Supplementary Information (SI) for Inorganic Chemistry Frontiers.
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Supporting Information

Preservation of High-Pressure Synthesizes Pentazolate Anions *Cyclo*-N_5^- Confined in Sp^3-hybridized Boron Nitride

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Content

1. Supplement Figures and Tables.

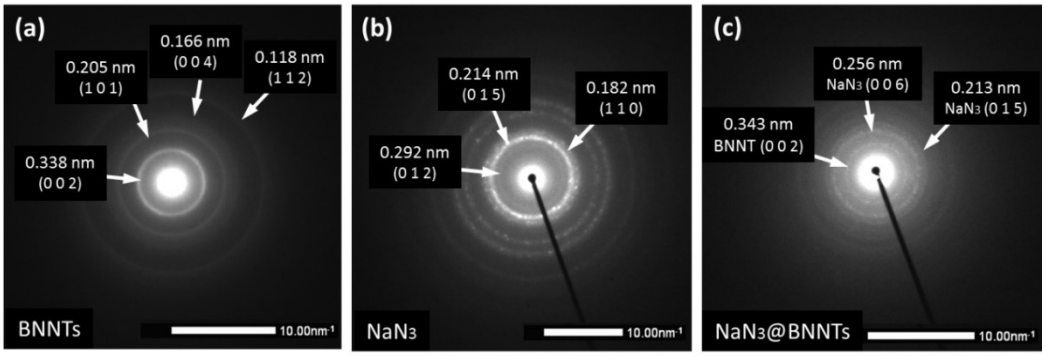

Figure S1. The SAED pattern of (a) BNNTs, (b) NaN_3 and (c) NaN_3@BNNTs.

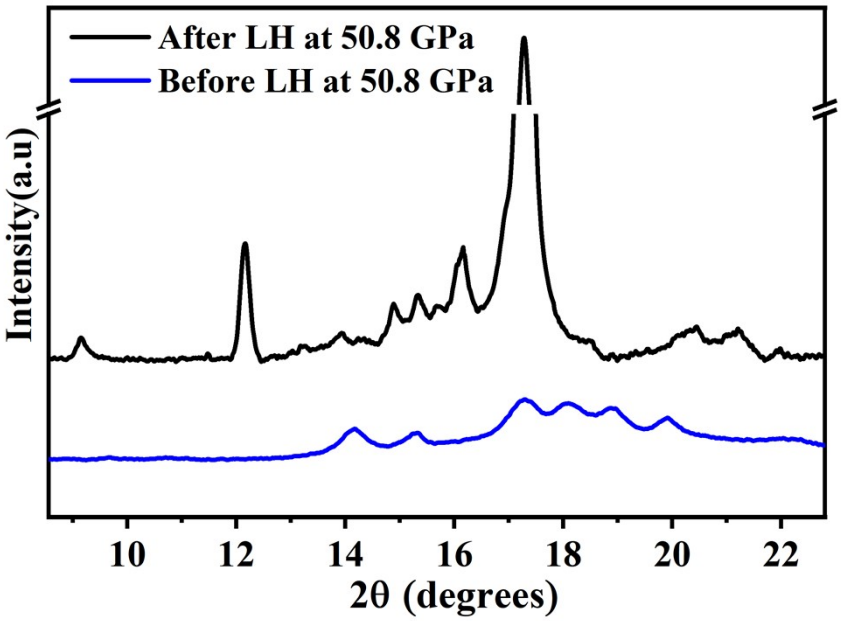

Figure S2. Experimental XRD patterns of NaN_3@MWBNNTs sample at 50.8 GPa before laser heating (LH) (blue curve) and of confined pentazole sodium after LH (black curve).

