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Synthesis of black phosphorus structured polymeric nitrogen*

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Since the discoveries of polymeric nitrogen, named cg-N (2004), LP-N (2014), HLP-N (2019), another polymorph named black phosphorus nitrogen (BP-N) was synthesized at high-pressure-high-temperature conditions. The narrow existing pressure region and similar synthesized pressure of BP-N compared with cg-N indicate that the stable energy and enthalpy of formation of these two structures are close to each other, which was confirmed by our theoretical calculation. In order to obtain the pressure region of BP-N phase, pure N_2 and TiN/Pb + N_2 precursors were used for laser-heating high pressure experiments in diamond anvil cell (DAC), and the phase identity was examined by Raman and XRD mapping. BP-N can be synthesized in the pressure range of 130 GPa to 140 GPa with the assistance of heating absorber. With the decrease of the pressure, BP-N can be quenched to $\sim$ 40 GPa. The synthesizing pressure–temperature and the stable pressure region of BP-N are important for further exploration of BP-N and its kinetic and thermal dynamic relationship with other polymeric nitrogen, especially cg-N.

Keywords: high pressure and high temperature, energetic materials, polymeric nitrogen, diamond anvil cell

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1. Introduction

Polymeric nitrogen is commonly considered to be a high-energy-density material (HEDM) because of large differences in energy (2.3 eV per atom) between the N–N single bonds and most stable chemical N≡N triple bonds in nitrogen molecules at ambient pressure. The single bonded polymeric nitrogen has been calculated to contain large chemical energy, three times that of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX),[1] one of the most powerful explosives used today. The search for polymeric forms of nitrogen upon compression has therefore attracted great attention. The structure of polymeric nitrogen was first suggested to be known as a simple cubic, black phosphorus (BP) structure, A7 structure of arsenic.[2] Then in 1992, Mailhiot predicted a high-pressure phase of cubic gauche (cg) structure based on first-principles calculations.[2] Thence, lots of theoretical high-pressure structures have been proposed,[3–9] such as cis-trans chain[3] and layered structure.[4] Experimentally, great efforts have been devoted to explore single bonded polymeric nitrogen at high pressure and high temperature (HPHT) conditions.[10–16] Single bonded cg-N was first synthesized by Eremets *et al.* under extreme conditions (110 GPa, 2000 K) and then repeated by other groups.[10,11] In 2014, the second experimentally obtained poly-nitrogen form of layered polymeric structure of *Pba2* space group, LP-N, was reported by Tomasino *et al.*,[13] which was synthesized along with cg-N and amorphous N above 125 GPa, although some controversies were raised regarding this structure.[14,15] In 2019, a hexagonal layered polymeric nitrogen (HLP-N) was identified near 250 GPa.[14] Very recently, Dominique Laniel and his co-workers discovered the new phase of BP-structured nitrogen up to 140 GPa and $\sim$ 4000 K through diagnostic probes of synchrotron single-crystal x-ray diffraction (SXRD) and Raman spectroscopy.[15] At the same time, Ji *et al.* also reported the synthesis of the black phosphorus structured nitrogen at 146 GPa and 2200 K.[16] The first predicted BP structure was experimentally realized after about more than 30 years. The overlooked BP structure suggested the complexity of phase diagram of N_2 at HPHT, the narrow HPHT region of BP-N, and lack of experimental data supporting, especially the dynamic properties of phase transitions to revise the theoretical modes. More importantly, the exploration of BP phase stability in the *P*–*T* space can provide more insights for understanding the fundamental mechanism of phase transitions and thermal properties, and therefore promoting the ability of new HEDM design and application.

In this paper, we have synthesized BP-structured poly-nitrogen using laser heated diamond anvil cell (DAC) techniques in the pressure range of 130–143 GPa. Besides, we have investigated the influence of different absorber of the laser radiation (TiN, Pb) in the sample chamber at relative lower pressures. The specific Raman peaks of BP-structured

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polymeric nitrogen were compared at different synthesis conditions. Further, x-ray-diffraction mapping measurements of the whole sample chamber confirmed the production of BP-structured polymeric nitrogen. Theoretical calculations were carried out to confirm the stability and energy performance of BP-N.

