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# High Energy Density Nitrogen-Rich Extended Solids

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**Abstract.** Many simple molecules such as N<sub>2</sub> and CO<sub>2</sub> have the potential to form extended “polymeric” solids under extreme conditions, which can store a large sum of chemical energy in its three-dimensional network structures made of strong covalent bonds. Diatomic nitrogen is particularly of interest because of the uniquely large energy difference between the single (160 kJ/mol) and triple (950 kJ/mol) bonds. As such, the transformation of singly bonded polymeric nitrogen back to triply bonded diatomic nitrogen molecules can release large energy (~33 kJ/cm<sup>3</sup> – three times that of HMX) without any negative environmental impact. Therefore, the goal of the present study has been to investigate the transformation of nitrogen and nitrogen-rich compounds to new singly bonded nitrogen-rich solids at high pressures and temperatures, using heated diamond anvil cells, Raman spectroscopy, and third-generation synchrotron x-ray diffraction. Recently, we have found a new form of singly bonded layered polymeric nitrogen (LP-N), synthesized in the stability pressure-temperature field higher than that of cg-N. This new phase is characterized by a 2D layered structure similar to the predicted *Pba2* and two colossal Raman bands, arising from two groups of highly polarized nitrogen atoms. This result also provides a new constraint for the nitrogen phase diagram, highlighting an unusual symmetry lowering 3D cg- to 2D LP-N transition and thereby the enhanced electrostatic contribution to the stabilization of this densely packed LP-N. In this paper, we will review this finding of LP-N, update the phase diagram of nitrogen, and offer a chemistry view of pressure-induced transformations in dense molecular solids.

## INTRODUCTION

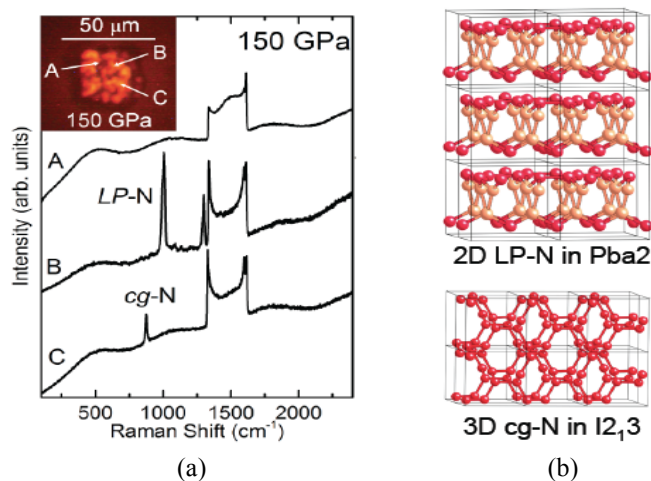
Understanding of condensed matter phenomena at extreme conditions offers unique opportunities for designing and synthesizing novel materials. These materials, both stable and metastable ones, possess with optimized properties over a wide range of length scales -- far beyond those achieved by other methods such as varying temperatures and chemical composition. Among novel phenomena uniquely occurring at high pressures is the pressure-induced electron delocalization from a simple molecular solid to a non-molecular extended solid such as a metal and a three-dimensional (3D) network polymer (e.g., diamond). Because of the strong chemical bonds connecting the network structure, the extended solid is often recoverable at ambient conditions and is metastable with very high chemical energy. Therefore, the objective of the present study is aimed to exploiting such a new class of energy materials under extreme conditions and providing the scientific basis for development of advanced energy storages and novel propellants in high energy density.

