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Novel Crystalline LiN$_5$ Predicted from First Principles as a Possible High-Energy Material

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The search for stable polymeric nitrogen and polynitrogen compounds has attracted great attentions due to their potential applications as high-energy-density materials. Here we report a theoretical prediction of an interesting LiN$_5$ crystal through first-principles calculations and unbiased structure searching techniques. Theoretical calculations reveal that crystalline LiN$_5$ is thermodynamically stable at pressures above 9.9 GPa, and remains metastable at ambient conditions. The metastability of LiN$_5$ stems from the inherent stability of the N$_5^-$ anions and strong anion-cation interactions. It is therefore possible to synthesize LiN$_5$ by compressing solid LiN$_3$ and N$_2$ gas under high pressure and quench recover the product to ambient conditions. To the best of our knowledge, this is the first time that stable N$_5^-$ anions are predicted in crystalline states. The weight ratio of nitrogen in LiN$_5$ is nearly 91%, placing LiN$_5$ as a promising high energy material. The decomposition of LiN$_5$ is expected to be highly exothermic, releasing an amount of energy approximately 2.72 kJ·g^{-1}. The present results open a new avenue to synthesize polynitrogen compounds and provide a key perspective toward the understanding of novel chemical bonding in nitrogen-rich compounds.

Solid nitrogen containing single N−N and double bonds (polynitrogen) are of significant interest as high-energy-density materials (HEDM). The high energy content in polynitrogen stems from the large energy difference between the single (~40 kcal mol^{-1}) and double (~100 kcal mol^{-1}) bonds in polynitrogens and the N≡N bonds (~225 kcal mol^{-1}) in N$_2$ molecules. The decomposition of polynitrogens is expected to be highly exothermic, releasing an enormously large amount of energy. Over the years many forms of polynitrogen have been proposed as targets for synthesis, ranging from purely single-bonded structures to chain structures containing alternating single and double bonds [1-8]. Several predictions have already made their real-world appearance, among which perhaps the most prominent case is the cubic gauche (*cg*) nitrogen [9], formed solely from single bonds, and synthesized under high-temperature high-pressure conditions. On the other hand, polynitrogens often have kinetic instability which make ambient-pressure recovery difficult. Since the kinetic stability of a molecule is determined by its weakest bond, it is possible to stabilize polynitrogens through ionization. Particular nitrogen-rich compounds containing ionized polynitrogens were shown to have significantly improved kinetic stability while maintaining the energy release capability [10-13]. Preparation of these compounds involve substantial difficulties due to the instability of the products, which often cause explosions. Nevertheless, a major came in 2004 when a kinetic stable N$_5^+$ solid, N$_5^+$SbF$_6^-$, synthesized and soon demonstrated as a promising HEDM [14]. On the other hand, although intense research effort also been devoted to pursuit novel N$_5^-$ materials, the realization of the bulk crystals has not yet be achieved.

In the present study, we therefore investigated the possible formation and stability of N$_5^-$ in solid phases. Lithium was specifically chosen to ionize the N$_5$ molecule since the large electron affinity of Li$^+$ is expected to increase the structure stability based on Born-Haber cycle consideration. Previous quantum-mechanical calculations have already established the Li-N$_5$ complex as an energy minimum in the potential energy surface [15, 16]. The stabilizing interactions in the complex may raise the activation barrier sufficiently such that the LiN$_5$ crystal can be formed. Theoretical prediction of LiN$_5$ crystal was achieved in the present study by using an unbiased structure search method based on swarm-intelligence CALYPSO algorithm [17, 18] in conjunction with density functional calculations. Significantly, LiN$_5$ is predicted to become thermodynamically stable at pressures above 9.9 GPa, well within the current capability of high-pressure synthesis. Due to strong ionic interactions, the LiN$_5$ crystal is mechanically stable at ambient pressure. The inherent metastability of the N$_5^-$ anion is expected to result in considerable kinetic stability of the crystal that may be sufficient for an ambient-pressure recovery. The energy density of the predicted LiN$_5$ phase is approximately 2.72 kJ·g^{-1}, making it a promising HEDM candidate.