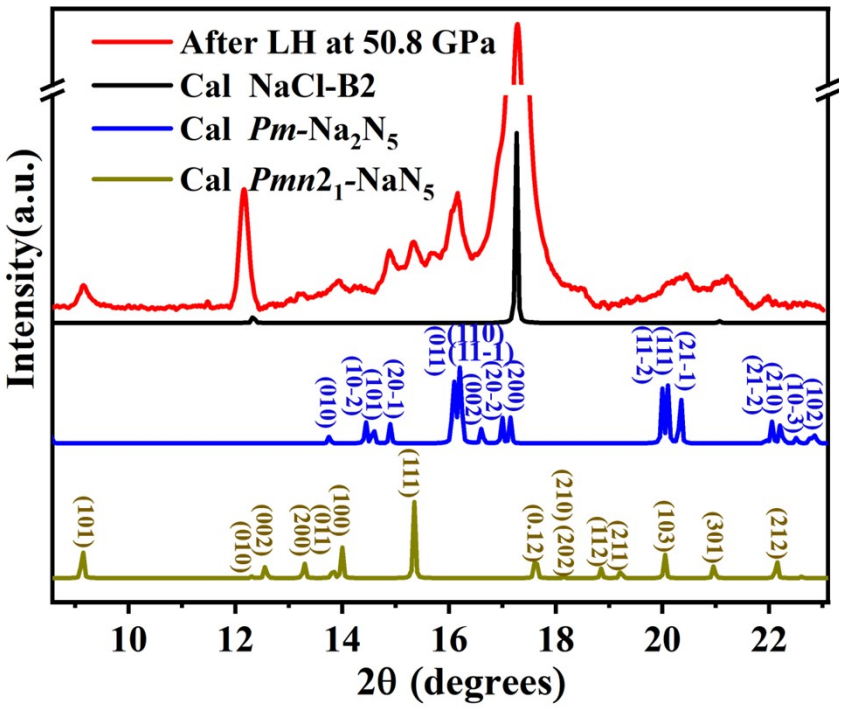

Figure S3. X-ray diffraction patterns of the confined sample taken at 50.8 GPa after laser heating (LH) compared to the calculated XRD pattern of the theoretical *Pmn*2_1-NaN_5, *Pm*-Na_2N_5 and NaCl-B2 crystal structure.