2. Experimental and computational methods

The HPHT experiments were conducted by using symmetric DAC and the micro-laser-heating equipment in the lab. The DAC with beveled diamond anvils (100 μm or 150 μm beveled to 300 μm) was used to generate pressures of 130 GPa and 143 GPa for pure N_2 loading and around 120–130 GPa with thermal absorbers, respectively. Rhenium gaskets were pre-indented to a approximate thickness of 20–30 μm and drilled a 50/80 μm diameter hole as the sample chamber. A thin flake of NaCl was used as the thermal insulator.[17–19] High pressure nitrogen gas (99.9%) was loaded into DACs at pressure of $\sim$ 200 MPa using a gas loader in the lab. Except for the pure N_2 loading in the first experiment, a piece of laser-absorbing material (compressed TiN powder or Pb) about one third of the sample hole was sandwiched between NaCl layer and the sample in the III–V experimental runs. The diamond Raman edge was measured to check pressures.[20] Laser heating was performed on five runs at 143 GPa (run I), 130 GPa (runs II–IV), and 121 GPa (run V), using 1064 nm YAG laser. The laser beam was focused to a spot of $\sim$ 15 μm on both sides and scanned to heat the sample. Thermal radiation spectra from one side of the sample were measured and fitted to the Planck black-body radiation function to determine the temperatures.[21]

Raman spectra were measured after the samples were quenched to room temperature. The high-pressure Raman experiments after laser heating and during decompression were conducted through HORIBA HR EVOLUTION Raman microscope with a liquid-nitrogen-cooled CCD detector and spectral resolution about 1 cm^{-1}. The exciting laser wavelength is 532 nm. Synchrotron x-ray diffraction measurements of run I and run III were carried out on BL15U1 beamline (0.6199 Å) at Shanghai Synchrotron Radiation Facility (SSRF). CeO_2 was used as the standard sample to do the calibration before data collection. Dioptas[22] was used for XRD data reduction.

Theoretical calculations were carried out using the Vienna *ab initio* approximation package (VASP)[23,24] within the generalized gradient approximation (GGA) parametrized by the Perdew–Burke–Ernzerhof (PBE) functional.[25] Projector augmented wave (PAW) potentials[26,27] and a plane wave basis set with an energy cutoff of 900 eV were used. A 0.03 $Å^{-1}$ *k*-point sampling of the Brillouin zone[26] was used for structural optimization without symmetry constraints. The convergences of energy and force were set to 1×10^{-6} eV and 0.001 eV/Å, respectively. The unit cell we selected contains 8 nitrogen atoms for BP-N and cg-N. Test calculations by using the optPBE-vdW method for checking the effects of van der Waals correction were done, and we found that simulations with and without vdW correction give similar results.

3. Results and discussion

Polymeric nitrogen was synthesized in five runs. In the first run, as described above the BP structured polymeric nitrogen was obtained at pressure of 143 GPa and temperature of 2500 K for 20 min at different points. The BP phase was identified through Raman spectra by measuring the room-temperature quenched sample, as shown in Fig. 1(a). The pressure in the center of the sample reduced to 139 GPa. The Raman peak position was compared with the recent reported Raman data reproduced from Refs. [15,16]. Figure 1(b) gives the schematic draws of the BP crystal structure at $\sim$ 140 GPa.[15] Briefly, the BP (A17) structure contains the characterized N-chains along the *c* axis, two single bonded N pair shifts relatively along the *b* axis, forming the hexagonal N ring, as shown in the top view along the *a* axis in Fig. 1(b). The similar chain geometry was also reported in other nitrogen hydrides polymer or metal nitrides.[28–31] According to previous theoretical calculation and experimental results,[15,16] the BP structural nitrogen phase has similar energy scales as to the cg-N, and

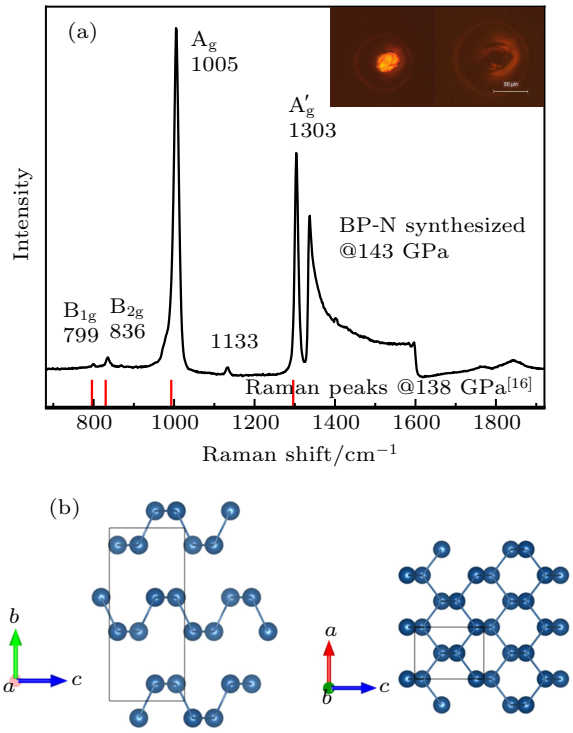


Fig. 1. (a) Raman spectra of nitrogen heated at 143 GPa from run I (black) compared with the experimental spectra for BP-structured polymeric nitrogen (red bars) at 138 GPa, 2200 K.[16] Inset shows the microscopic images of the sample under illumination with both reflected and transmitted light before and after laser heating. (b) Crystal structure of BP-N under 140 GPa.

