

Polymeric nitrogen: A review of experimental synthesis method, structure properties and lattice dynamic characterization from large scientific facilities and extreme spectroscopy perspectives

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ABSTRACT

Single-bonded polymeric nitrogen (PN) synthesized under high pressure was highly delivered for its valuable application prospects on high-energy-density materials (HEDM) and profound effects for understanding the interaction behavior of simple diatomic. Since the 1980s, polymeric phases of nitrogen have displayed remarkable complexity under extreme conditions of pressure and temperature that fascinated theoreticians and experimentalists. The high-pressure X-ray diffraction (XRD) and Raman spectroscopy experiments on PN made it possible to elucidate their evolution, in particular, to measure important structural information through scientific facilities. Here, the synthesized PN hitherto, including cubic gauche nitrogen (cg-N), layered polymeric nitrogen (LP-N), hexagonal layered polymeric nitrogen (HLP-N), post-layered-polymeric nitrogen (PLP-N), and black phosphorous structure nitrogen (BP-N) are reviewed. The synthesized methods, diagnosed technologies, lattice dynamics, and experimental challenges are introduced, with a particular focus on their structural similarity and lattice dynamic characterization, and the Raman criterion for nitrogen polymerization is also given. Finally, we propose the expectation of developing free-electron laser (FEL) and high-pressure neutron technology which is a potential key in the research of fundamental elements under high pressure.

1. Introduction

Energetic materials could release a large amount of energy in the process of explosive chemical reactions or bond converting, providing huge kinetic and thermal energy. However, traditional explosives have reached the limit of the energy released by molecules.¹ Novel energetic candidates have been attracting significant attention for wide application prospects as explosives and propellants. Nitrogen (N) is one of the extremely particular and important elements. With five outermost valence electrons and a relatively complex electronic structure, N atoms have many possible bonding modes. Interestingly, the triple bond of nitrogen ($N \equiv N$) is known as the strongest covalent bond (946 kJ mol^{-1}).² The strength is much higher than that of its single bonds (159 kJ mol^{-1}) or the double (417 kJ mol^{-1}) bonds.³ It's different totally from the case of other group V elements. Thus, N exists as diatomic molecules at ambient conditions. Gaseous nitrogen consisting of molecule nitrogen (N_2) is the first and the only all-nitrogen material found in nature up to now, assuming a stable energy level and chemically inert. Breaking $N \equiv N$ to form different bonding forms thus requires overcoming the great energy

barrier. In turn, precisely owing to the great differences in the nitrogen bond-dissociation energies, a large amount of energy would be released under the transformation from single (N–N) or double (N=N) bonds to the triple-bonded molecular nitrogen. The material composed of pure nitrogen single bond even has more than 3 times the energy density than trinitrotoluene (TNT).⁴ Therefore, there is considerable interest in a class of substances containing a high proportion of N–N or N=N in ions, clusters and units. Among them, polymeric nitrogen consisting of only nitrogen atoms has great advantages: high energy density and environmentally harmless product. Besides, it is found in experiments that nitrogen commonly existing in the air will polymerize as various single-bonded forms under extreme conditions. On the other hand, itself and the evolution of nitrogen bonds are unique whereas its near atoms or same group elements have been found in a series of non-triple-bonded forms at ambient conditions. The study of nitrogen might be helpful to elucidate the behavior of other important low atomic number diatomic molecules (such as H_2 and O_2) in the warm dense regime. Unlocking the nature of the similar behavioral characteristics of simple diatomic molecules in condensed phases also is valuable. In this

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sense, PNs have received much attention within the high-pressure physics community and chemistry.

The released energy of explosion during the dissociation of nitrogen compounds is linked to the amount of N–N and N=N. Consequently, nitrogen-rich materials composed mainly of nitrogen, especially all-nitrogen compounds have been highly interested. Much effort has been paid theoretically and experimentally to searching the stable candidates. At present, the candidates mainly contained 3 classes: nitrogen cluster compounds, ionic compounds, and their energetic derivatives, and solid PN with a crystal structure under high pressure. The aspect of ionic all-nitrogen compounds has made some practical progress. Hitherto, there are three N_3^- , N_5^+ , and *cyclo*- N_5^- that stabilized in ionic nitrogen-rich compounds put into application.^{5–7}

Polymeric nitrogen consisting of N atoms connected in the form of N–N is the all-nitrogen compound with the highest energy content and the hardest preparation conditions. Since the first successful synthesis of cg-N in 2004 which verified the fact that the intermolecular triple bonds of $N \equiv N$ can be ruptured by an application of laser-heating diamond anvil cell (LHDAC) forming a cubic polymeric network of single-bonded nitrogen atoms,⁸ the successful prediction of cg-N has stimulated the theoretical search for other singly-bonded polymeric forms of nitrogen. Yet, more than two dozen extended nitrogen structures have been predicted by those theoretical calculations.^{9–17} However, up to now, there only are other four PN phases have been experimentally observed except for the cg-N,⁸ LP-N,¹⁸ BP-N,^{19,20} PLP-N,²¹ and HLP-N,²² covering a wide range of pressure-temperature (*P-T*) regime (110–244 GPa, 2000–4000 K).

The experimental explorations on the PN could be divided into two directions, one is the high-pressure synthesis of extended solid, and the other one is the *in-situ* measurements of the physical properties. Extreme compression exerting on the material could profoundly reduce the interatomic distance, inducing electron delocalization and a series of transformations in characteristics. Meanwhile, the entropy of materials will increase greatly at high temperatures which affects the balance of electron behaviors. Eventually, the combined effect of extreme conditions will be reflected in the structure, phase boundaries, and stabilities.²³ With the development of the high-pressure apparatus, typically, diamond anvil cell (DAC) capable of generating ultra-high pressure and conducting laser heating, the extreme thermodynamic condition is not unachievable. For achieving the desired high pressure, the volume of the sample chamber is usually sacrificed, and the diameter of diamond anvil is typically 20–50 μm above 200 GPa. Microprobe technologies matching the high-pressure sample are therefore required. The excellent compatibility of DAC with a vast range of *in-situ* diagnostic techniques makes it possible to understand the high-pressure behaviors of PN at different scales. The most common experimental tools in the study of PN are XRD and Raman scattering. The high-pressure sample cavity surroundings not only contain diamonds, and the pressure gasket, but also the stainless-steel bracket, which is difficult to effectively probe by the traditional analysis and test means.

Due to the limitation of the sample size, the current high-pressure experimental studies are based on XRD and/or Raman scattering. Among various *in-situ* diagnostic methods, large-scale scientific apparatus like the synchrotron radiation facility plays a key role in providing structural information due to the very high spatial resolution and energy resolution. Based on large-scale and in-house scientific experimental technologies, recent experimental works aim to discover the possibility of new-type all-nitrogen HEDM and further elucidate *P-T* synthesized paths with experimental discovery and property characterization of polymeric forms. However, at the current stage, there are some experimental challenges to some extent that handicap the further understanding of PN. Here, a brief review of PN is introduced in terms of field background, synthetic technology and conditions. Then, we analyze the structural and vibrational properties of PN, and mainly conclude the Raman criterion of PNs. Finally, a fresh look at PN is presented. The article will assist in understanding the high-pressure behavior in the

formation of polymeric nitrogen phases as pressure is applied, and thereby to hone our understanding of the physical and chemical mechanism on the pressure-induced polymerization.