To construct a phase diagram of the binary Li-N system, we searched for the thermodynamically stable structures of various stoichiometry of LiN$_x$ (x = 1/3, 1/2, 1, 3/2, 2, 5/2, 3, 4, 5 and 6) using simulation cells containing up to four LiN$_x$ units. Structure searches were carried out five pressures (0, 10, 20, 50, and 100 GPa) using the swarm optimization methodology as implemented in the

CALYPSO code [17, 18]. Density functional total energy calculations and geometrical optimizations were performed using the VASP (Vienna Ab Initio simulation package) program [19] with the Perdew-Burke-Ernzerhof [20] parameterization of generalized gradient approximation. Zero-point corrections to the total energies were estimated using the harmonic approximation. The projector-augmented wave (PAW) method [21] was employed with the PAW potentials [22] taken from the VASP library where $1s^2 2s^1$ and $2s^2 2p^3$ are treated as valence electrons for Li and N atoms, respectively. A kinetic energy cutoff of 750 eV was used for the plane-wave basis set. A dense k-point grid with the spacing of $2\pi \times 0.03$ Å^{-1} was used to sample the Brillouin zone and shown to yield excellent convergence for total energies.

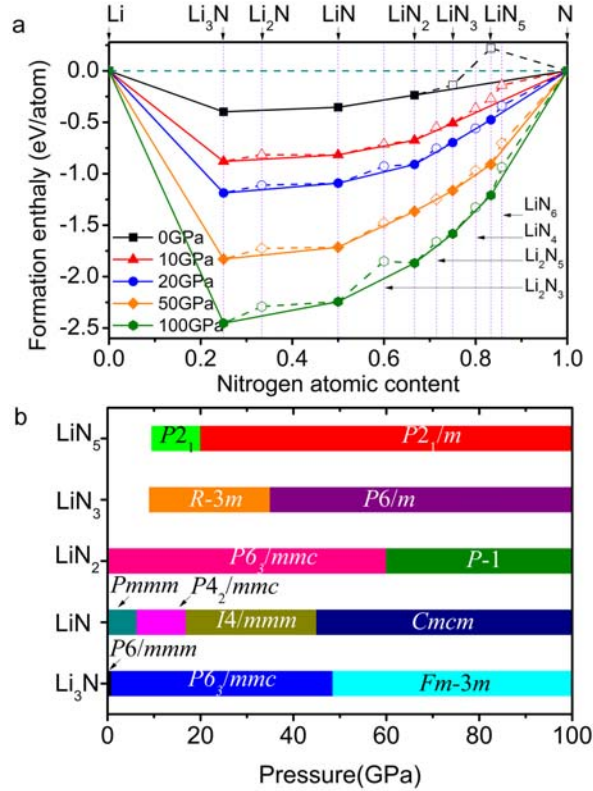FIG.1 (Color online). (a) Enthalpies of formation of various LiN$_x$ compounds under pressure. All calculated points are connected by the dotted lines, whereas the convex hull is constructed by solid lines. Van der Waals interactions were included in the calculations at ambient pressure. (b) Calculated thermodynamically stable ranges for LiN$_x$ compounds.

Thermodynamic stability of the LiN$_x$ crystals obtained in the structure searches were examined using their enthalpies of formation with respect to the crystals of N$_2$ and Li. To account for all possible decompose routes, a convex hull of the enthalpies of formation of LiN$_x$ is constructed at each pressure (Fig. 1a). The LiN$_x$ stoichiometries that are part of the convex hull (solid lines)

are stable with respect to decomposition into other binary stoichiometries and/or elements. The stoichiometries located above the convex hull (dashed lines) are either unstable, or metastable if the kinetic barrier is sufficiently high. Apparently, high metastability is a crucial asset for the applications of HEDMs. On decomposition, a metastable structure above the convex hull reduces to the products on the hull, and release an amount of energy corresponding to their energy difference. Fig. 1a shows that several LiN$_x$ crystals, including Li$_3$N, LiN, LiN$_2$, LiN$_3$ and LiN$_5$, are either thermodynamically stable or can be thermodynamically stable under pressure. The predicted pressure ranges of thermodynamic stability for these crystals are presented in Fig. 1b, noting several structure changes at high pressure. Among all LiN$_x$ crystals, Li$_3$N is the most thermodynamically stable phase throughout the entire pressure range. Our results show that Li$_3$N transforms from the α-phase ($P6/mmm$) to the β-phase ($P6_3/mmc$) near 1 GPa, and to the γ-phase near 48.5 GPa, both in good agreement with the experiment [23]. The Bader charge analysis [24] reveals an almost complete electron transfer between Li and N atoms, resulting in the N^{3-} anion with completely filled subshells. The N atoms are therefore not bonded together which eliminates Li$_3$N as a candidate for HEDMs. Significantly, two hitherto unknown stoichiometries, LiN and LiN$_2$, were also uncovered in our calculations as thermodynamic ground state. We have predicted four stable structures of LiN ($Pmmm$, $P4_2/mmc$, $I4/mmm$, and $Cmcm$) and two stable structures of LiN$_2$ ($P6_3/mmc$ and P-1) at different pressure ranges which hopefully can be synthesized in future experiments. Most of the predicted LiN and LiN$_2$ crystals contain diatomic N$_2$ anions and this predominates their thermodynamic stability. Detailed information of the predicted stoichiometries/structures are presented in Table S1, and Figs. S1 to S4 of the Supplementary Material [25].
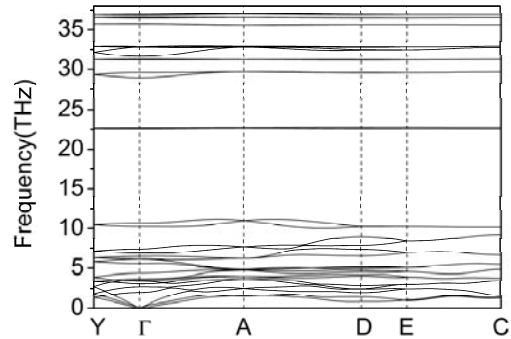