can only be stabilized in a narrow HPHT condition. The BP phase has totally six Raman active modes, among which A_g and A_g' have large intensities. The observed A_g, A_g', B_{1g}, and B_{2g} vibrations are located at 799 cm^{-1}, 836 cm^{-1}, 1005 cm^{-1}, and 1303 cm^{-1} at $\sim$ 139 GPa, respectively, as plotted in Fig. 1(a). The B_{3g} peak is overlapped with the first order Raman signal of the stressed diamond anvil and cannot be seen in this pressure range. The marked peak at 1133 cm^{-1}, also reported in Ji's work as a Raman mode induced by impurities, defects, or other phases of nitrogen, could be observed in the other runs and always synthesized along with the BP-structured nitrogen. While in Laniel's work,[15] this specific Raman peak was assigned to be the B_{2g} vibration of BP-N. Further assigning of this Raman peak should be addressed.

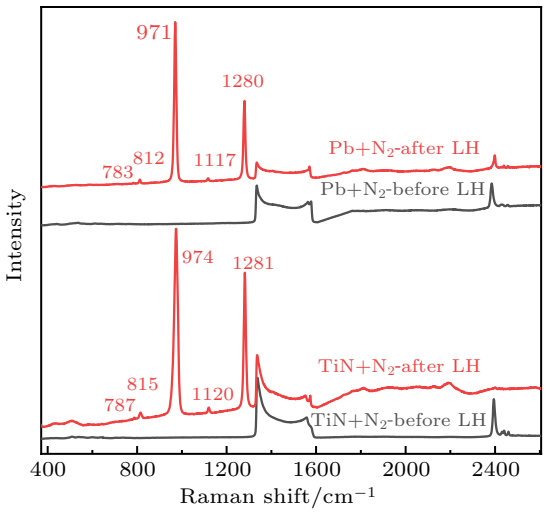


Fig. 2. Raman spectra of nitrogen before and after heating at 130 GPa using TiN and Pb as laser absorber, respectively.

As mentioned, the pressure range of BP-N thermal stability is quite narrow, and a mapping of the synthesis pressure range is necessary for dynamic study of BP-N and as a reference for the following researches. The run II of a pure N_2 loaded experiment was conducted at $\sim$ 130 GPa by laser heating, but the heating efficiency was quite low and instantaneous temperature reached about $\sim$ 1800 K for seconds. The results indicated that only cg-N has been synthesized at this pressure and temperature range as show in Fig. S1. Some literatures[10] stated that pure N_2 loading in the chamber of DAC can be efficiently heated while pressure is higher than 140 GPa, at which the darken N_2 sample becomes a good absorber, while others[11,13] concluded that direct laser heating above 120 GPa can be performed for HPHT experiments. Our results confirmed that pure N_2 could be directly laser heated at 130 GPa, but it is very hard to maintain high temperature for several minutes. To exclude the sample–laser interaction and correspondingly heating efficiency influence, heating absorbers, TiN and Pb were loaded simultaneously with pure N_2 for the III, IV experimental runs at $\sim$ 130 GPa, respectively. The Raman spectra of the laser-heated quenched samples were plotted in Fig. 2, suggesting the successful formation of BP structured polymeric nitrogen at pressure of 130 GPa. The careful Raman mapping of the laser-heated sample did not give any by-passing products except for the unreacted raw materials, excluding any reaction routine changes or other effects by introducing TiN/Pb in as pure heating absorbers. Therefore, we proposed that the formation of BP-N at relatively low pressure of 130 GPa was purely from the enhance of heating efficiency. As the YAG laser cannot heat transparent samples, a CO_2-laser heating apparatus for this experiment can be employed in the future to double confirm this conclusion. The TiN + N_2 were lastly loaded and laser heated at $\sim$ 120 GPa in the V experimental run, and the results indicated that the BP-N cannot be synthesized at that pressure, which is shown in Fig. S2. To make it more clearly, the experimental details of the five runs are summarized in Table 1.