2. The species of PN

In general, PNs refer to a series of all-nitrogen compounds with polymeric structures. All-nitrogen compounds refer to a class of materials whose molecules are composed entirely of nitrogen. The high nitrogen content makes the decomposition of such compounds involve more breaking and re-bonding of nitrogen bonds, which is the earliest candidate to find HDEM materials. However, as the research deepens, the research of all-nitrogen polymers is limited by experimental techniques and application conditions. The polymeric nitrogen structure in some nitrogen-rich compounds has also been incorporated into the field of PN. This section will briefly introduce these high-pressure PN structures in nitrogen-rich compounds, which are considered to have greater application possibilities, as well as nitrogen molecular clusters — the allotrope isomer of PN. The research status of PN will be listed at the end. It favors understanding the background and motivation of PN research, the current progress, and the research direction more comprehensively.

2.1. Polymerized nitrogen structure in nitrides

As a matter of fact, the research on nitrogen-based HEDM started from polynitrogen units. Nitrogen atoms are covalently bonded to form ion clusters with a net charge, which are then paired with other ions to form compounds. These nitrogen compounds are called ionic nitrides. These nitrogen-rich compounds have made a series of breakthroughs since the late 19th century. In 1890, azide anion (N_3^-) was discovered in N_3H by Curtius for the first time detection ever of a stable high-energy nitrogen-based chemistry component.²⁴ The N_3^- has two double bonds linked between central and two side atoms separately consisting of a linear structure. Its metastability in the free state raised much interest in the energy application field (467 kJ mol^{-1} of N_3^-).⁵ After one century's perse, the pentazenium cation N_5^+ contained higher energy (1473 kJ mol^{-1})²⁵ was synthesized in N_5AsF_6 crystal in 1999.²⁶ Some N_5^+ ionic salts were reported subsequently.^{6,27,28} In 2016, the pentazolate anion *cyclo*- N_5^- was discovered by Bazanov et al.⁷ as a more stable energetic material which caused enthusiasm in the HEDMs field immediately. Later, Zhang et al.^{29–31} reported its successful synthesis in bulk in $(N_5)_6(H_3O)_3(NH_4)_4Cl$ salt.

Nevertheless, it is generally difficult for stable high-energy polynitrogen clusters or their ions in generated through classical chemistry methods. Compared with that, pressure has the significant advantage which is developing as a versatile tool to profoundly modify atypical materials' properties and effectively discover new materials.³² As known, despite the strong N_2 molecular bond, bonding patterns of molecular nitrogen at ambient conditions change easily and dramatically under compression.³³ Under compression, the electronic delocalization of N is promoted gradually. It's favorable to induce the transformation of polynitrogen units (at moderate pressure) and polymeric networks of nitrogen (at extreme pressure).

In the first case, a successful strategy is introducing heteroatoms in synthesis to form a nitrogen-rich system for further stabilizing polynitrogen units. The introduction of extra electrons can facilitate the separation of nitrogen triple bonds through charge transfer, leading to a lower energy barrier and the formation of new polymeric nitrogen structures. At the same time, the extra electrons can also improve the strength of the nitrogen single bond and enhance the stability of the polymerization structure. Currently, the introduced heteroatoms can be mainly divided into metallic and non-metallic types. Metals, especially transition metals, not only can coordinate with the corresponding nitrogen ions but also provide extra electrons to complex the bonding form and enhance the bonding strength. Some metal azides have been deeply investigated as low-energy explosives in detonating or nitrogen source

precursors in synthesizing PNs, including CsN₃,³⁴ NaN₃,³⁵ LiN₃,³⁶ KN₃,³⁷ RbN₃.³⁸ Many more stable metal nitrides have been synthesized subsequently, such as LiN₅,^{39,40} NaN₅,⁴⁰ CsN₅,³⁹ CuN₅.⁴¹ Recently, a discovery of hexazine rings (N₆²⁻) stabilized in potassium polynitride K₂N₆ under compression enlarges again the species of polynitrogen entity.⁴² Hitherto, parts of metal nitrogen-rich compounds could be quenched at ambient pressure,^{43,44} also inspiring the wide exploration of metal complexes in theoretic⁴⁵ for extending the metastability range of nitrogen-contained HEDMs.

The energy of the class of nitrides mentioned above comes mainly from nitrogen bonds in polynitrogen units. So N atoms among them are not aggregated in a polymerized form. In a strict definition, most metal nitrogen-rich compounds thus do not belong to the PN species. Nevertheless, compression could induce the nitrogen-rich compounds to end up transforming into oligomers of nitrogen or extended nitrogen structures in some systems. And some polymeric structures are predicted to exist in the metal nitrides, such as a range of polynitrogen with the N₄²⁻ chain,⁴⁶ N₄ ring and N₂₂ ring,⁴⁷ N₆ ring.^{48,49} In addition, 1D-NF chain with polymeric zigzag nitrogen chains is reported, and 3D-N₆F is predicted to be stable at pressures up to 180 GPa with a positively charged nitrogen network.⁵⁰ Li et al.⁵¹ and Niu et al.⁵² proposed a new method for synthesizing polymeric nitrogen structures using light non-metallic atomic nitrides through the structure search method. The principle is to invert the construction unit of the polymeric nitrogen framework in HeN₄ on decompression. Because the element He is easy to be moved away from the channel of the N-structure, HeN₄ is regarded as an ideal carrier with PN structure. Aside, some advanced techniques such as introducing substrates have been proven effective in stable PN structures.^{53–55}

Apparently, the energetic N ions induced by pressure have a significant advantage. The vast majority of them could unite with a single element as the counter ion. The poly-N products formed under compression thus are much simpler than those of the chemistry-induced. And because of the moderate synthesis conditions and the high stability, metal nitrogen-rich compounds synthesized through the high-pressure method are regarded to be an important clue to searching available novel PNs. However, although the introduction of metal atoms enhances the stability of nitrogen-rich compounds, their dissociation products and dissociation mechanisms are also relatively complex. On another hand, the nitrogen-rich system could be achieved in a relatively low temperature-pressure regime (<60 GPa, 300 K), but unavoidably reduce the energy content. The polymeric structure of all-nitrogen remains the best candidate and ultimate pursuit of ideal HDEM.

2.2. Polymeric nitrogen

Under compression, pure dimolecular nitrogen N₂ displays a series of complex phase behaviors with the decreasing of intermolecular distances. There are at least eleven experimentally observed solid molecular phases at the pressure up to megabar.^{56,57} In this stage, pressure-induced symmetry breaking leads to a series of solid molecular phases emerging in nitrogen.⁵⁷ It is mainly the changes in the interaction between nitrogen molecules that lead to these phase transitions.^{57,58} The application of sufficient pressure and high temperature will further lead to the intramolecular dissociation of nitrogen. The covalent N≡N bonds gradually collapse, eventually polymerizing into a single-bonded (N–N) network system, in preference to losing its covalent altogether.