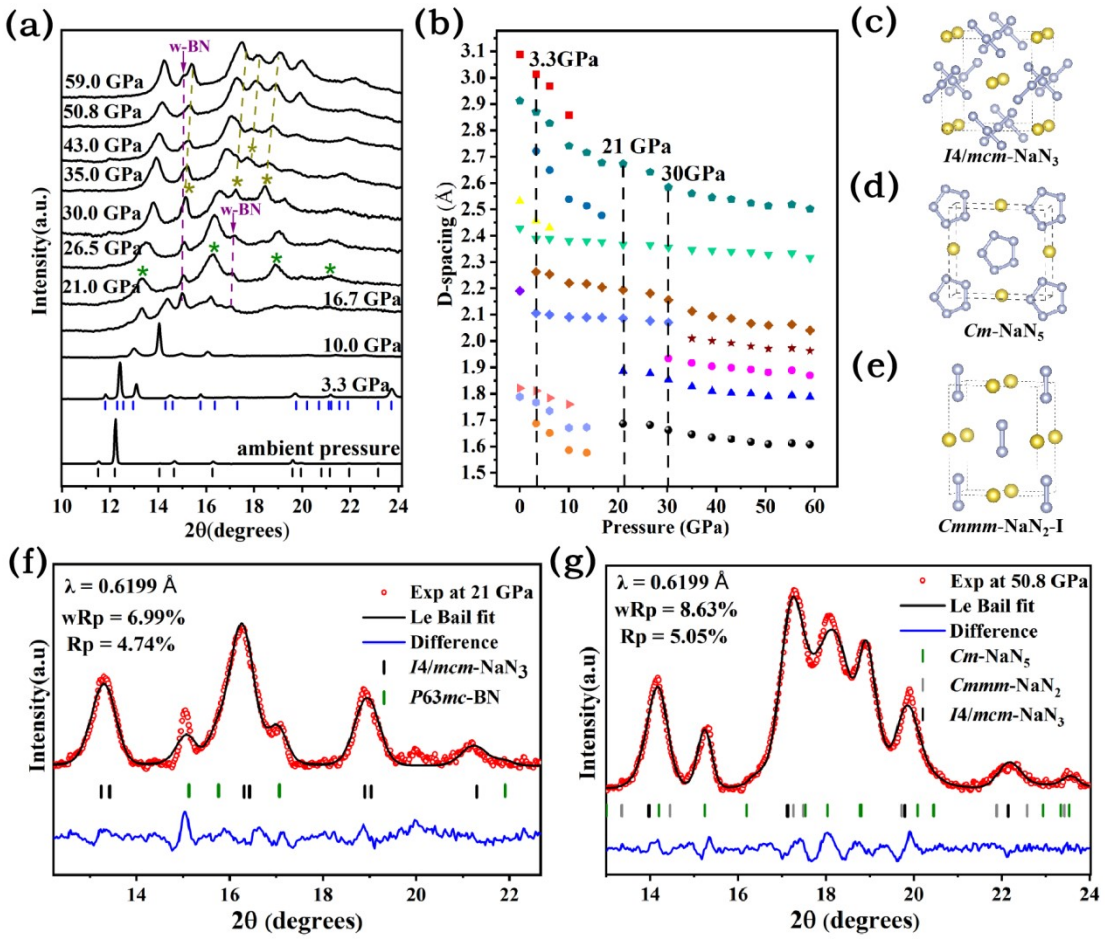

Figure S4. (a) Cold-compression experiments XRD patterns of NaN_3@MWBNNTs up to 59.0 GPa. Vertical black and blue ticks mark Bragg peaks positions of *R*-3*m*-NaN_3 and *C*2/*m*-NaN_3 respectively. The green and yellow asterisks mark represents the diffraction peaks of *I*4/*mcm*-NaN_3 and *Cm*-NaN_5, respectively. The yellow and purple dash lines represented are guides for the diffraction peaks of *Cm*-NaN_5 and w-BN. (b) The d-spacing variation under pressure of confined sample at room temperature. The black dash lines represents the phase transition pressure observed in the Cold-compression experiments. The crystal structure of the (c) *I*4/*mcm*-NaN_3, (d) *Cm*-NaN_5, and (e) *Cmmm*-NaN_2-I. Le Bail refinement of integrated X-ray diffraction pattern obtained from the confined sample at (f) 21 GPa and (e) 50.8 GPa.

Cold-compression experiments of NaN_3@MWBNNTs were performed up to 59.0 GPa at room temperature (Figure S2a). At ambient pressure, NaN_3 confined in MWBNNTs shows a typical rhombohedral structure with *R*-3*m* space group

symmetry (ICSD #1144). Le Bail refinement of the experimental XRD pattern was performed for the confined NaN_3 and the lattice parameters were provided (Table S1). Phase transition from *R*-3*m*-NaN_3 to *C*2/*m*-NaN_3 was observed at 3.3 GPa. Above 16.7 GPa, two diffraction peaks appeared at ~ 15 and 17° (masked by purple dash lines), which can be attributed to the (100) and (002) reflections in w-BN [2-4]. Then at 21.0 GPa, the diffraction peaks of *C*2/*m*-NaN_3 disappear gradually and four new peaks appear (marked by green asterisks), indicating the second phase transition from monoclinic *C*2/*m*-NaN_3 to tetragonal *I*4/*mcm*-NaN_3 (Figure S2c and f) [5]. With compressing to 30-35 GPa, three diffraction peaks of *I*4/*mcm*-NaN_3 (around 16.34, 19.01, and 21.19°) become much weaker and four new diffraction peaks appear (marked by yellow asterisks). Le-Bail fits of the diffraction pattern at 50.8 GPa (Figure S2g) indicating that under cold compression, the confined *I*4/*mcm*-NaN_3 begins to partially transform above 30.0 GPa, yielding a mixture of *Cm*-NaN_5 and *Cmmm*-NaN_2 (Figure S2d and e), as Zhou et al. Reported [6]. This three-phase coexistence (*I*4/*mcm*-NaN_3, *Cm*-NaN_5, and *Cmmm*-NaN_2) persists throughout the compression process up to our maximum pressure of 59.0 GPa. The crystallographic data of *Cmmm*-NaN_2 and *Cm*-NaN_5 unit cells at 50.8 GPa are listed in Table S2.

During the compress process, the sp^3-bonded w-BN capsule with super hardness and strength act as a pressure shield, increasing the phase transition pressures of NaN_3. Zhou et al. reported two phase transitions in NaN_3: (1) from *C*2/*m*-NaN_3 to *I*4/*mcm*-NaN_3 at 15.5 GPa, and (2) *I*4/*mcm*-NaN_3 to *Cm*-NaN_5 and *Cmmm*-NaN_2 above 19.6 GPa [6]. In contrast, our work reveals that under confinement, the phase transitions occur at notably higher pressures: the *C*2/*m* → *I*4/*mcm* transition shifts to 21 GPa, and the *I*4/*mcm* → *Cm* + *Cmmm* transition occurs at 30 GPa. This represents a substantial pressure increase of 5.5 GPa and 10.4 GPa, respectively, compared to the unconfined sample, demonstrating the significant confinement effect of sp^3-hybridized BN encapsulation under high pressure.

