

# SCIENTIFIC REPORTS

OPEN

## Novel lithium-nitrogen compounds at ambient and high pressures

Yanqing Shen<sup>1,4</sup>, Artem R. Oganov<sup>2,3,4,5</sup>, Guangri Qian<sup>4</sup>, Jin Zhang<sup>4</sup>, Huafeng Dong<sup>4</sup>, Qiang Zhu<sup>4</sup> & Zhongxiang Zhou<sup>1</sup>

Received: 29 May 2015

Accepted: 20 August 2015

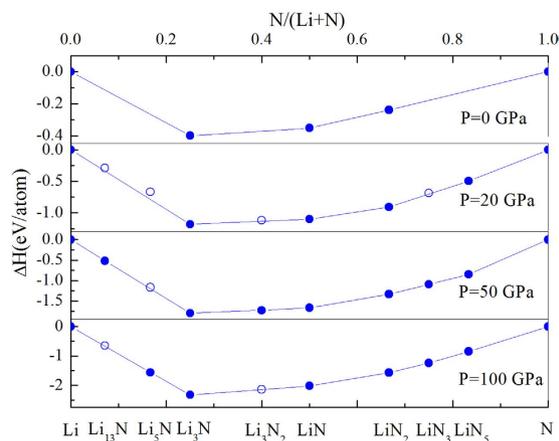
Published: 16 September 2015

Using *ab initio* evolutionary simulations, we predict the existence of five novel stable Li-N compounds at pressures from 0 to 100 GPa ( $\text{Li}_{13}\text{N}$ ,  $\text{Li}_5\text{N}$ ,  $\text{Li}_3\text{N}_2$ ,  $\text{LiN}_2$ , and  $\text{LiN}_5$ ). Structures of these compounds contain isolated N atoms,  $\text{N}_2$  dimers, polyacetylene-like N chains and  $\text{N}_5$  rings, respectively. The structure of  $\text{Li}_{13}\text{N}$  consists of Li atoms and  $\text{Li}_{12}\text{N}$  icosahedra (with N atom in the center of the  $\text{Li}_{12}$  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  $\text{LiN}_3$  shows peculiar electronic structure changes with increasing pressure: metal-insulator-metal-insulator. This work also resolves the previous controversies of theory and experiment on  $\text{Li}_2\text{N}_2$ .

Li-N system contains two well-known compounds: lithium nitride ( $\text{Li}_3\text{N}$ ) and lithium azide ( $\text{LiN}_3$ ).  $\text{Li}_3\text{N}$  has potential use as an electrolyte in Li-batteries and a hydrogen storage medium<sup>1–4</sup>. Extensive experimental and theoretical investigations show that  $\text{Li}_3\text{N}$  undergoes a sequence of phase transitions with increasing pressure. At ambient conditions, X-ray diffraction identified in  $\text{Li}_3\text{N}$  a mixture of two phases:  $\alpha$ - $\text{Li}_3\text{N}$  (P6/mmm) and metastable  $\beta$ - $\text{Li}_3\text{N}$  (P6<sub>3</sub>/mmc); at about 0.5 GPa,  $\alpha$ - $\text{Li}_3\text{N}$  fully transforms to  $\beta$ - $\text{Li}_3\text{N}$ ; a new phase  $\gamma$ - $\text{Li}_3\text{N}$  (Fm $\bar{3}$ m) occurs near 40 GPa<sup>5,6</sup>. Normal ionic materials usually become metallic with increasing pressure, but  $\text{Li}_3\text{N}$  is abnormal since the increasing pressure makes it into a much more strongly ionic state<sup>7</sup>.  $\text{LiN}_3$  has been widely used in industry as a nitrogen source, initial explosives and photographic materials<sup>8</sup>. Before 2013,  $\text{LiN}_3$  was known in a single phase C2/m, and seemed so simple and well understood. However, several other phases of  $\text{LiN}_3$  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  $\text{LiN}_3$  with pseudo-benzene  $\text{N}_6$  ring has been predicted by two research groups independently<sup>9,10</sup>. 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, respectively<sup>10</sup>. Above 375 GPa, Wang *et al.* identified the phase of  $\text{P}2_1$  which consists of zigzag N polymeric chains with  $\text{N}_5$  ring sharing N-N pairs<sup>11</sup>. The band structures indicate that there are two metal-insulator transitions in  $\text{LiN}_3$ : 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  $\text{N}^{3-}$  anion) and azides ( $[\text{N}_3]^-$ ), in 2001, Knip *et al.* proved the existence of diazenides  $[\text{N}_2]^{2-}$  by synthesizing  $\text{SrN}_2$  and  $\text{BaN}_2$  under high  $\text{N}_2$  pressure<sup>12,13</sup>. Since then, discovery of new diazenides has been of constant interest. In 2010, alkali diazenides  $\text{Na}_2\text{N}_2$  and  $\text{Li}_2\text{N}_2$  (Pmmm) were predicted<sup>14</sup>, but then, a different structure of  $\text{Li}_2\text{N}_2$  (Immm) was obtained under HP/HT conditions