The clue of nonmolecular nitrogen could be backtracked to the first experimental evidence provided by Nellis et al.⁵⁹ in 1984. A phase transition associated with N₂ dissociation was observed in shock wave experiments at 30 GPa, 6000 K. Based on that, the emergence of PN at high pressure with sole N–N covalent bond was first theoretically predicted by McMahan et al.³ in 1985. It's the first molecular system predicted to transform into a polymeric form before metallization. Interestingly, in other single-bonded V group elements, the structure of simple cubic (SC), α -arsenic (A7, R-3m), and BP (*Cmca*) have been

observed under high pressure, among which SC is the structure of atmosphere gas arsenic (As), antimony (Sb), and bismuth (Bi). For this reason, the arsenic A7 structure consisting of a rhombohedral distortion of the SC phase was regarded as the most promising high-pressure candidate of PN (but has not been found yet). Later, in 1992, a cubic gauche lattice structure with the lowest energy after considering all possible polymeric structures was proposed by Mailhoit et al.^{60,61} In cg phase, all nitrogen atoms are three-fold coordinated and bond-lengths are the same for all pairs of bonded atoms. Such structure has never been observed previously for any other elements, rendering it a very special material with very high stiffness ($B_0 = 298$ GPa with fixed $B' = 4$).⁸ And a great amount of effort had been paid for experimental verification of the PN after the first prediction.^{26,35,62–65} It was not until 2004 that the pressure-induced molecular-to-polymeric transformation of nitrogen was finally observed experimentally at around 110 GPa and 2000 K in a hydrostatic compression.⁸ Other predictions about novel PN were stimulated by the successful prediction of cg-N, promoted in the form of 0D nitrogen clusters,^{66,67} 1D chains,⁶⁸ 1D-2D chaired webs,⁶⁹ 2D layered^{70–72} (*Pba2*, *Iba2*), 3D single-bonded⁷³ and cageliked¹⁴ (*P4₂bc*), helical tunnel.⁷² Under high pressure, some possible theoretical evolution path was put forward: cg→*Pba2/Iba2* (>180 GPa) or *P-42₁/m* (>196–257 GPa)→*P2₁2₁2₁* (>320 GPa) or clusters.^{12,14,15,66,72} At present, the experiment synthesize method was verified by: cg→*Pba2/Cmca*→*P4₂bc* (<244 GPa).

In conclusion, after nearly three decades, four PN phases under extreme conditions, and a spate of polymeric structures of nitrogen in a series of nitrogen-rich nitrides have been confirmed. The harsh synthetic conditions and the dilemma of retainment at ambient conditions make the current research on PN only stay in the laboratory, so the search for more accessible energetic all-nitrogen materials is the development goal of the next stage. The current research directions are mainly divided below: First, optimize the stability conditions of PN. This direction has made great progress through element doping and substrate design. Some polymeric nitrogen structures have been able to be quenched at ambient pressure. Although there is still a certain distance between large-scale synthesis and practical application, present research still inspires PN. Another one is a deeper understanding of the synthesis mechanism and the design of a novel structure for PN. Breakthroughs in this direction and an in-depth understanding of polymerized nitrogen systems are very important for future applications. This poses great challenges to experimental technology and design. Therefore, this is described further in the next section.

3. Synthetic technology and conditions

High energy usually means an existing large energy barrier in the transition of formation or dissociation. It is hard, therefore, to break through the barrier under ambient conditions but is more possible in extreme circumstances. High pressure could dramatically decrease the distance of N atoms and enhance stability whereas heating promotes the cross of the energy barrier. That provides the possibility to form a pure polymeric system under extreme conditions. Therefore, the realization of ultra-high temperature compression conditions has become the first key point in the research of polymeric nitrogen synthesis. This section will first introduce the corresponding devices and experimental conditions, and summarize the difficulties and challenges of the experiment.

3.1. DAC sample loading

Two typical experimental methods could be applied to load nitrogen in DAC: high-pressure gas loading and low-temperature liquid immersing. The first one is loading the pure molecular nitrogen gas at the pressures of 100–300 MPa, with a special gas loading device. In the gas-loading system, a DAC is placed inside the pressure vessel that is filled with compressed gas. The second method is immersing DAC in liquid nitrogen to load the fluid sample. Because of the low-temperature

condition (77 K) at the sample loading, solid nitrogen experiences a low-temperature and high-pressure process, and the monoclinic λ -N₂ (space group P2₁/c) could be formed by cold compression from the liquid phase.⁷⁴ Notably, starting from the different initial phases, the loading result might be various considering the path-dependent effect.

3.2. High-pressure synthetic condition

Owing to the cruel conditions required for high-pressure polymerization, equipment applied to generate the static high pressure above 110 GPa generally is fabricated DAC. To reduce the stress from the diamond inside, symmetric DAC with beveled diamond anvils were used for pressure generation in experiments above 100 GPa.⁷⁵ The anvil flats were beveled out to a diameter of 20–100 μ m at an angle of 7–8.5° to overcome the large elastic strain at the culet tip. Because of good ductility and chemical inertia, rhenium foil was the common gasket material in high-pressure experiments. Some fabricated gasket (such as boron) was also to be selected. Precompressed gasket materials to less than one-twentieth of diamond diameter thickness. A hole in the center of pre-indented gasket was drilled using electric discharge machining, laser, or ion-milled⁷⁶ to produce a sample chamber. Its size is generally a third of culet size.

The practical limit of routine experiments using the current DAC technology is \sim 900 GPa,⁷⁷ but is lower in the study of fluid. A high-pressure experimental compilation of metallic hydrogen (MH) and PN from different research groups has been shown in Fig. 1. In principle, the diamond phase of carbon should be stable at below 1 terapascal (TPa).⁷⁸ There are many reasons why diamond fails under low pressure,^{79,80} which can be summarized as local stress. Therefore, the ideal correlation of the culet size and the maximum pressure is associated with many factors: the parameters of the diamond, operation, experimental conditions, and some uncontrolled variables. To reduce the risk of diamond failure, suitable gasket material, optimized anvil cutting process and even compression operation should be selected. The tradeoff between experimental pressure and diagnosed signals' intensity also needs to be considered.

