Supporting Information

Pressure-stabilized polymerization of nitrogen in manganese nitrides at ambient and high pressures

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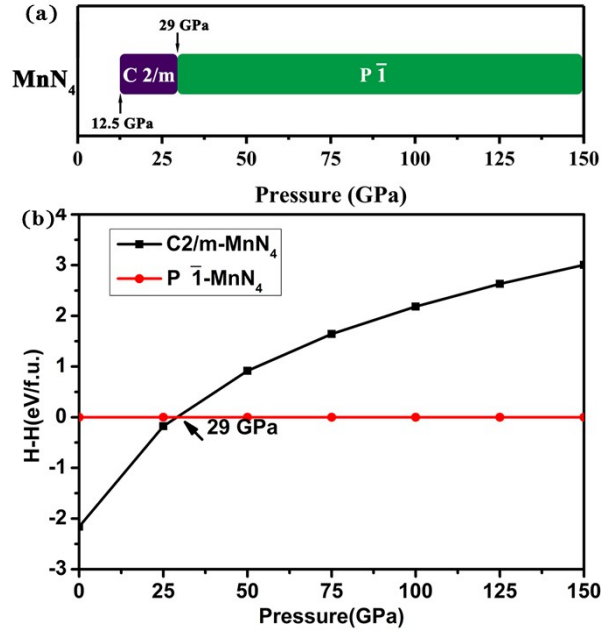
Fig. S1. (a) The stable pressure range of C2/m-MnN$_4$ and P $\bar{1}$-MnN$_4$, and (b) enthalpy of the C2/m-MnN$_4$ phase relative to the P $\bar{1}$-MnN$_4$ phase with pressure.
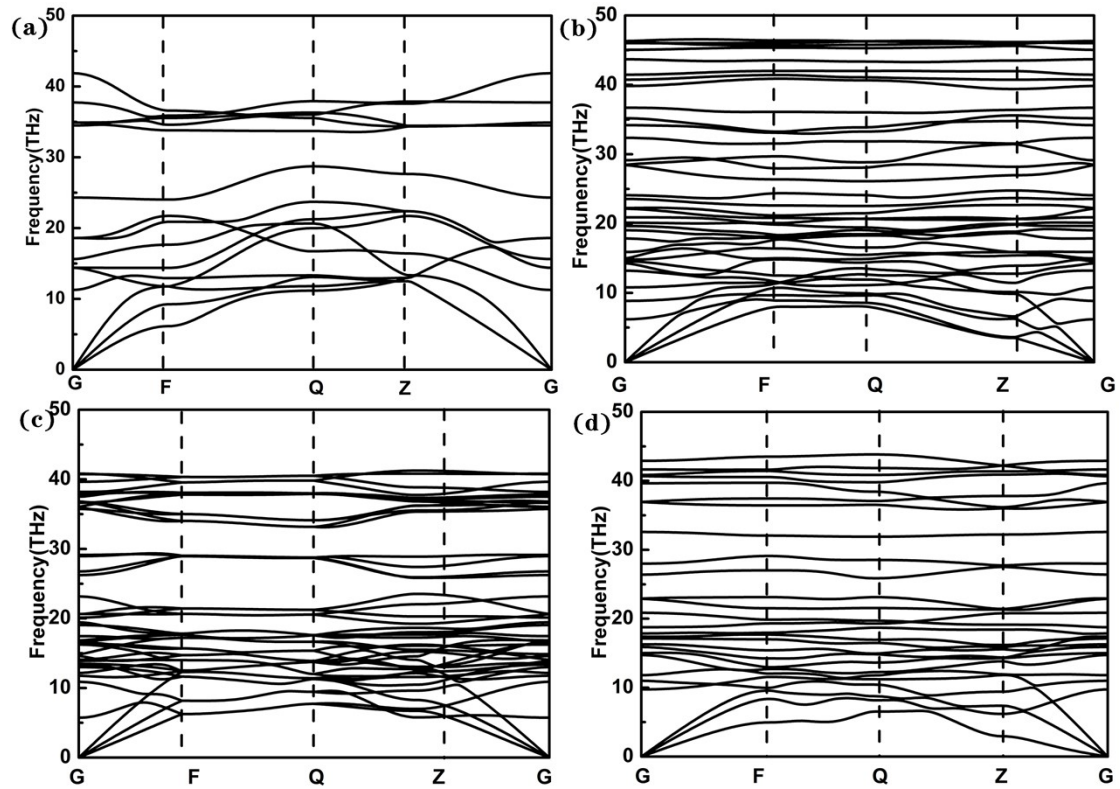