<sup>1</sup>Department of Physics, Harbin Institute of Technology, Harbin 150001, China. <sup>2</sup>Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 3 Nobel St., Moscow 143026, Russia. <sup>3</sup>Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny City, Moscow Region 141700, Russia. <sup>4</sup>Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York 11794, USA. <sup>5</sup>School of Materials Science, Northwestern Polytechnical University, Xi'an 710072, China. Correspondence and requests for materials should be addressed to Y.S. (email: shenyanqing2004@163.com)



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

(9 GPa, 750 K) by decomposition of  $\text{LiN}_3$ <sup>15</sup>. This discrepancy encourages us to study  $\text{Li}_2\text{N}_2$  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<sup>16–19</sup>. 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<sup>20–22</sup>. The predicted counterintuitive compounds  $\text{NaCl}_3$  and  $\text{Na}_3\text{Cl}$  in the Na-Cl system have been confirmed by experiment<sup>22</sup>. 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,  $\text{N}_2$ ,  $\text{Li}_3\text{N}$ ,  $\text{LiN}_3$ , and  $\text{Li}_2\text{N}_2$  are reproduced readily in our evolutionary structure searches. Interestingly, five previously unreported compositions of Li-N system:  $\text{Li}_{13}\text{N}$ ,  $\text{Li}_5\text{N}$ ,  $\text{Li}_3\text{N}_2$ ,  $\text{LiN}_2$ , and  $\text{LiN}_5$  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.