3.3. Laser heating

Simply compressing molecular nitrogen at room temperature would

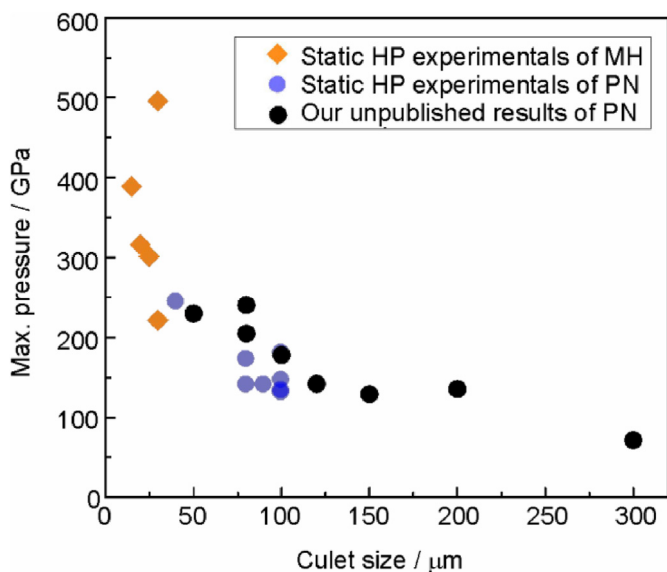


Figure 1. Maximum experimental pressures as a function of diamond anvil culet from various groups in the field of MH,^{76,81–85} PN,^{8,18–22,86,87} and our unpublished work.

not be able to conquer the barrier to the polymerization system. To overcome the large kinetic barrier between triple-bonded N₂ and single-bonded PN, laser heating the sample to 2000 K is necessary for all the polymeric phases (Table 1). The coupling of laser and solid nitrogen has to overcome the energy barrier which is a conditional dynamic process. A typical near-infrared (\sim 1064 nm) ytterbium fiber laser (YFL) is suitable to heat a transparent sample like solid nitrogen, while the carbon dioxide laser (10.6 μ m) that suits to heat a transparent sample but is hard to focus the laser beam within several-micrometers sample size.

The first successful synthesized PN experiment applied some modifications to DAC set-up, including the gasket compacted from the powder of cubic boron nitride (cBN) and epoxy resin, as well as the use of a laser absorber of thick boron flat.⁸ The artifact set-up eminently enhanced the heated chamber temperatures (a promotion from 1000 K to 2000 K). However, the small sample cavity, especially, those under ultra-high pressure (in diameter from 10 to 30 μ m), put the challenge of the beam spot size. The diffraction spectrum of internal materials may be put at a contaminated risk for additional diffraction lines stemming from the gasket. And possible chemical reactions between the absorbing materials and the nitrogen should be taken into account in the transformation conditions of the polymeric phase. The following attempted experiments^{18,22,23,89,90} make things simpler by using direct laser heating at higher pressure where the nitrogen transformed to dark red.^{23,90} With the pressure increases to above 130 GPa, an opaque amorphous state ('red'-N) was observed with the disappearance of XRD peaks and vibrational modes.^{21,23,57} The low transparency of the sample indicates the possibly increased optical absorption, providing the possibility of absorbing laser radiation (1064 nm) without any absorber.

3.4. Challenges in experimental synthesis

With the studies digging in, it appears to be realized gradually: the studies on PN derived from theoretical calculations have been effectively guiding the relevant field (e.g., precisely predicted the most stable polymeric phase cg-N), but sometimes the experiments about PN took the lead in probing clues. Such as in the case of BP-N, there always are structures that are much superior in calculated enthalpy to the BP structure. In the perspective of evolutionary algorithm, the entropy of BP structure is always beyond the lowest one. It means BP structure is unstable at high pressures in theory. Nevertheless, it was observed in two dependently experiments in recent years.^{19,20} This stresses the importance of experimental techniques to study the evolution rule of PN under high pressure, especially, of the possible revision for the theoretical method. And leaving a mystery-how to compare theoretical and numerical approaches with experimental data for a better understanding of the bonding change of PN at high pressure.

In theory, it is easier to break the thermodynamics barrier to form a new bonded type in extreme conditions. The higher pressure is better for PN synthesis. It is not easy to achieve in the actual situation for nitrogen. First, high pressure is limited. For initial non-solid samples, achieving ultra-high pressure is not easy. Measuring sample signals at ultra-high pressures is even more difficult. In addition, N is a light element, and the scattering cross-section of X-rays is small. It is a reason why neutron scattering should be developed - its section is relatively large. While the high fluorescence of diamond would be strong at up to 200 GPa. Therefore, it is the first challenge to measure the vibration performance of nitrogen by spectroscopy at high pressure. Meanwhile, precise temperature measurement of the sample is another challenge for LHDAC.

The laser-sample coupling is unstable and the temperature gradient is unevenly distributed across the sample cavity. As a result, the heating process is usually accompanied by the appearance of flashes implying temperature fluctuation. In most situations, the temperature calibration was determined by black-body radiation of the laser chamber or inferred by the optical flashes in the heating (estimated to be above \sim 2000 K). These factors limit the expansion and refinement of polymerized nitrogen phase diagrams. What's more, multi-phases are the common result in an

Table 1

The summary of structural and vibration information for PNs.

Phase	Theoretical Raman-active modes	Optical character	Observed Raman signatures (pressure)	Experimental methods	Ref.
cg-N	$A + E+2T$	Transparent	840 cm^{-1} (115 GPa) ~850 cm^{-1} (134 GPa)	XRD/Raman Raman	8 57
LP-N	$3A_1+3A_2+3B_1+3B_2$	Transparent	~1005 cm^{-1} and 1300 cm^{-1} (150 GPa) 857 cm^{-1} , 1033 cm^{-1} and 1150 cm^{-1} (157 GPa)	XRD/Raman Raman	18 21,88
BP-N	$2A_g + B_{1g} + B_{2g}+2B_{3g}$	Opaque	975 cm^{-1} and 1300 cm^{-1} (140 GPa) 1000 cm^{-1} and 1300 cm^{-1} (138 GPa) ~890 cm^{-1} and 1275 cm^{-1} (126 GPa)	XRD/Raman XRD/Raman Raman	19 20 74
PLP-N	\	Very transparent	~985 cm^{-1} , 1021 cm^{-1} and 1054 cm^{-1} (161 GPa)	XRD/Raman	21
HLP-N	$3A_1+3A_2+3B_1+3B_2+6E$	Very transparent	~930 cm^{-1} , 960 cm^{-1} and 1140 cm^{-1} (160 GPa)	XRD/Raman	22

LHDAC experiment due to the large pressure and temperature gradients in the sample chamber, and the low crystallinity of the polycrystalline sample raises difficulties in structural characterizations. For instance, the cg-N is always energetically stable and has the lowest synthesis conditions compared to other polymeric phases, while the entropy gap between different polymeric phases is very small. It therefore always emerges as an almost purified phase or by-product.²⁰

The difficulties of structural analysis increase at higher *P-T* conditions. The higher pressure usually sacrifices the culet size. At the pressure above 150 GPa, the culet size of diamond anvil cells is typically less than 100 μm , so the sample size is restricted to 20–50 μm .²² It is profoundly restricted by the focusing spot size of the heating laser. The small sample size brings challenges to either the synthesis or diagnosis. Although the laser-heating happened in a small layer of molecular nitrogen, a continuous energy-increasing process across molecular nitrogen in the chamber. The large temperature gradient in the sample chamber caused by the uneven laser heating process might be followed by the mixture of polymeric phases, even containing unreacted molecular phases under a high-strain-rate environment, which greatly enhanced the difficulties in distinguishing the feature X-ray diffraction peaks of specific phases from different phases.