Fig. S2. The phonon dispersion curves of (a) P4/mmm-MnN$_4$ at 100 GPa, (b) P $\bar{1}$-MnN$_5$ at 150 GPa, (c) C2/m-MnN$_6$ at 50 GPa, and (d) P $\bar{1}$-MnN$_8$ at 50 GPa.
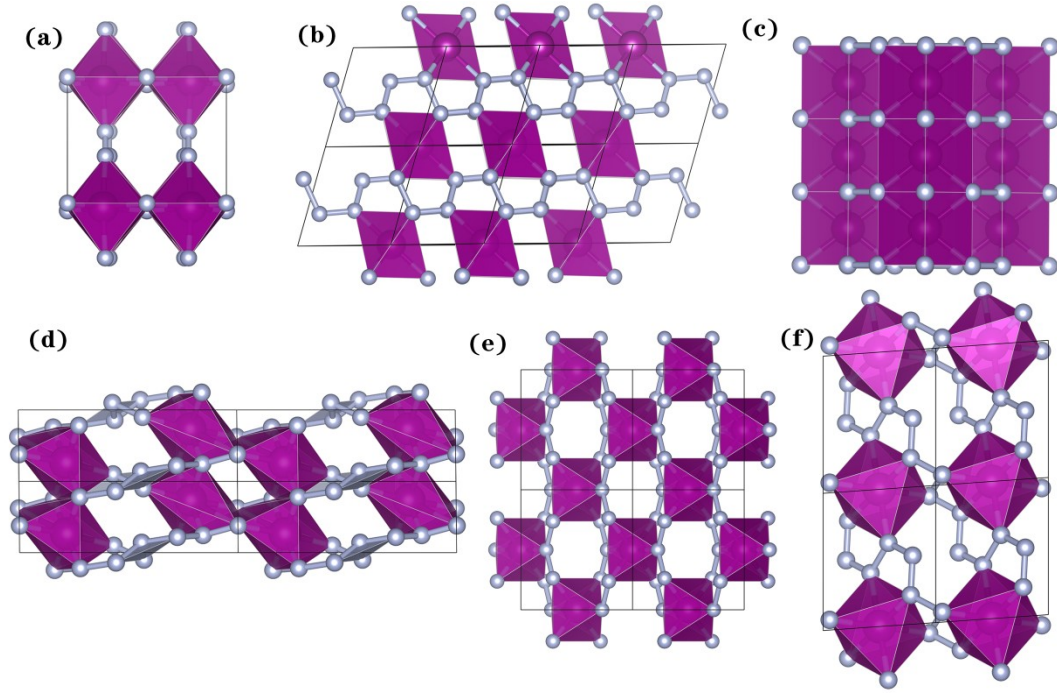
Fig. S3. The polyhedral supercell structures of the predicted phases: (a) C2/m-MnN$_4$, (b) P $\bar{1}$-MnN$_4$, (c) P4/mmm-MnN$_4$, (d) P $\bar{1}$-MnN$_5$, (e) C2/m-MnN$_6$, and (f) P $\bar{1}$-MnN$_8$.
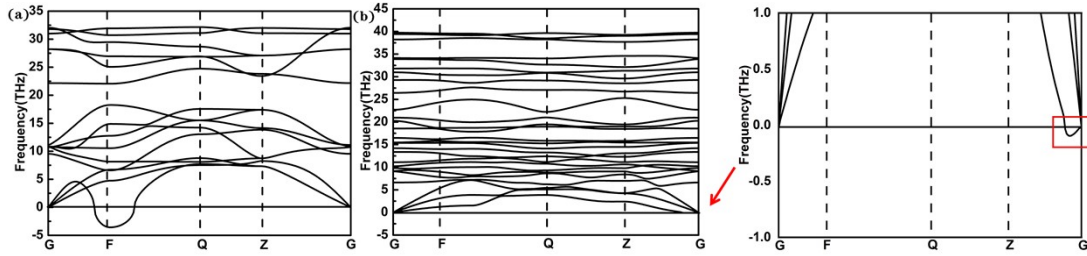
Fig. S4. The phonon dispersion curves of (a) P4/mmm-MnN$_4$ at 0 GPa and (b) P $\bar{1}$-MnN$_8$ at 0 GPa.