FIG. 2. Phonon dispersion curves for the $P2_1$ structure of LiN$_5$ at ambient pressure.

Amazingly, our structure predictions for this first time uncovered LiN$_5$ as a thermodynamic ground state at high pressure. The predicted LiN$_5$ crystal is stable above 9.9 GPa (with zero-point corrections), which is very similar to the pressure required for stabilizing LiN$_3$, a known high-energy material [26]. Crystal structures in this pressure range are well accessible in high-pressure

synthesis. Phonon calculations in Fig. 2 reveals no imaginary vibrational modes for the LiN_5 crystal at ambient pressure, suggesting that it is mechanical stable and might be quench recoverable. To examine the metastability of LiN_5, we performed first principles molecular dynamics simulations [19] using a canonical ensemble at ambient pressure and room temperature (300 K). After typically long simulation time (10 ps), the structure of LiN_5 remains unchanged. The predicted metastability of LiN_5 is consistent with previous quantum-mechanical calculations [16] in which the N_5^- anion is shown to possess significant kinetic stability toward dissociation. The calculated activation barrier for the dissociation of N_5^- into N_3^- and N_2 is 19.4 kJ mol^{-1}, allowing for a kinetic stable region for LiN_5 at ambient conditions. The weight ratio (w.t.) of nitrogen in LiN_5 is as high as 91%. The ambient-pressure decomposition of LiN_5 is estimated to release 2.17 eV energy per LiN_5 unit, which corresponds to an energy density of approximately 2.72 kJ·g^{-1}. Such a high energy content, if realized, would place LiN_5 among modern high-energy materials such as TATB, RDX, and HMX which typically have the energy densities ranging from 1 to 3 kJ·g^{-1} [27].
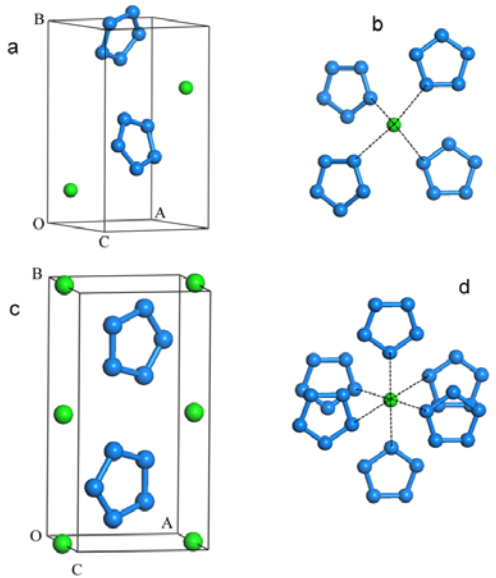

FIG. 3 (Color online). (a) The unit cell of the $P2_1$ structure and (b) tetrahedral arrangement of four N_5^- surrounding Li. (c) The unit cell of the $P2_1/m$ structure and (c) octahedral arrangement of six N_5^- surrounding Li.

The predicted LiN_5 crystal has peculiar structures composed of cyclic N_5 molecules and Li atoms. Below 20 GPa, the crystal structure has the $P2_1$ space group (Fig. 3a). Above 20 GPa, the structure changes to a more ordered $P2_1/m$ symmetry (Fig. 3c). Both $P2_1$ and $P2_1/m$ structures have monoclinic unit cells containing two formula units [25]. In LiN_5, the valence electrons are depleted from the Li atoms and almost all transferred to nearby N_5 molecules, resulting in nominal N_5^- anions in the crystal. Both the Bader charge analysis [24] and density of states (DOS)