The X-ray diffraction rings sometimes are not visible instead showing opaque defined spots. Meanwhile, because the heating laser is hard to be evenly absorbed, the novel structure usually coexists with other phases. The mixed-phase synthetic productions that are close in energy require specific distinction. Otherwise, the allocation of X-ray diffraction patterns may result in disputations of the structural identification, a case in point is the structural analysis of LP-N.^{19,22,91}

Because of the strong chemical bonds of polymer connecting the network structure, the polymeric phase (like cg-N) is predicted to be recoverable and metastable at atmospheric pressure,^{60,61} however, the synthesized sample at high pressure often can't be preserved as pressure releases. PNs were either observed to transform from cg to molecular phases⁸ or vanish with a catastrophic diamond anvil failure under decompression.^{18,20,22,87} As a result, all the polymeric phases cannot be quenchable at ambient conditions. The stability and characteristics of PN at ambient conditions are then still unknown, challenging for potential applications. Recently, pristine surface instability has been initially discussed in the decomposition of PNs. It was found that dangling bonds and transfer electrons to the surface play a key role in stabilizing the cg-N surface, while H saturation provides a possible solution.⁹²

Noticeably, the dependence on the synthesized path cannot be ignored for pressure-induced polymeric nitrogen. Now, more and more studies show that path dependency complicates phase transformations, with no exception for nitrogen. For example, recovered low-temperature molecular $\lambda\text{-N}_2$ has a very wide *P-T* region, occupying nearly the entire high-pressure molecular phase space,⁵⁶ introducing an additional complication for nitrogen at high densities.

4. Diagnostic methods

Laser, X-ray, and neutron scattering techniques have long been used to understand the physical properties of matter under high pressure.

From the equation of state to polymer orientation to the exploration of metallic hydrogen, scattering methods offer perspectives on physical properties not attainable with other approaches. Restricted by the small cavity for the high-pressure generation, the *in-situ* experimental diagnoses are limited. This part introduces the scattering techniques coupled with high pressure and the information it could provide about PNs.

4.1. X-ray diffraction

From its discovery in 1895 to nowadays, X-ray has been recognized by humankind both in science and sociology for its exceptional importance. The structural information including the crystal symmetry, unit cell parameters, atomic positions, as well as phase composition and stress of polymorphic samples (single crystal, polycrystalline, amorphous, nanocrystals) can be derived by XRD only if the diffraction conditions of the Bragg equation were met. Especially in high-pressure science, XRD was known for its accuracy in the equation of state (EOS), melting point, high-temperature and/or high-pressure (HTHP) phase transition, elasticity and lattice response of substances under high pressure. Besides achieving the limits of pressure and temperature, the detection of novel high-pressure structures is consistently developing. To determine the form of the synthesized PN, some properties are key factors to make a judge,⁶⁰ including lattice parameters, lattice volumes, vibration patterns, calculated enthalpy, etc. High-pressure synchrotron radiation XRD technique gradually becomes the most commonly verified method in the structure inference of PN.

Typical synchrotron radiation XRD techniques in HP studies including angular dispersive X-ray diffraction (ADXRD) used two-dimensional detectors which have been universally applied for studying materials at hydrostatic or quasi-hydrostatic HP conditions *in situ*, such as pressure-induced structural phase transitions,⁹³ electronic topological transitions,⁹⁴ and morphotropic transitions.⁹⁵ Energy dispersive X-ray diffraction (EDXRD) uses a point detector, which is mainly utilized in liquid and amorphous materials characterization. By using the advanced large-volume scanning technique, the combination of ADXRD and EDXRD gathered multi-energy XRD data that could provide much specific structural information in *in-situ* DAC experiments.⁹⁶ Besides, application modes of XRD including polycrystalline XRD, single-crystal XRD, amorphous XRD, radial XRD, and multiple grain XRD are well recognized.^{97–99} Worth to note, the multiple grain XRD method uses ultra-small XRD spots to analyze several single-crystal structures in polycrystalline samples. The application of this technique makes it possible to achieve high-quality XRD characterization of materials that are difficult to prepare, have poor crystallinity or those in small scattering cross-sections (common in light element components) in DAC.

Generally, advanced synchrotron radiation X-ray diffraction techniques can provide a sequence of important structural information on the PN. Compared with the energy produced by the gadget X-ray transmitting tube, the X-ray provided by synchrotron sources has better monochromaticity, as well as smaller focus spot (only a few microns) and higher beam brilliance (shorter wavelength, λ), supporting the fine structural analysis of a tiny sample in DAC chamber. In the example of the

Shanghai Synchrotron Radiation Facility (SSRF), the first third-generation synchrotron radiation light source device of Chinese mainland, the beam diameter is approximately $2 \mu\text{m} \times 2 \mu\text{m}$. The developments have progressed from the first-generation synchrotron radiation device developed in electron storage rings, the second-generation dedicated to special sources to the third one optimized brightness by retrofitting both undulators and wigglers. Under the promotion of continuous research in photon science, FEL known as the fourth-generation synchrotron light source has been desired to be applicable in a related field.

4.2. Neutron powder diffraction (NPD)

Although XRD technique takes advantage of a wide range and important applications as a nondestructive detection method for crystal structure information, its inherent constraints cannot be neglected: the scattering object of X-ray photons is electrons, while the equivalent cross-section of the process is proportional to the atomic number Z . Then the significant correlation between the relative diffraction intensity of XRD intensity and the type of element has determined, in the most typical example, deuterium being invisible under X-rays testing. NPD could avoid strong attenuation of the diffracted signal with Z decreasing, as well as has together with great spatial resolution. Consequently, as an alternative diffraction measurement, NPD has attracted the attention of materials science and high-pressure science. In addition, benefits from its inherent magnetic moment, neutron is directly sensitive to long-range magnetic sequences.¹⁰⁰ If the crystallographic order between the magnetic moments of the atoms in the sample exists, the NPD can be used to determine the magnetic moment and relative orientation of the atom to be measured.

Theoretically, NPD has unique advantages for a better understanding of the structural information of light-element systems like nitrogen. However, *in-situ* detection at high pressures faces a great challenge. The first problem is that non-solid systems, especially fluid samples, are difficult to load in DAC or other devices. In the past two decades, the neutron sample-packaging technology for fluid nitrogen has been upgraded, and the high-pressure NPD studies on solid nitrogen mostly concentrated on the molecular crystalline phases under relatively low P - T conditions, such as 20 GPa and 1000 K. Under the premise that the high-pressure NPD technology based on a reactor neutron source requires a comparatively larger sample volume, a stronger neutron source is extremely necessary.

The typical neutron sources are fission reactor sources and spallation sources.^{101,102} Up to now, the European Spallation Source (ESS) in Sweden of 5 MW level remains in the type of spallation sources but might be five times higher than that of the current spallation source. At present, the SNS Facility in the USA and the Materials and Life Science Experimental Facility (MLF) in Japan, have once again attracted the attention of the study of neutron diffraction under extreme conditions. Nevertheless, high-pressure NPD technology even based on a spallation neutron source (below 100 GPa) cannot reach the P - T condition of polymerization of nitrogen, which requires the future development of advanced neutron sources and improved reliable *in-situ* high-pressure devices.