Table S1. Structural parameters of the Mn-N compounds at corresponding pressure.

Structure	Pressure (GPa)	Lattice parameters (Å, °)	Atomic Positions
P6$_3$/mmc-Mn$_2$N	50	a = 2.5102 b = 2.5102 c = 8.6143 α = 90.00° β = 90.00° γ = 120.00°	Mn$_1$(4f) (0.6667, 0.3333, 0.6074) N$_1$(2d) (0.6667, 0.3333, 0.2500)

C2/m-MnN$_4$	20	a = 7.6064 b = 5.5432 c = 10.3809 α = 90.00° β = 154.99° γ = 90.00°	Mn$_1$(4g) (0.0000, 0.2238, 0.0000) N$_1$(8j) (-1.5704, 0.2380, -1.5968) N$_2$(4i) (-2.2758, 0.5000, -1.9694) N$_3$(4i) (0.3055, 0.0000, -0.0290)
P $\bar{1}$-MnN$_4$	50	a = 3.7071 b = 3.8140 c = 5.1901 α = 98.21° β = 110.51° γ = 73.47°	Mn$_1$(2i) (0.7632, 0.0026, 0.7613) N$_1$(2i) (0.1861, 0.6554, 0.6873) N$_2$(2i) (0.6775, 0.6498, 0.1855) N$_3$(2i) (0.0992, 0.3231, 0.9615) N$_4$(2i) (0.5984, 0.3191, 0.4640)
P4/mmm-MnN$_4$	100	a = 3.5131 b = 3.5131 c = 2.3547 α = 90.00° β = 90.00° γ = 90.00°	Mn$_1$(1c) (0.5000, 0.5000, 0.0000) N$_1$(4k) (0.8050, 0.1940, 0.5000)
P $\bar{1}$-MnN$_5$	150	a = 2.3722 b = 3.7598 c = 7.2847 α = 88.00° β = 90.62° γ = 91.50°	Mn$_1$(2i) (0.2644, 0.6189, 0.2150) N$_1$(2i) (0.2188, 0.0321, 0.7226) N$_2$(2i) (0.8591, 0.1085, 0.4408) N$_3$(2i) (0.3789, 0.8451, 0.0020) N$_4$(2i) (0.7555, 0.2581, 0.1595) N$_5$(2i) (0.0997, 0.4199, 0.4312)
C2/m-MnN$_6$	50	a = 5.1820 b = 4.8642 c = 4.3284 α = 90.00° β = 61.10° γ = 90.00°	Mn$_1$(2d) (0.0000, 0.5000, 0.5000) N$_1$(8j) (0.7870, 0.2375, 0.8349) N$_2$(4i) (0.7265, 0.0000, 0.7307)

		a = 3.7604	Mn$_1$(1e) (0.5000, 0.5000, 0.0000)
		b = 3.7855	N$_1$(2i) (0.4204, 0.5923, 0.6062)
P $\bar{1}$-MnN$_8$	50	c = 4.4830	N$_2$(2i) (0.7774, 0.2247, 0.7866)
		α = 97.15°	N$_3$(2i) (0.9421, 0.8681, 0.0742)
		β = 92.31°	
		γ = 102.71°	N$_4$(2i) (0.2046, 0.7742, 0.4997)

Table S2. The elastic constants C_{ij} (GPa) of the Mn-N compounds at 0 GPa.