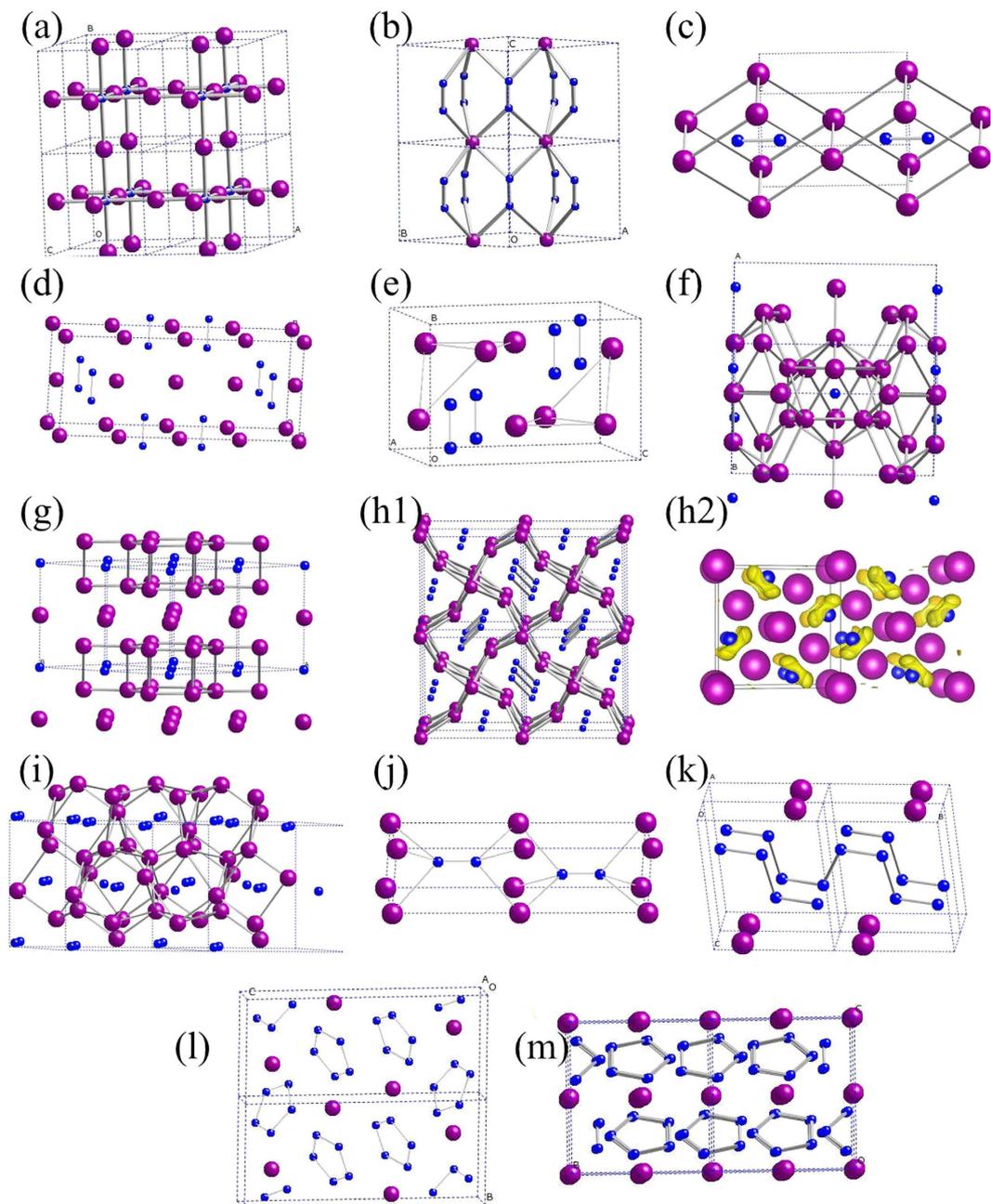
Simultaneously with our work (in fact, with submission date after our paper appeared on arxiv.org) Peng *et al.*<sup>23</sup> investigated the Li-N system and found two new stable compounds,  $\text{LiN}_2$  and  $\text{LiN}_5$ . However, the phase diagram of the Li-N system published by Peng *et al.*<sup>23</sup> missed a number of stable compounds ( $\text{Li}_{13}\text{N}$ ,  $\text{Li}_5\text{N}$ ,  $\text{Li}_3\text{N}_2$ ). 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  $\text{Li}_3\text{N}$  and  $\text{Li}_2\text{N}_2$ ,  $\text{LiN}_2$  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  $\text{LiN}_3$  is metastable below 49 GPa, which is in agreement with the known fact that it decomposes into  $\text{N}_2$  and Li under external influences (heat, irradiation, etc) at 0 GPa. (iii) At 20 GPa,  $\text{LiN}_5$  becomes stable, meanwhile  $\text{Li}_{13}\text{N}$ ,  $\text{Li}_3\text{N}_2$  and  $\text{LiN}_3$  lie very close to (or nearly on) the convex hull. At 50 GPa,  $\text{Li}_{13}\text{N}$ ,  $\text{Li}_3\text{N}_2$  and  $\text{LiN}_3$  are all stable, and  $\text{Li}_5\text{N}$  lies very close to the convex hull. At 100 GPa,  $\text{Li}_5\text{N}$  is stable, however,  $\text{Li}_{13}\text{N}$  and  $\text{Li}_3\text{N}_2$  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 ( $\text{Im}\bar{3}\text{m}$ ) transforms into fcc ( $\text{Fm}\bar{3}\text{m}$ ), cI16 ( $\text{I}\bar{4}3\text{d}$ ),  $\text{Aba}2\text{-}40$ , and  $\text{Pbca}$  phases in sequence, which is in accordance with previous experimental and theoretical data<sup>24–26</sup>. For pure N, the known  $\text{Pa}\bar{3}$ ,  $\text{P}2_1/\text{c}$ ,  $\text{P}4_12_12$ , and  $\text{I}2_13$  structures are reproduced in our searches and agree well with other theoretical predictions<sup>27,28</sup>.