4.3. Raman scattering

Raman scattering spectroscopy associated with the molecular or lattice vibration could probe the elementary excitations in materials in the process of inelastic scattering and rapidly provide the wealthy inner information for small-volume samples. According to the phonon wave vector selection rule ($q \sim 0$), all the Raman phonons in the Brillouin zone center (Γ) that meet the phonon dispersion relationship can participate in the Raman scattering process which reflects the structural and vibrational properties of materials. Upon compression, the atoms gradually approach, the localized irregular strain occurs inside the matter, and the spatial translation invariance is destroyed. As the distance of atoms is

further reduced, the pressure-induced phase transition may happen, while the bonding mode, atomic arrangement, and electronic structure inside the matter usually change greatly, leading to changing the bonding forms, or producing new vibration types and symmetrical structures. These structural anomalies can be reflected in the Raman phonon changes after being coupled to the incident laser. By analyzing Raman spectrum, it is easier to identify the anomaly linked to the change of bonding form, structural transition or vibrational characteristic. In DAC apparatus, IIA-type anvil diamonds provide an ideal optical and electromagnetic window with the corresponding excellent transmittance. Therefore, high-pressure spectroscopy based on the DAC has great advantages in quick and non-destructive detection of the trace amount of sample in DAC. Vibrational spectroscopy, like Raman scattering and infrared absorption, is very suitable for identifying the phase transition and investigating the optical properties of high-pressure phases.^{103,104} In conclusion, the high-pressure and optical window of DAC, combined with the micro-trace sensitivity of Raman spectroscopy, perfectly build an *in-situ* HP spectrum platform. With this combination, the HP Raman spectroscopy is widely used for studies on the pressure-induced polymerization of diatomic molecules such as N_2 , H_2 , H_2O , etc.^{19,20,84,105} However, the achievement of effective encapsulation of non-solid samples and further increase the ultimate pressure to meet the needs of major topics is still a great challenge and needs the further attention of researchers.

5. Polymorphism of polymeric nitrogen

Some cluster was also predicted to contain amounts of energy including the N_3 ,⁵ N_4 ,¹⁰⁶ N_6 ,⁶⁷ N_8 ,⁶⁶ N_{10} ,¹⁴ and N_{60} ,¹⁰⁷ among which perhaps the most promising allotrope is novel molecular N_8 consisting of two N_4 units that highly desired to be synthesized at ambient conditions. However, the great energy barrier results in the not yet clear synthesis conditions. It is for this reason that no molecular cluster of nitrogen is found in high-pressure high-temperature experiments.

So far, not many polymerized nitrogen phases have been experimentally synthesized. This chapter describes the synthetic conditions of five experimentally synthesized PNs and analyzes their structural properties to understand the mechanism of the structural transformation. In the polymeric nitrogen structure found so far, different PN products were achieved from different synthetic conditions or P - T paths (Fig. 2). However, the whole phase diagram is gradually clear but not enough.

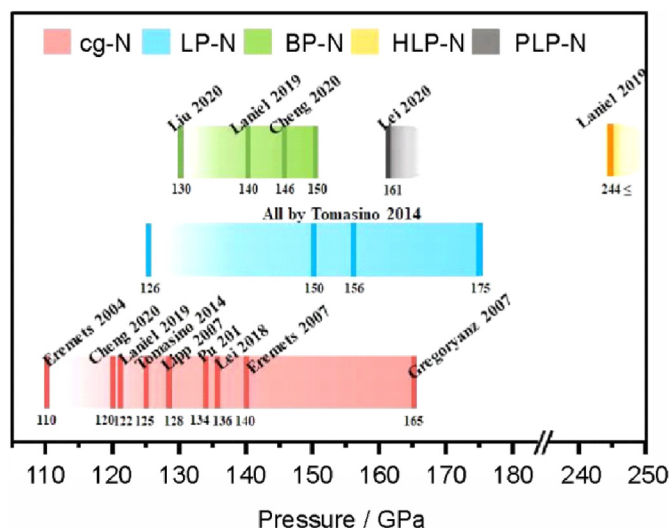


Fig. 2. The experimental synthetic pressure conditions for the five types of PN. The red, blue, green, gray, and orange lines represent the reported synthetic pressures for cg-N, LP-N, BP-N, PLP-N, and HLP-N, respectively. The experimental information is abstracted from literatures.^{18–23,35,57,90,108} The filling color bands serve as the guide of the corresponding pressure scope.

5.1. Cg-N

As the predicted most stable phase, the existence of the cubic gauche structure of nitrogen has been first confirmed by the experiments with synthesized conditions at 110 GPa and 2000 K by Eremets et al.⁸ The synthesized conditions for cg-N were verified with the P - T condition of 170 GPa above 2500 K⁸⁹ and 127 GPa above 1400 K²³ in subsequent experiments. At the pressure between 110 and 140 GPa cg-N were also synthesized (Fig. 2).^{21,22,57,86,90,108}

Corresponding to the theoretical prediction, the structure of cg-N has been verified as space group $I2_13$ from high-pressure X-ray diffraction patterns (Table 1). From optical images, the cg-N was a translucent crystalline phase, indicating that it might no longer absorb the NIR laser heating to accomplish the phase transition once synthesized. However, upon laser heating at a higher pressure, a phase transition from cg-N to LP-N was observed at 159 GPa and 2000 K by Lei et al., based on the Raman criterion for LP-N.²¹ Despite the subsequent argument in the determination of LP-N and BP-N, the phase boundary of the found cg-N had been further defined. In addition, the pressure dependences of Raman spectroscopy for cg-N were investigated up to 172 GPa, and down to 46 GPa, and the zero pressure mode-Grüneisen parameter of the cg-N Raman mode was also extrapolated to be 1.24 ± 0.02 .⁵⁷ Moreover, the phonon behaviors of cg-N were studied through Raman spectroscopy in a temperature range from 173 K to 300 K.¹⁰⁹

The above studies show that the structure of the cage-like cubic kink confers greater stability on cg-N. Therefore, it is believed that cg-N is expected to be intercepted at atmospheric pressure. However, due to the technical difficulties mentioned before, it is difficult to retain high-pressure synthetic products under decompression. However, due to its good stability, it is expected that cg-N can be synthesized at atmospheric pressure by other means (such as plasma technology¹¹⁰). Therefore, from the perspective of stability, cg-N is the closest polymeric nitrogen structure to applications.

5.2. LP-N

After the first report in 2004 by Eremets et al.,⁸ several possible high-pressure phases of PN have been predicted in the past decade.^{11–15,72,73} In 2014, Tomasino et al.¹⁸ claimed to acquire a novel layered PN (space group $Pba2$) after laser heating solid molecular nitrogen at 126–175 GPa (Fig. 2). This new phase is characterized by two colossal Raman bands (at ~ 1000 and 1300 cm^{-1} at 150 GPa) and optical transparency.