Nitrogen molecule represents the strongest covalent bond known, which makes it extremely stable and chemically inert at ambient conditions. It is also the first molecular system predicted to transform into a polymeric form prior to the metallization [1], which has been discovered later in laser-heated DAC experiments above 110 GPa and 2000 K [2,3]. This successful prediction of cg-N has stimulated the search for other singly bonded polymeric forms of nitrogen and other molecular solids. As a result, a large number (over dozen) of extended nitrogen structures have been predicted to be stable in various forms; yet, the cg-N was the only extended phase of nitrogen discovered until very recently. Recently, we discovered new singly bonded extended nitrogen [4], synthesized using

laser-heated diamond anvil cells at pressures between 120-180 GPa, well above the stability field of *cg*-N. This new phase was characterized by its singly bonded, layered polymeric (LP) structure similar to the predicted *Pba2* and two colossal Raman bands arising from two groups of highly polarized nitrogen atoms in the bulk and surface of the layer. This finding of LP-N, in turn, provided a new constraint for the nitrogen phase diagram, highlighting an unusual symmetry lowering *3D cg*- to *2D LP*-N transition and thereby the enhanced electrostatic contribution to the stabilization of this densely packed layer structure of LP-N ( $\rho = 4.85 \text{ g/cm}^3$  at 120 GPa). In this paper, we will review this finding of LP-N, update the phase diagram of nitrogen, and offer a chemistry view of pressure-induced transformations of dense molecular solids that occur at large compression energies rivaling strong chemical bonds energies.

## SINGLY BONDED LAYERED POLYMERIC NITROGEN (LP-N)

Here, we briefly summarize our recent finding of layered polymeric nitrogen (LP-N), reported in Ref. [4]. Singly bonded LP-N was synthesized by laser heating nitrogen samples at pressures between 125-175 GPa and temperatures above 2000 K, which formed together with *cg*-N and amorphous N (Fig. 1a). The presence of transparent LP-N phase can be easily confirmed by two strong Raman peaks at  $\sim 1005$  and  $1300 \text{ cm}^{-1}$ , in contrast to the characteristic single phonon of *cg*-N. The Raman cross section of LP-N is estimated to be approximately three times that of diamond single crystal and possibly the largest of all solids. The crystal structure of LP-N was found similar to the predicted layer structure of *Pbca2* with excellent agreement in density and lattice parameters (Fig. 1b). Based on the third-order Birch-Murnaghan EOS fits to the present results, LP-N ( $\rho = 4.85 \text{ g/cm}^3$ ) is found  $\sim 7.8\%$  denser than *cg*-N ( $4.50 \text{ g/cm}^3$ ) at 120 GPa and is also  $\sim 22.5\%$  stiffer,  $B_0 = 342 \text{ GPa}$  and  $B' = 6.0$ , than *cg*-N,  $B_0 = 279 \text{ GPa}$  and  $B' = 4.8$ . Efforts to recover these extended phases to pressures below 50 GPa were unsuccessful due to catastrophic diamond failure.

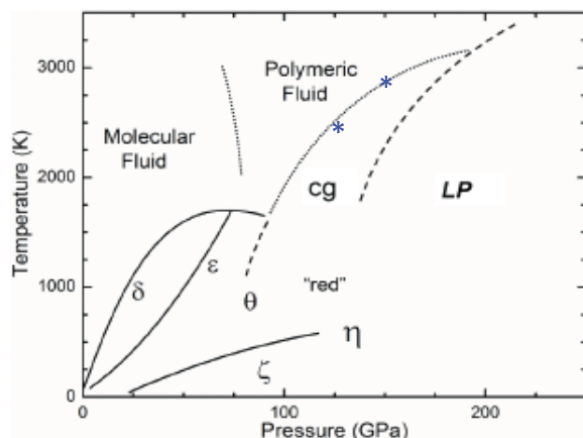


**FIGURE 1.** (a) Raman spectra of laser-heated nitrogen at 150 GPa, showing the presence of *cg*-N, LP-N and amorphous-N as presented in Ref. [4]. (b) Crystal structures of 2D layered LP-N in *Pba2* and 3D network *cg*-N in *I213*.