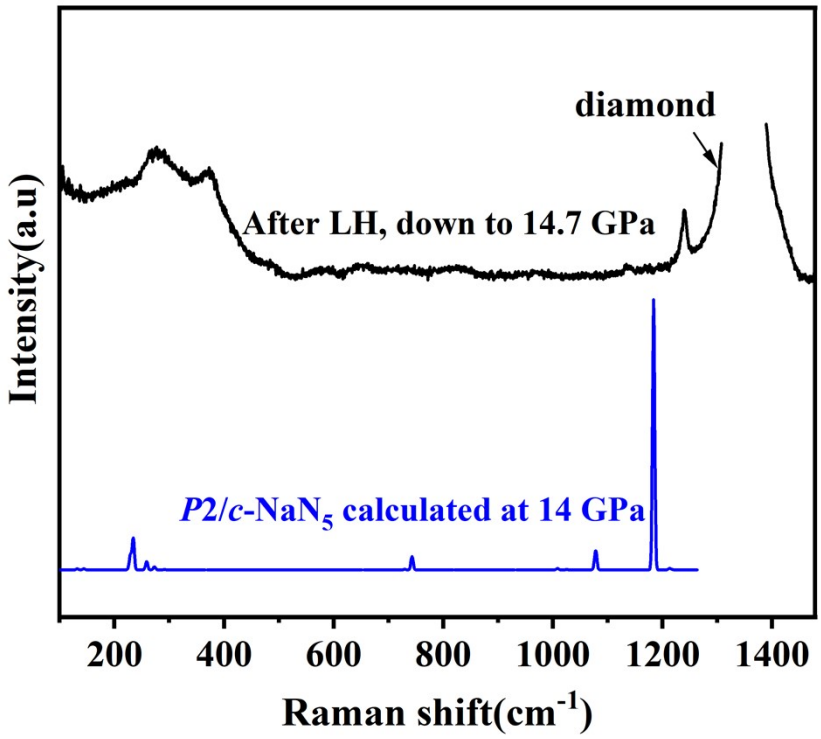

Figure S5. Experimental Raman spectrum of the laser-heated sample down to 14.7 GPa (black curve) compared with theoretical Raman spectra of *P*2/*c*-NaN_5 (blue line) at 14 GPa.

Table S1. Lattice constant for the pure NaN_3 and confined NaN_3 under ambient condition.

	Space group	**a=b (Å)**	**c (Å)**	**V (Å^3)**
NaN_3(ICSD #1144)	R-3m	3.646(0)	15.223(0)	175.2(5)
Confined NaN_3	R-3m	3.639(1)	15.207(8)	174.4(2)

Table S2. Crystallographic Data for the *I*4/*mcm*-NaN_3, *Cmmm*-NaN_2, *Cm*-NaN_5, obtained from our experiments and Ref.38.

	***I*4/*mcm*-NaN_3**		***Cmmm*-NaN_2**		***Cm*-NaN_5**	
Pressure	50.8 GPa This work	57.9 GPa Ref.38	50.8 GPa This work	57.9 GPa Ref.38	50.8 GPa This work	57.9 GPa Ref.38
a (Å)	5.102(3)	5.021(3)	4.130(1)	4.078(1)	6.210(7)	6.167(4)
b (Å)	5.102(3)	5.021(2)	4.929(7)	4.854(4)	5.471(7)	5.345(1)
c (Å)	5.092(1)	5.012(2)	2.668(1)	2.621(1)	2.922(8)	2.871(2)
β (deg)	90	90	90	90	78.112(1)	78.07(2)

Table S3. Crystallographic Data for the *Pmn*2_1-NaN_5, *Pm*-Na_2N_5 and *P*2/*c*-NaN_5 obtained from our experiments and calculations..

	***Pmn*2_1-NaN_5**		***Pm*-Na_2N_5**		***P*2/*c*-NaN_5**	
Pressure	50.8 GPa	Cal. 50 GPa	50.8 GPa	Cal. 50 GPa	14.7 GPa	Cal. 15 GPa
a (Å)	5.359(3)	5.440(1)	4.779(5)	4.645(6)	7.631(1)	7.862(2)
b (Å)	2.891(4)	2.847(5)	2.588(1)	2.595(1)	4.912(3)	5.121(5)
c (Å)	5.665(7)	5.671(8)	4.935(6)	4.811(8)	5.750(5)	5.947(6)
β (deg)	90	90	90	90	147.874(4)	149.580(6)

2. Refferencs.

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