Two different amorphous with cg-N and a metastable phase⁷³ ($C2/c$) were claimed to coexist as by-productions because of uneven laser heating.¹⁸ Because the LP-N synthesized experiment has not been repeated independently now, there still are some arguments regarding the discrepancies of the volumes and Raman spectra between experiments and calculations when identifying the component contributions. An analysis attributed that synthesized product to the mixture of cg-N, $Pba2$, and $Pccn$ allotropes.⁹¹ Recently, Laniel et al.^{19,22} claimed that the LP structure might be a misunderstanding for the X-ray diffraction pattern data which in fact comes from the BP structure. However, the distinct still exist in the optical characteristics between transparent LP-N and opaque BP-N (Table 1). This has caused some controversy about whether LP-N is there or not. The biggest reason cause of the controversy is that LP-N has not been synthesized in any independent experiments, further to mirror the experimental difficulties encountered on PN. Firstly, the unstable laser heating coupling prevented to synthesis pure polymeric phase. challenging the precise phase identification. Besides, the highly preferred orientation from XRD patterns enhances the difficulties in structural analysis. The high-precision independent diagnosis method was highly desired.

5.3. PLP-N

In 2019, the post-layered-polymeric nitrogen (PLP-N, or Panda-N),

was observed by further heating a PN phase with the Raman peaks of BP and LP to above 2300 K at 161 GPa by Lei et al.²¹ This phase was found to be very optically transparent and exhibits ultra-large-spacings ranging from 2.8 to 4.9 Å at 172 GPa, suggesting a lower-symmetry large-unit-cell 2D chain-like or 0D cluster-type structure with wide bandgap.

However, the observed X-ray diffraction pattern and Raman scattering data cannot match any predicted structures in the published literature. This finding further complicates the phase diagram of nitrogen and also highlights the path dependence of the high-pressure dissociative transition in nitrogen.

5.4. HLP-N

According to a theoretical high-pressure sequence (at 0 K), the 3D network structure cg-N would undergo a transition to the 2D layered nature at 188 GPa, then translate to N10 structures at ~ 263 GPa.¹⁴ The structural transformation of PN from 3D to 2D under high pressure remained elusive until the HLP-N structure ($P4_2bc$) was observed in 2019.²² Laniel et al.²² synthesized a multigrain texture PN sample at 209–244 GPa above 3300 K. A novel tetragonal phase (space group $P4_2bc$ ¹⁴) was demonstrated to match the predicted hexagonal layered structure by XRD patterns and the comparison of experimental and theoretical Raman modes. Compared to the precursor amorphous state, HLP-N has a drastic rise in transparency and obvious novel diffraction peaks.

5.5. BP-N

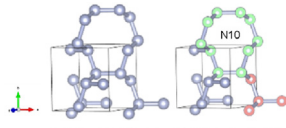
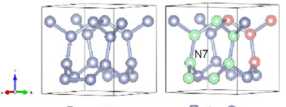
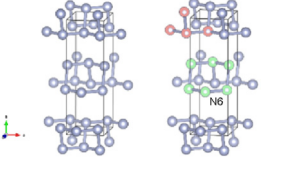
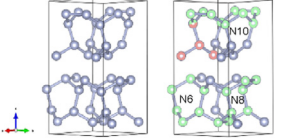
The prediction of black phosphorus structure nitrogen was inspired by a high-pressure rule: in the same periodic table column, elements would exhibit the same structure as the element posited below them at high pressure. However, in all group V elements, nitrogen was the first one but the only one that had not been found in the BP structure (space group $Cmca$), until recent works^{19,20} reported a mixture phase and purely crystalline form of BP-N, respectively. BP-N requires a high pressure of up to 140 GPa for synthesis. According to the Raman data from Liu et al.^{74,87}, the BP-N could be analyzed at a relatively low pressure of 130 GPa. It is noted that the forming region of BP-N and LP-N has the most overlap (Fig. 2) and the BP-N has the almost identical Raman character as the LP-N (Table 1).

5.6. Structural similarity

The PN is linked by strong N–N covalent bonds. Such bonding form replaces the weaker intermolecular interactions of molecular nitrogen, building a larger activation barrier toward the reverse transformation, resulting in a large energy gap toward the reverse transformation. In all the polymeric phases, each nitrogen atom is connected to the other three nearest neighbor atoms with a single bonded N–N covalent bond (Table 2). From other points of view, crystal structures of the polymeric phases show a 3D network made of N–N rings (Table 2). Aside from the LP-N mainly with odd-membered N–N rings (N7), other polymeric phases, including cg-N (N10), BP-N (N6), HLP-N (N6, N8, N10), are made of even-membered N–N rings (Table 1 and Table 2). The crystal structure of PN established by experimental results appears to indicate that the N6-bearing layered structures are the thermodynamical favored arrangement upon compression.

The main identified evidence of different PN phases is based on the match of the experimental and simulated XRD pattern, Raman spectra, and the optical energy (namely, calculated lower enthalpy than other structures) in the stability P - T domain. Other experimental details, such as the anomalies in volume and Raman data, were used to provide the clue. Therefore, the development and expansion of research methods and diagnostic techniques are of great significance for the research of polymerized nitrogen.

Table 2The crystal information and structures of cg-N in $I2_13$, LP-N in $Pba2$, BP-N in $Cmca$, and HLP-N in $P4_2bc$.

Phase	Space group	Wyckoff position	Structural characters	Structural images
cg-N	$I2_13$	8a	N10	
LP-N	$Pba2$	4c	N7	
BP-N	$Cmca$	8f	N6	
PLP-N HLP-N	\ $P4_2bc$	\ 8c	2D chain-like or 0D cluster-type N6, N8, N10	

Note: The green sphere represents the formation of the N ring, and the red sphere represents a unit of one N atom and its nearest neighbors (are both 4 nearest atoms for the above PNs as shown).

6. Lattice dynamics

Molecular solid Nitrogen has strong covalent triple bonds (vibron) and weak intermolecular interactions (lattice phonon), it can exhibit sharp high-frequency stretching vibron modes ($2300\text{--}2500\text{ cm}^{-1}$) and broad low-wavenumber lattice phonon modes ($100\text{--}1000\text{ cm}^{-1}$).^{57,62}

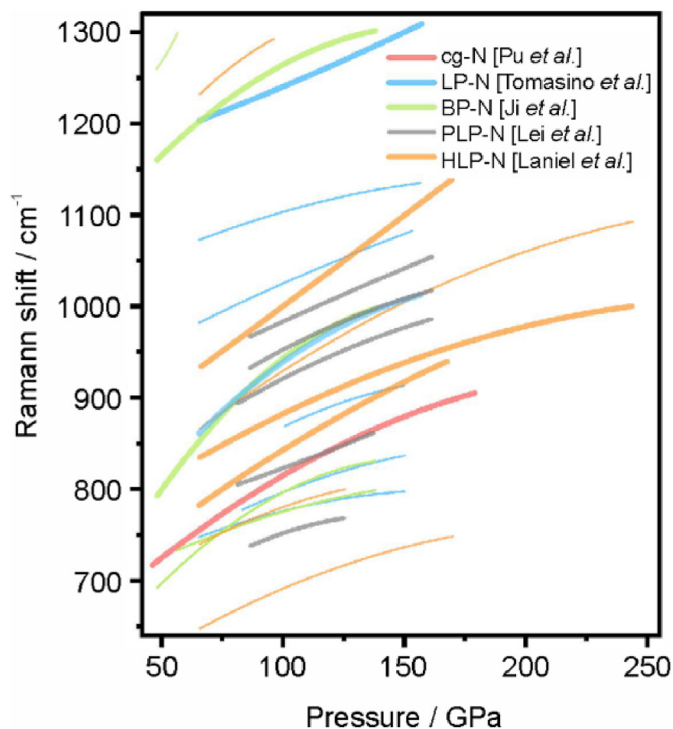


Fig 3. Pressure dependent Raman phonon modes for PN, cg-N (red line), LP-N (blue line), BP-N (green line), PLP-N (gray line), and HLP-N (orange line). The thick lines represent the main Raman peaks (high intensity) and the thin line represents the relatively weak Raman peak (low intensity).