Table 1. Experimental details of the five experimental runs, including the experimental conditions and major results.

#	Pressure/GPa	Temperature/K	Absorber	Results
I	$\sim$ 143	$\sim$ 2500	–	BP-N
II	$\sim$ 130	$\sim$ 1800	–	cg-N
III	$\sim$ 130	$\sim$ 2500	TiN	BP-N
IV	$\sim$ 130	$\sim$ 2500	Pb	BP-N
V	$\sim$ 120	$\sim$ 2500	TiN	–

The BP-N synthesized from N_2 and Pb at $\sim$ 130 GPa was used to exam the frequency dependence of pressure, as shown in Fig. 3. The measured pressure dependence of Raman shift of BP-N and cg-N was also compared with calculations and previously reported values[10,13,15,16] of polymeric nitrogen polymorphs, such as BP-N, cg-N, and LP-N. All the measurements were performed during decompression. We could only release the pressure down to 40 GPa, thereafter the sample escaped because of the weakening of the gasket during decreasing pressure.[32] There are three main features of our experimental data to conclude that the synthesized phase is BP-N: i) cg-N synthesized in the II experimental run and other literatures only has one observed A Raman mode, which gives a slightly higher wavenumber than those of B_{1g} and B_{2g} modes of BP-N in Fig. 3(b); ii) LP-N has both observed Raman modes similar to A_g and A_g' modes in BP-N, the frequency and pressure dependence of A_g mode in both structures overlapped quite well. However, Laniel and his coworkers proposed that the previously reported LP-N structure is incorrect and that solid crystal in fact adopts the BP-N structure; iii) x-ray-diffraction mapping measurements of the whole sample chamber of experimental runs I and III confirmed the production of BP-structured polymeric nitrogen as shown in Fig. S3. The *d* values of the marked peak range from 3.299 Å to 3.311 Å in the III experimental run and from 3.270 Å to 3.279 Å in the I experimental run, which is believed to belong

to the (020) peak of BP-structured nitrogen. Conclusively, the obtained high-pressure phase of N_2 is BP-N.

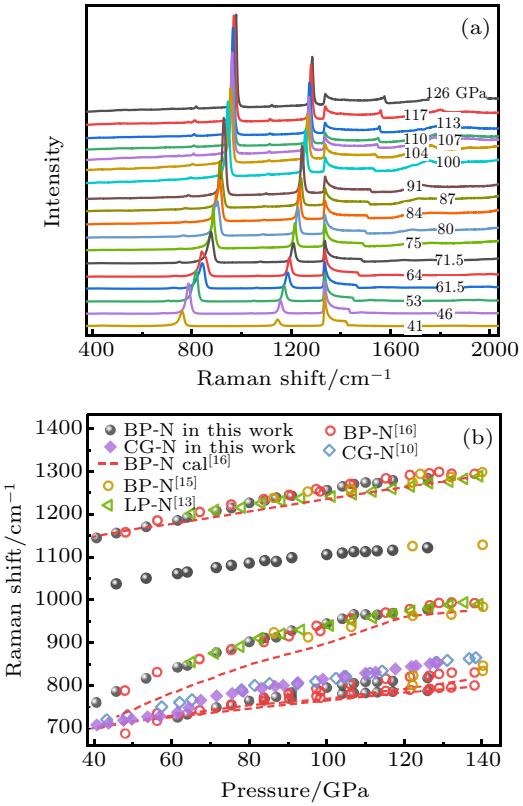


Fig. 3. (a) Raman spectra of BP-N during the decompression. (b) Measured pressure dependence of Raman shift (run III) of BP-N and (run II) of CG-N compared with calculations and previously reported values[10,13,15,16] of polymeric nitrogen. All measurements were performed during decompression.

For the theoretical calculation, the structure of BP-N with *Cmca* symmetry is fully optimized at high pressure 0–140 GPa, and the equation of state (pressure–volume relation) is presented in Fig. 4(a). With the pressure decreasing from 140 GPa to 30 GPa, the volume increases smoothly. However, a discontinuous change of the equation of state is observed at 30 GPa, and the volume increases more rapidly at lower pressure range (0–30 GPa) than the counterparts of higher pressure. Detailed analysis shows that a phase transition starts at 30 GPa and ends at 20 GPa, and the BP-N with *Cmca* symmetry spontaneously changes to a new phase with chain-like structure (CH-N) where each chain has the zigzag structure, as shown in Figs. S4(a) and S4(b). Similar structure was reported by using the variable-cell-shape molecular dynamics simulation of BP-N phase at pressure below about 20 GPa.[3] The results indicate that the high-pressure synthesized BP-N will become unstable when the pressure decreases to $\sim$ 30 GPa.