For  $\text{Li}_3\text{N}$  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 3. Crystal structures of Li-N compounds.** (a)  $Pm\bar{3}m$ - $\text{Li}_3\text{N}$  at 0 GPa, (b)  $P\bar{6}2m$  - $\text{LiN}_3$  at 0 GPa, (c)  $Pmmm$ - $\text{Li}_2\text{N}_2$  at 0 GPa, (d)  $Immm$ - $\text{Li}_2\text{N}_2$  at 10 GPa, (e)  $Pnma$ - $\text{Li}_2\text{N}_2$  at 10 GPa, (f)  $Immm$ - $\text{Li}_{13}\text{N}$  at 50 GPa, (g)  $P6/mmm$ - $\text{Li}_5\text{N}$  at 90 GPa, (h1)  $P4/mbm$ - $\text{Li}_3\text{N}_2$  at 30 GPa, (h2) ELF isosurfaces (ELF = 0.85) of (h1), (i)  $C2/c$ - $\text{Li}_3\text{N}_2$  at 40 GPa, (j)  $P6_3/mmc$ - $\text{LiN}_2$  at 0 GPa, (k)  $P\bar{1}$ - $\text{LiN}_2$  at 60 GPa, (l)  $P2_1/c$ - $\text{LiN}_5$  at 50 GPa, (m)  $C2/c$ - $\text{LiN}_5$  at 80 GPa.

For  $\text{Li}_{13}\text{N}$ ,  $Immm$  and  $C2/m$  phases have similar structures. The  $Immm$  structure of  $\text{Li}_{13}\text{N}$  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  $\text{Li}_{12}\text{N}$  icosahedral group (with N atom inside the  $\text{Li}_{12}$  icosahedron). A similar  $\text{Li}_{12}\text{Cs}$  icosahedron is present in the  $Pnna$  structure of  $\text{Li}_3\text{Cs}$  compound<sup>29</sup>, where neighboring icosahedra share Li-Li edges. However, the  $\text{Li}_{12}\text{N}$  icosahedra are isolated and do not share Li atoms with each other in our  $\text{Li}_{13}\text{N}$  compound. The Li-N bond lengths in the  $\text{Li}_{12}\text{N}$  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  $\text{Li}_3\text{Cs}$ <sup>29</sup>).

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

of us for the Na-Cl system (e.g., Na<sub>3</sub>Cl, also confirmed experimentally<sup>22</sup>) and for the K-Cl system<sup>30</sup>. Bader analysis shows that Li<sub>5</sub>N at 90 GPa has charge configuration [Li<sub>4</sub>N]<sup>-0.68</sup> Li<sup>+0.68</sup>, indicating that most of the valence electrons of Li layer transfer to the Li<sub>4</sub>N sandwich layer<sup>31</sup>. Interestingly, the Bader charge of Li atom in upper Li-graphene sheet of Li<sub>4</sub>N 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 Li<sub>3</sub>N<sub>2</sub> 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 Mg<sub>3</sub>O<sub>2</sub> predicted by some of us recently<sup>32</sup>, except that in Li<sub>3</sub>N<sub>2</sub> 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-Mg<sub>3</sub>O<sub>2</sub>, we can clearly see columns of face-sharing body-centered cubes of metal atoms. The electron localization function (ELF) of Li<sub>3</sub>N<sub>2</sub> (Fig. 3h2) shows strong charge transfer from Li to N. However, unlike Mg<sub>3</sub>O<sub>2</sub> which is an electrider, there is no strong interstitial electron location in Li<sub>3</sub>N<sub>2</sub>. Bader analysis also confirms the above result. The charges of P4/mbm-Li<sub>3</sub>N<sub>2</sub> 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 N<sub>2</sub> groups also sitting in its channels (Fig. 3i), with the N-N distance of 1.391 Å at 40 GPa.

The P6<sub>3</sub>/mmc structure of LiN<sub>2</sub> can be described as a NiAs-type structure, where anionic positions are occupied by the N<sub>2</sub> 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 LiN<sub>3</sub><sup>10</sup>. 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.