Upon the phase transition from molecular solid to polymeric form, the Raman vibron that reflects the existence of strong covalent triple bonds will disappear. Meanwhile, the lattice phonon that reflects the formation of a single bond network will appear. Thereby, the Raman criterion (RC) for nitrogen polymerization is based on the disappearance of high-wavenumber Raman vibron ($2330\text{--}2500\text{ cm}^{-1}$) and the presence of low-wavenumber Raman phonon ($700\text{--}1300\text{ cm}^{-1}$).

The polymorphism of nitrogen under high pressure all has special Raman excited modes (Table 1). Because the intense Raman mode from diamond which begins from 1330 cm^{-1} would prevent the observation of the vibrational mode at higher frequencies. Here, Fig. 3 shows the devolution of the Raman frequencies between 650 and 1300 cm^{-1} with pressure, where most polymeric compounds containing single-bonded nitrogen atoms have detected Raman modes. Under compression, nitrogen would present a strong fluorescence, disturbing the detection of low-intensity Raman peaks. The intensity of the background signal from fluorescence directly restricts the maximum experimental pressure and significantly decreases during sample decompression. The Raman data would be collected until diamond anvil failed.

Group theory analysis indicates that the cg-N has four Raman-active modes, $A + E + 2T$.⁶¹ The intensity of the A mode is much stronger than E and T modes, so the A mode is the main identified peak as the reference; The synthesized cg-N usually has a relatively pronounced Raman peak at 840 cm^{-1} corresponding to the mode of A symmetry, with the disappearance of the molecular N_2 vibron at 2390 cm^{-1} .⁸ This is a typical example that the end of the intermolecular dissociations is often the onset of the intramolecular dissociative transitions. The BP-N has six Raman active modes: $2A_g$ (named A_g and A_g') + $B_{1g} + 2B_{2g}$ (named B_{2g} and B_{2g}') + B_{3g} . Among the calculated Raman peaks, B_{3g} is near the diamond Raman region (calculated at $\sim 1431\text{ cm}^{-1}$ at 138 GPa) and B_{2g}' is too weak (calculated at $\sim 1053\text{ cm}^{-1}$ at 138 GPa) to be observed experimentally.^{19,20} LP-N was observed to have two strong Raman peaks at ~ 1005 and 1300 cm^{-1} at 150 GPa .¹⁸ Its most Raman characterized peaks are overlapped with those of BP-N, except for two weak peaks between 970 and 1150 cm^{-1} .¹⁹ It indicates that the vibrational mode as well as the structure of LP and BP are highly similar. HLP-N has twelve detected vibrational Raman modes among which seven at frequencies between 650 and 1300 cm^{-1} .²² Only three strong most intense Raman modes were

barely observed at 244 GPa because of a strong fluorescence. As pressure releases below 176 GPa, the fluorescence dramatically decreases and the seven characteristic Raman peaks beyond the frequencies of the diamond first-order region appear (orange lines in Fig 3).

As shown in Fig 3, the pressure-dependent phonon frequency changes in PLP-N shift nearly linearly with pressure at approximately $1.1 \text{ cm}^{-1} \text{ GPa}^{-1}$. That value is smaller than those of cg-N ($\sim 1.3 \text{ cm}^{-1} \text{ GPa}^{-1}$) and LP-N ($1.2\text{--}1.6 \text{ cm}^{-1} \text{ GPa}^{-1}$), while that of HLP-N ($1.9\text{--}2.3 \text{ cm}^{-1} \text{ GPa}^{-1}$) and BP-N ($3.7\text{--}5.3 \text{ cm}^{-1} \text{ GPa}^{-1}$) are comparatively larger, suggesting PLP-N is a stiff lattice. In the case at 100 GPa, the slope of the Raman main peak of HLP, BP, LP and cg is $1.61 \text{ cm}^{-1} \text{ GPa}^{-1}$, $1.32 \text{ cm}^{-1} \text{ GPa}^{-1}$, $1.17 \text{ cm}^{-1} \text{ GPa}^{-1}$, and $1.54 \text{ cm}^{-1} \text{ GPa}^{-1}$, respectively. Just as corresponding with structure characteristics, it indicates the more stable structure the phase has, the larger pressure response efficiency its main vibration mode shows.

7. Expectation

In conclusion, the studies about the characteristics of PN have achieved some cheerful results but still have many questions waiting to be solved. In the respect of probing the phase evolution of PN at higher P - T ranges, further experimental work could be carried out in several ways. First, the groundbreaking progress in the technology of thermodynamic synthesis conditions is necessary to identify and probe the evolution and phase diagram of PNs. The HLP phase has not been reported in other independent experiments, as well as the structure characters of novel PN are not clear now. Meanwhile, some signs of path-independent have been found in PN research. Systematic research on synthesis and mechanism requires theorists and experimentalists to work together. Second, the comprehensive understanding of synthesized products needs advances in various diagnostic methods. FEL (typically, 100 J, 10 ns, 10 Hz) could create and diagnose matter shock or ramp compressed to multi-megabar pressures, which has a good advantage at focusing on structural determination, mapping of phase diagrams, exploration of phase stability, development of compression pathways, and understanding the phase evolution and influence of bonding behavior. It is an available method to perform dynamic and static compression of samples using the FEL. Furthermore, to better understand the structural characteristics of PN, the nano-polycrystalline diamond is expected to reach a high pressure up to 100 GPa by upgrading the high-pressure neutron sample-packaging and compression technology for fluid nitrogen, developing the strong point of reactor-based neutron diffraction on light element molecular crystals. Moreover, the bandgap of PN at high pressure has not been investigated experimentally until now, which is a promising direction for studying the high-pressure electronic band structure of PN. Besides, the metallization characteristics of nitrogen can also be deeply studied through the field in optical band gap and energy band structure.

Author contribution

Li Lei conceived and supervised the research and finalized the manuscript; Jing-yi Liu drafted the paper with help from Heng-yuan Zhang provided chart drawing and useful discussion.

Declaration of competing interest

No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously and not under consideration for publication elsewhere in whole or in part. All the authors listed have approved the manuscript that is enclosed.

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