## PHASE DIAGRAM OF NITROGEN

The discovery of LP-N provides new constraints for the phase diagram of nitrogen (Fig. 2). At low pressures, nitrogen represents a classical diatomic molecular system with a strong triple bond ( $\text{N}\equiv\text{N}$ ), exhibiting fascinating polymorphism with four solid molecular phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) below 10 GPa and 300 K [5,6]. Upon further compression,  $\delta$ -N<sub>2</sub> undergoes a series of structural phase transitions to  $\epsilon$ -,  $\zeta$ - and black amorphous  $\eta$ -N<sub>2</sub> at ambient temperature. Upon heating at high pressures,  $\zeta$ -N<sub>2</sub> transforms to  $\epsilon$ -,  $\delta$ -,  $\theta$ -, and amorphous “red”-N<sub>2</sub> [7-9]. These transitions are, however, known to show strong path dependencies, which underscore the intermediary nature of bonding in these phases between molecular (below 60-80 GPa) and extended solids (above 100-120 GPa). Above 120 GPa, nitrogen becomes fully extended to form *cg*-N and LP-N. The phase boundaries are difficult to determine,

as the transitions are often controlled kinetically (signified by dashed lines). Nevertheless, we suggest a positive slope for the *cg*- and LP- phase boundary, based on (i) the higher density of LP-N compared to *cg*-N, (ii) the strong presence of *cg*-N in the stability field of LP-N (not the other way), and (iii) the absence of LP-N in the stability field of *cg*-N between 100 and 125 GPa. The melting line of *cg*-N and the liquid-liquid transition line (dotted lines) are reproduced from those predicted theoretically and we have recently confirmed by the melting temperatures (blue asterisks in Fig. 2) determined by *in-situ* synchrotron x-ray/laser-heating experiments using the 16IDB beamline at the Advanced Photon Source (APS). In this x-ray/laser-heated melting experiment, the onset of melting was referred by disappearance and reappearance of the major diffraction peak (200) of *cg*-N upon laser heating. Further details will be presented in the forthcoming paper.



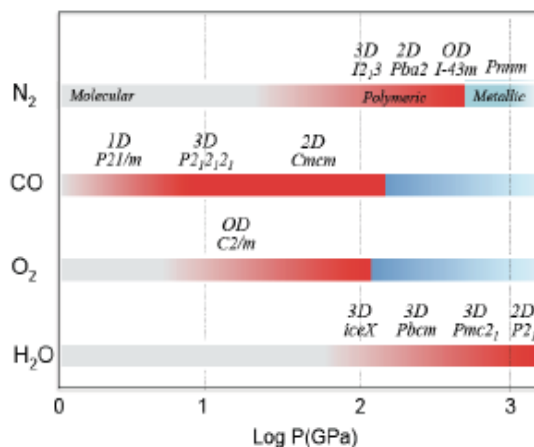
**FIGURE 2.** Phase diagram of nitrogen at high pressures and temperatures. Two asterisks signify the recently measured melting temperatures by *in-situ* laser-heating/x-ray diffraction, confirming the predicted melt curve.

The present phase diagram of dense nitrogen underscores the pressure-induced *3D-to-2D* structural transition, in contrast to more commonly observed *2D-to-3D* transitions at high pressures as in, for example, the graphite-to-diamond transition. However, several recent theoretical calculations have predicted the stabilization of *2D* layer structures at very high pressures. Those predictions include *2D* polymeric-CO in *Cmcm* [10], partially ionized extended layers of H<sub>2</sub>O in *P2<sub>1</sub>* [11], and the graphene-like structure suggested for recently discovered H<sub>2</sub>-IV [12]. In this regard, the *cg*- to LP-N transition is not surprising, but provides significant implications to those transitions in other molecular systems and, together, the pressure-induced chemistry in dense solids.

## CHEMISTRY IN DENSE SOLIDS

The present discovery of LP-N offers a new fundamental insight into the pressure-induced ionization overtaking the pressure induced hybridization in densely packed molecular systems. Upon large compression molecular solids transform into extended polymeric structures to soften highly repulsive intermolecular interaction by delocalizing valence electrons or making bonds between nearby molecules (i.e., the pressure-induced electron delocalization). These polymeric structures can further undergo symmetry-breaking distortions to enhance their packing efficiencies, which result in commensurate or incommensurate structures depending on the polarity of the bonds and the miscibility. Upon further compression the electrostatic packing energy dominates over the electron hybridization energy, converting these covalent network structures into ionic solids (pressure-induced ionization) or extended mixtures of constituting elements (phase separation). In fact, recent theoretical calculations have shown that many, if not all, molecular solids transform into extended solids with more itinerant electrons in covalent or metallic network structures. Figure 3 summarizes a selected set of extended structures previously predicted in terms of first principles density functional theories [10-15]. Note that not all of these structures have been found experimentally except a few -- the 3D *I2<sub>13</sub>* (*cg*-N), 2D *Pba2* (LP-N), and 0D-*C2/m* ( $\epsilon$ -O<sub>2</sub> or a cluster of (O<sub>2</sub>)<sub>4</sub> [16]. In turn, the limited findings advocate for searching these predicted structures and gaining systematic insights into those unusual transformations. Importantly, these low *Z* extended solids are likely high energy density solids with energy content