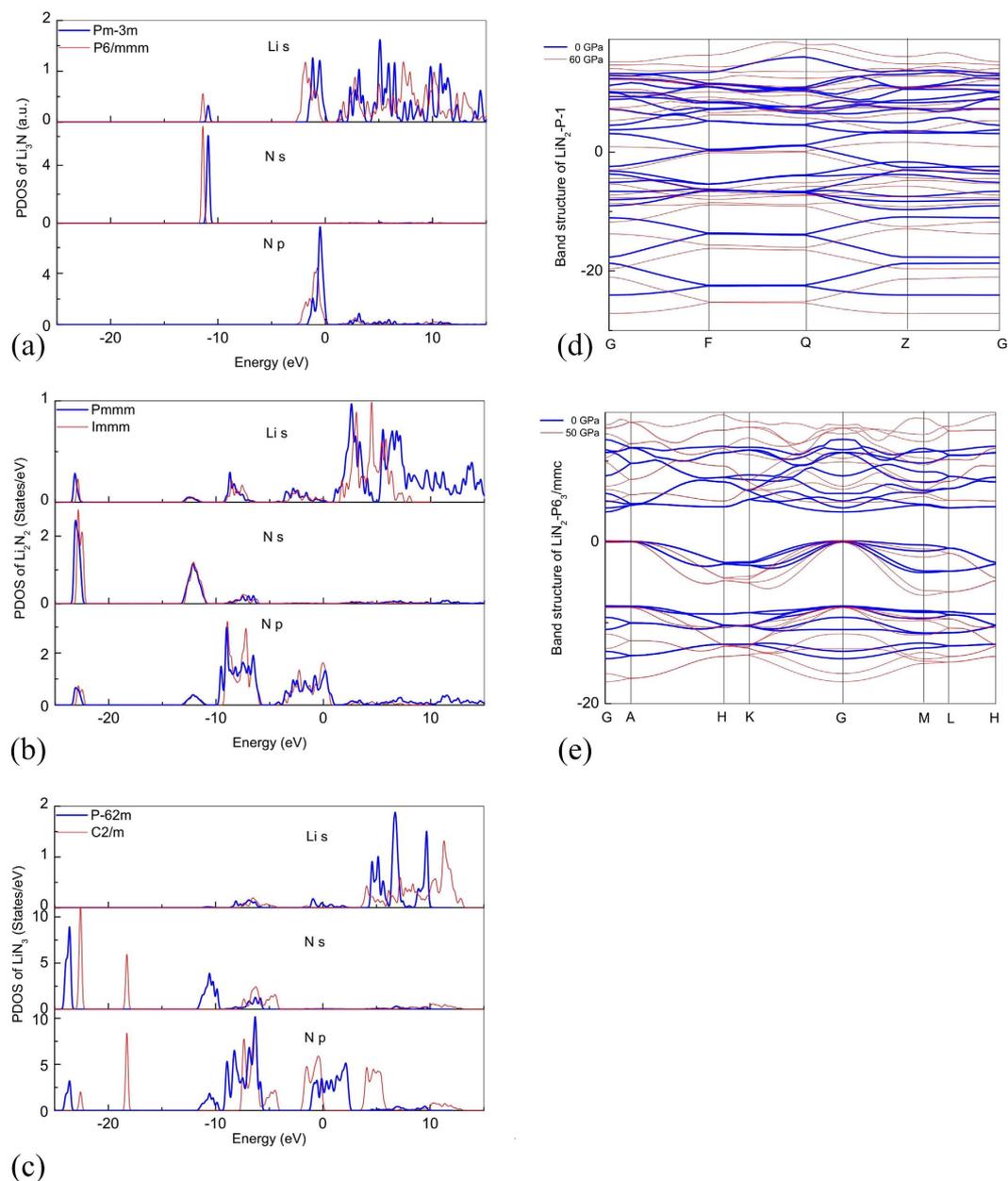
As observed in Fig. 3l, the P2<sub>1</sub>/c structure of LiN<sub>5</sub> consists of isolated Li atoms and N<sub>5</sub> rings, which up to now were only detected in molecular complexes<sup>19</sup>. At 50 GPa, the N-N distances are 1.286, 1.291, 1.299, 1.303 and 1.305 Å, respectively. The higher-pressure C2/c phase also consists of isolated Li atoms and N<sub>5</sub> rings (Fig. 3m). Unlike in P2<sub>1</sub>/c, the N<sub>5</sub> 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 Li<sub>13</sub>N, Li<sub>5</sub>N and Li<sub>3</sub>N<sub>2</sub> are metallic. The Pm $\bar{3}$ m phase of Li<sub>3</sub>N is a semiconductor with the DFT band gap of 0.84 eV. All three stable phases of Li<sub>2</sub>N<sub>2</sub> are also metallic, in agreement with experiment<sup>15</sup>. Interestingly, LiN<sub>2</sub> has a metal-insulator transition: P6<sub>3</sub>/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 $\bar{6}2$ m phase of LiN<sub>3</sub> is also metallic, combining with previously known phases of LiN<sub>3</sub>, we find that the sequence of transitions of LiN<sub>3</sub> under pressure is extremely unusual: from metallic to insulating to metallic to insulating. The P2<sub>1</sub>/c and C2/c phases of LiN<sub>5</sub> 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 Li<sub>3</sub>N (or Li<sub>2</sub>N<sub>2</sub> or LiN<sub>3</sub>) at 0 GPa are obviously different. The newly found phases Pm $\bar{3}$ m-Li<sub>3</sub>N, Pmmm-Li<sub>2</sub>N<sub>2</sub> and P $\bar{6}2$ m-LiN<sub>3</sub> 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 $\bar{1}$ -LiN<sub>2</sub> and P6<sub>3</sub>/mmc-LiN<sub>2</sub> 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 $\bar{1}$ -LiN<sub>2</sub> 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 Li<sub>3</sub>N, Li<sub>2</sub>N<sub>2</sub> and LiN<sub>3</sub>, we found five novel compositions which should be experimentally synthesizable under pressure, including Li<sub>13</sub>N, Li<sub>5</sub>N, Li<sub>3</sub>N<sub>2</sub>, LiN<sub>2</sub>, and LiN<sub>5</sub>. Notably, the N-N bonding patterns evolve from isolated N ions to N<sub>2</sub> dumbbells, to linear N<sub>3</sub> groups, infinite nitrogen chains, N<sub>5</sub> rings with increasing N content. Interestingly, for the experimentally known compounds Li<sub>3</sub>N and LiN<sub>3</sub> at ambient conditions we find new lowest-energy structures (Pm $\bar{3}$ m and P $\bar{6}2$ m, 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 Li<sub>2</sub>N<sub>2</sub>. 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  $\text{Li}_3\text{N}$ ,  $\text{Li}_2\text{N}_2$  and  $\text{LiN}_3$  at 0 GPa. (d–e) Band structures of  $\text{P}\bar{1}$ - $\text{LiN}_2$  and  $\text{P6}_3/\text{mmc}$ - $\text{LiN}_2$  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<sup>33–35</sup>. 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<sup>36</sup>. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was employed to treat the exchange-correlation energy<sup>37</sup>, and the all-electron projector augmented wave (PAW) potentials were used to describe the core-valence interactions<sup>38</sup>. 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 code<sup>39</sup>. Our tests