calculation (Fig. 4a) confirmed this assignment. Moreover, this is also consistent with the gas-phase calculation in which the cyclic geometry was identified to be the global minimum of N_5^- [16]. Yet, the N_5^- anion is isoelectronic with cyclopentadiendide $C_5H_5^-$ and therefore is considered as the nitrogen analog of the latter. Notably, the N_5^- anions were found to be very robust to the stacking effects in the crystal. The N–N bond lengths of the N_5 rings are almost perfectly equal in LiN_5 and insensitive to pressure changes. The $P2_1$ structure, for example, have the N–N bond lengths varying slightly between 1.33 and 1.34 Å, which agree very well with the gas-phase values [16]. Upon compression, LiN_5 experiences interesting coordination changes (Figs. 3a and 3b). In the $P2_1$ structure, the Li atoms are each coordinated with four N_5 rings in a distorted tetrahedral arrangement (Fig. 3b). The four Li-N distances are between 2.18 and 2.30 Å (calculated at 0 GPa). In the $P2_1/m$ structure, the coordination increases to octahedral where the Li atoms are each coordinated with six N_5 rings with the Li-N distances decreasing to between 2.07 to 2.18 Å (calculated at 20 GPa) (Fig. 3d). This four-to-six fold change of local bonding environment reveals the stabilization effects of pressure, as commonly seen in ionic solids [28].
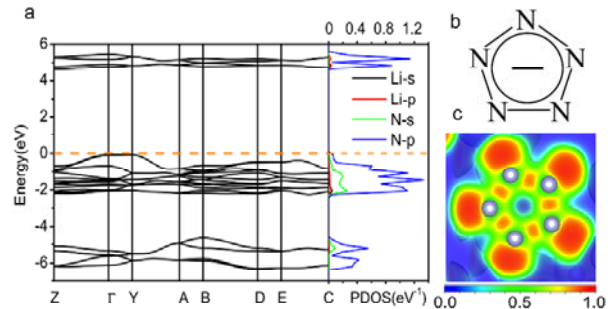

FIG. 4 (Color online). (a) Electronic band structure and projected DOS of the $P2_1$ structure calculated at ambient pressure. (b) Minimum energy structure of the D_{5h} planer N_5^-. (c) The ELF contours illustrated on a plane containing N_5^- in the $P2_1$ structure.

Crystalline LiN_5 is an insulting phase resulted from the ionic nature of the structure. The bonding in the N_5^- anion is covalent and stabilized by the electron transferred from nearby Li atoms. Calculated electronic band structure and projected DOS for the $P2_1$ structure at ambient pressure are presented in Fig. 4a, which reveals that the entire energy range is dominated by the bands of the N_5^- anion. A large band gap of nearly 4.6 eV appears between the valence and conduction bands. The undistorted N_5^- anion has the D_{5h} symmetry (Fig. 4b). To illustrate its bonding feature, we adopted an intuitive approach via calculation of the electron localization function (ELF) [29]. The ELF is a measure of relative electron localization in extended structures, and large ELF values usually occur in regions where there is a high tendency of electron pairing, such as cores, bonds, and lone pairs. Fig. 4c shows the ELF contours drawn in the plane of the N atoms for the

N_5^- anion which recovers neatly its bonding pattern. The high ELF regions (red) reveal five nonpolar σ-bonds, and five lone pairs in the molecular plane. Outside the plane the six π electrons have cyclic delocalization, forming an aromatic set of π bonds spanning all N atoms. All five N−N bonds in the N_5^- are of the same length, i.e., 1.33-1.34 Å, greater than a double bond (1.20 Å) but shorter than a single bond (1.45 Å). This intermediate distance is consistent with the electron delocalization where the π electrons are distributed equally between each of the five N atoms. Calculated Mayer bond order (MBO) [30] also confirms that the bonding in N_5^- (1.42) is an intermediate between the single (1.0) and double (2.0) bonds. In comparison, the calculated MBO for the N_3^- (open chain structure) in LiN_3 is 1.93, revealing typical double bond feature. A six-π-electron five-member ring obeys the Hückel's rule, thus the N_5^- anion is expected to be stable against nonplanar distortion. The intrinsic stability of the N_5^- anions is a key to the kinetic stability of the LiN_5 crystal, whereas the cation-anion electrostatic interactions also make significant contributions.

In summary, based on swarm-intelligence structure searches, we predicted a new crystal LiN_5, which is expected to be mechanically stable at ambient conditions. At pressures above 9.9 GPa, LiN_5 is thermodynamically stable with respect to all decomposition routes, suggesting that it may be prepared by high-pressure synthesis. Due to the intrinsic stability of the N_5^- anions, the LiN_5 crystal has considerable kinetic stability that may be sufficient for an ambient-pressure recovery. On decomposition, LiN_5 is expected to release an enormously large amount of energy (2.72 kJ·g^{-1}), and thus may find applications as a high energy material. This therefore represent an exciting prediction and hopefully can encourage experimental efforts in its synthesis.

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