of ~10-100 kJ/g and may also exhibit other novel properties such as super hardness, superconductivity and nonlinear optical properties [4,17,18].



**FIGURE 3.** A schematic to show a small subset of recently predicted extended structures of  $N_2$ ,  $CO$ ,  $O_2$ , and  $H_2O$  [10-15], highlighting the symmetry breaking phase transition from 3D networks to 2D layers in  $N_2$ ,  $CO$ , and  $O_2$ . However, these structures have not been found experimentally except the 3D- $I2_3$  ( $cg$ -N) and 0D- $C2/m$  ( $\epsilon$ - $O_2$  or a cluster of  $(O_2)_4$ ), advocating further studies. Gray, red, and blue bars signify insulating molecular, polymeric, and metallic states of the solids.

## ACKNOWLEDGMENTS

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## REFERENCES

1. C. Mailhiot, L. H. Yang, A. K. McMahan, *Phys. Rev. B* **46**, 14419 (1992).
2. M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, et al., *Nature Materials* **3**, 558 (2004).
3. M. J. Lipp, J.-H. Klepeis, B. Baer, et al., *Phys. Rev. B* **76**, 014113 (2007).
4. D. Tomasino, M. Kim, J. Smith, and C.S. Yoo, *Phys. Rev. Lett.* **113**, 205502 (2014).
5. D. Schiferl, S. Buchsbaum, and R.J. Mills, *J. Phys. Chem.* **89**, 2324 (1985).
6. R. Bini, L. Ulivi, J. Kreutz, and H.J. Jodl, *J. Chem. Phys.* **112**, 8522 (2000).
7. E. Gregoryanz, A. F. Goncharov, R. J. Hemley, et al., *Phys. Rev. B* **66**, 224108 (2002).
8. A.F. Goncharov, J.C. Crowhurst, V.V. Struzhkin et al., *Phys. Rev. Lett.* **101**, 95502 (2008).
9. D. Tomasino, Z. Jenei, W. Evans, and C.S. Yoo, *J. Chem. Phys.* **140**, 244510 (2014).
10. J. Sun, D.D. Klug, C.J. Pickard, et al., *Phys. Rev. Lett.* **106**, 145502 (2011).
11. A. Hermann, N.W. Ashcroft, R. Hoffmann, *Proc. Nat. Acad. Sci.* **109**, 745 (2012).
12. C.J. Pickard, M. Martinez-Gonzales, and R.J. Needs, *Phys. Rev. B* **85**, 214115 (2012).
13. Y. Ma, A.R. Oganov, Z. Li, Y. Xie, and J. Kotakoski, *Phys. Rev. Lett.* **102**, 065501 (2009).
14. S. Bernard, G.L. Chiarotti, S. Scandolo, and E. Tosatti, *Phys. Rev. Lett.* **81**, 2092 (1998).
15. Y. Wang, H. Liu, J. Lv, Li Zhu, H. Wang, and Y. Ma, *Nature Comm.* **2**, 563 (2011).
16. G. Weck, S. Desgreniers, P. Loubeyre, M. Mezouar, *Phys. Rev. Lett.* **102**, 255503 (2009).
17. R.P. Dias, C. S. Yoo, V.V. Struzhkin, et al., *Proc. Nat. Acad. Sci.* **110**, 11720 (2013).
18. V. Iota, C. S. Yoo, H. Cynn, *Science* **283**, 1510 (1999).