showed that the effect of van der Waals interactions<sup>40,41</sup> on stability of lithium nitrides is negligible, which is consistent with other works<sup>23</sup>.

## References

- Boukamp, B. A. & Huggins, R. A. Lithium ion conductivity in lithium nitride. *Phys. Lett. A* **58**, 231–233 (1976).
- 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).
- Chen, P., Xiong, Z., Luo, J., Lin, J. & Tan, K. L. Interaction of hydrogen with metal nitrides and imides. *Nature* **420**, 302–304 (2002).
- Hu, Y. H. & Ruckenstein, E. Ultrafast reaction between Li<sub>3</sub>N and LiNH<sub>2</sub> to prepare the effective hydrogen storage material Li<sub>2</sub>NH. *Ind. Eng. Chem. Res.* **45**, 4993–4998 (2006).
- Lazicki, A. *et al.* New cubic phase of Li<sub>3</sub>N: Stability of the N<sub>3</sub><sup>-</sup> ion to 200 GPa. *Phys. Rev. Lett.* **95**, 165503 (2005).
- Lazicki, A. *et al.* Pressure-induced loss of electronic interlayer state and metallization in the ionic solid Li<sub>3</sub>N: Experiment and theory. *Phys. Rev. Lett.* **78**, 155133 (2008).
- Cui, S., Feng, W., Hu, H., Feng, Z. & Wang, Y. Structural transition of Li<sub>3</sub>N under high pressure: A first-principles study. *Solid State Commun.* **149**, 612–615 (2009).
- Evans, B. L., Yoffe, A. D. & Gray, P. Physics and chemistry of the inorganic azides. *Chem. Rev.* **59**, 515–568 (1959).
- Zhang, M., Yan, H., Wei, Q., Wang, H. & Wu, Z. Novel high-pressure phase with pseudo-benzene “N<sub>6</sub>” molecule of LiN<sub>3</sub>. *EPL-Europhys Lett.* **101**, 26004 (2013).
- 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).
- Wang, X. *et al.* Polymerization of nitrogen in lithium azide. *J. Chem. Phys.* **139**, 164710 (2013).
- Auffermann, G., Prots, Y. & Kniep, R. SrN<sub>2</sub> and SrN<sub>2</sub>: Diazenides by synthesis under high N<sub>2</sub> pressure. *Angew. Chem. Int. Ed.* **40**, 547–549 (2001).
- Vajenine, G. *et al.* Preparation, crystal structure, and properties of barium pernitride, BaN<sub>2</sub>. *Inorg. Chem.* **40**, 4866–4870 (2001).
- Zhang, X., Zunger, A. & Trimarchi, G. Structure prediction and targeted synthesis: A new NaN<sub>2</sub> diazenide crystalline structure. *J. Chem. Phys.* **133**, 194504 (2010).
- Schneider, S. B., Frankovsky, R. & Schnick, W. High-pressure synthesis and characterization of the alkali diazenide Li<sub>2</sub>N<sub>2</sub>. *Angew. Chem. Int. Ed.* **51**, 1873–1875 (2012).
- Chiesa, M. *et al.* Reductive activation of the nitrogen molecule at the surface of “electron-rich” MgO and CaO. The N<sub>2</sub><sup>-</sup> surface adsorbed radical ion. *J. Phys. Chem. B* **105**, 497–505 (2001).
- Kaim, W. & Sarkar, B. N<sub>2</sub><sup>3-</sup>: Filling a gap in the N<sub>2</sub><sup>n-</sup> Series. *Angew. Chem. Int. Ed.* **48**, 9409–9411 (2009).
- Chirik, P. J. One electron at a time. *Nature Chem.* **1**, 520–522 (2009).
- Vij, A., Pavlovich, J. G., Wilson, W. W., Vij, V. & Christe, K. O. Experimental detection of the pentaazacyclopentadienide (pentazolate) anion, cyclo-N<sub>5</sub><sup>-</sup>. *Angew. Chem. Int. Ed.* **41**, 3051–3054 (2002).
- Hu, C.-H. *et al.* Pressure-induced stabilization and insulator-superconductor transition of BH. *Phys. Rev. Lett.* **110**, 165504 (2013).
- Zhu, Q. *et al.* Stability of xenon oxides at high pressures. *Nature Chem.* **5**, 61–65 (2013).
- Zhang, W. *et al.* Unexpected stoichiometries of stable sodium chlorides. *Science* **342**, 1502–1505 (2013).
- Peng, F., Yao, Y., Liu, H. & Ma, Y. Crystalline LiN<sub>5</sub> predicted from first-principles as a possible high-energy material. *J. Phys. Chem. Lett.* **6**, 2363–2366 (2015).
- Hanfland, M., Syassen, K., Christensen, N. E. & Novikov, D. L. New high-pressure phases of lithium. *Nature* **408**, 174–178 (2000).
- Pickard, C. J. & Needs, R. J. Dense low-coordination phases of lithium. *Phys. Rev. Lett.* **102**, 146401 (2009).
- Lu, J., Wang, Y., Zhu, L. & Ma, Y. Predicted novel high-pressure phases of lithium. *Phys. Rev. Lett.* **106**, 015503 (2011).
- Pickard, C. J. & Needs, R. J. High-pressure phases of nitrogen. *Phys. Rev. Lett.* **102**, 125702 (2009).
- Wang, X. *et al.* Cagelike diamondoid nitrogen at high pressures. *Phys. Rev. Lett.* **109**, 175502 (2012).
- Botana, J. & Miao, M.-S. Pressure-stabilized lithium caesides with caesium anions beyond the -1 state. *Nat. Commun.* **5**, 4861 (2014).
- Zhang, W. & Oganov, A. R. *Stability of numerous novel potassium chlorides at high pressure*. arXiv:1405.3007 (2014).
- Bader, R. F. W. *Atoms in Molecules-A Quantum Theory* (Oxford Univ. Press, Oxford, 1990).
- 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).
- Oganov, A. R. & Glass, C. W. Crystal structure prediction using ab initio evolutionary techniques: principles and applications. *J. Chem. Phys.* **124**, 244704 (2006).
- Oganov, A. R., Lyakhov, A. O. & Valle, M. How evolutionary crystal structure prediction works - and why. *Acc. Chem. Res.* **44**, 227–237 (2011).
- 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).
- 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).
- Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
- Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl<sub>2</sub>-type SiO<sub>2</sub> at high pressures. *Phys. Rev. B* **78**, 134106 (2008).
- Bučko, T., Hafner, J., Lebegue, S. & Ángyán, 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).
- Bučko, T., Lebegue, S., Hafner, J. & Ángyán, 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/>