (No. 2013M531028). A.R.O. thanks DARPA (No. W31P4Q1210008 and No. W31P4Q1310005) and the Government of Russian Federation (No. 14.A12.31.0003) for financial support.
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
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Shen, Y. et al. Novel lithium-nitrogen compounds at ambient and high pressures. Sci. Rep. 5, 14204; doi: 10.1038/srep14204 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/