In the following, we calculate the formation enthalpies (FE) of BP-N and CH-N at different pressures and compared them with that of cg-N. We define the FE of BP-N or cg-N based on the following formula:

$$\Delta E = \left(E_{\text{poly}} - 4E_{\text{N}_2}\right)/8,$$

where E_{poly} represents the enthalpy of BP-N, CH-N, or cg-N, and E_{N_2} is the enthalpy of nitrogen molecules. By comparing the enthalpy of high-pressure N_2 phases, we find that the α phase $(Pa\bar{3})$, ε phase $(R\bar{3}c)$, and ζ phase $(P222_1)$ are the most stable configurations at the pressure ranges of 0–20 GPa, 20–120 GPa, and 120–140 GPa, respectively, which agree well with the experimentally observed N_2 phase transition sequence at high pressure.[33] The formation energy of BP-N, CH-N, and cg-N is shown in Fig. 4(b). At the pressure higher than 20 GPa, the FE of BP-N with black phosphorus-like structure is larger than that of cg-N, whereas the trend is reversed when the CH-N becomes stable at 0–20 GPa.

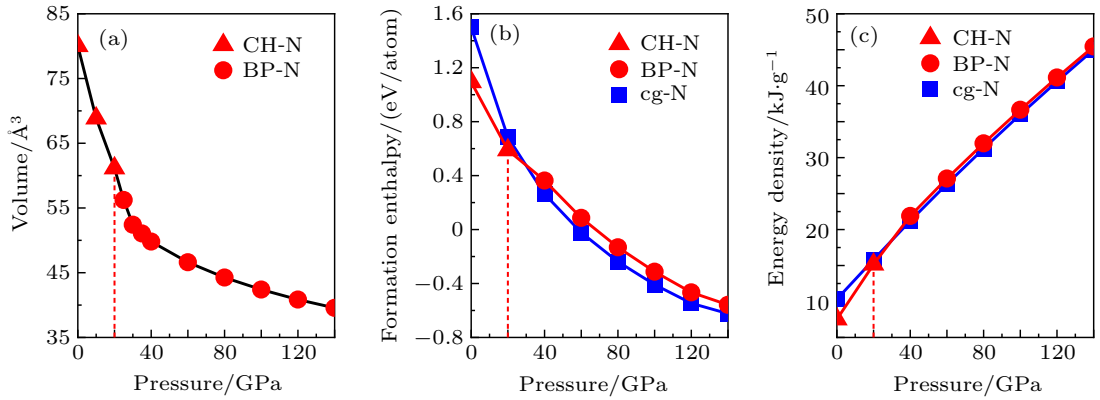


Fig. 4. (a) The equation of state, (b) formation enthalpy, and (c) energy density of CH-N, BP-N, and cg-N. The values of CH-N, BP-N, and cg-N phases are shown in red triangle, red circle, and blue square, respectively. The red vertical dotted line indicates the pressure (20 GPa), where CH-N becomes stable.

In Fig. 4(c), by taking the N_2 at ambient condition as a reference, we present the calculated energy density of BP-N, CH-N, and cg-N as a function of pressure. The energy density increases as the pressure increases, and the calculated energy density of cg-N at 0 GPa is 10.33 kJ/g similar to the results in existing literatures (9.7 kJ/g).[10,34] At the high pressure ranging from 0 GPa to 20 GPa, the energy density of CH-N is lower than that of cg-N. However, in the BP-N stable pressure

range (> 20 GPa), the energy density of BP-N is higher than the cg-N counterpart. We can prospect that at 0 GPa, the BP-N may have higher energy density than cg-N if BP-N is stabilized to ambient condition via nanotechnology or interface engineering.[35,36]

4. Conclusion

Our experiments suggested that BP-N can be synthesized in the pressure range 130–143 GPa by laser-heating method. Pressure lower to 120 GPa cannot initiate the phase transition even heating to relatively high temperature. The relationship between BP-N and cg-N structures and the phase transition therein need further experiments to study the kinetic and thermodynamic routines. Further exploration of other heating absorber acting as catalysis at the same time, such as noble metals and metal nitrides, is necessary to change or lower the kinetic barrier to form BP-N and obtain BP-N at relatively low pressure. In view of the high energy density of BP-N, it would also be of great interest to experimentally stabilize this HEDM to ambient condition via auxiliary confinement.

Acknowledgments

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