MnN$_x$	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
C2/m-MnN$_4$	404	214	320	103	15	26	8	4	10	82	-4	-4	0.02
P $\bar{1}$-MnN$_4$	439	629	295	172	185	214	80	120	-137	68	-35	-88	-74
P4/mmm-MnN$_4$	720	720	396	109	109	205	100	4	-	-	-	-	-
P $\bar{1}$-MnN$_5$	408	292	584	122	238	164	117	141	-36	70	-33	-102	-28
C2/m-MnN$_6$	211	520	441	176	136	134	101	87	-8	107	25	-6	-20
P $\bar{1}$-MnN$_8$	108	423	280	105	55	60	37	49	18	111	-8	-60	-23

Monoclinic structure:

The mechanical stability criteria of monoclinic structure are shown as follows:

$C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $[C_{11} + C_{22} + C_{33} + 2 (C_{12} + C_{13} + C_{23})] > 0$

$C_{33}C_{55} - C_{35}^2 > 0$, $C_{44}C_{66} - C_{46}^2 > 0$, $C_{22} + C_{33} - 2C_{23} > 0$,

$C_{22} (C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - (C_{23}^2) C_{55} - (C_{25}^2) C_{33} > 0$

$2 [C_{15}C_{25} (C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35} (C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35} (C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^2 (C_{22}C_{33} - C_{23}^2) + C_{25}C_{25} (C_{11}C_{33} - C_{13}^2) + C_{35}C_{35} (C_{11}C_{22} - C_{12}^2)] + C_{55}g > 0$

At ambient pressure, the monoclinic C2/m-MnN$_4$ and C2/m-MnN$_6$ are mechanically unstable due to that their elastic tensors Cij do not satisfy to the criteria.

Triclinic structure:

The mechanical stability criteria of triclinic structure are shown as follows:

$C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$

$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0$

$(C_{33}C_{55} - C_{35}^2) > 0, (C_{44}C_{66} - C_{46}^2) > 0, (C_{22} + C_{33} - 2C_{23}) > 0$

$[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{23}^2C_{33}] > 0$

At ambient pressure, the triclinic P $\bar{1}$-MnN$_4$, P $\bar{1}$-MnN$_5$ and P $\bar{1}$-MnN$_8$ are mechanically stable due to that their elastic tensors Cij satisfy to the criteria.

Tetragonal structure:

The mechanical stability criteria of tetragonal structure are shown as follows:

$C_{11} > |C_{12}|$

$2C_{13}^2 < C_{33}(C_{11} + C_{12})$

$C_{44} > 0$

At ambient pressure, the tetragonal P4/mmm-MnN$_4$ is mechanically stable due to that its elastic tensor C_{ij} satisfies to the criteria.

Table S3. The Bader charges transfer of the Mn-N compounds, the "N" is the number of each equivalent atom (Mn and N atoms) in one cell and the "sigma (e)" is the corresponding number of electrons lost and gained by the Mn and N atoms, respectively.

Structure	Atom	N	Charge value(e)	σ(e)
C2/m-MnN$_4$	Mn$_1$	4	11.67	-1.30
	N$_1$	8	5.20	0.20
	N$_2$	4	5.49	0.49
	N$_3$	4	5.41	0.41
P $\bar{1}$-MnN$_4$	Mn$_1$	2	11.81	-1.19
	N$_1$	2	5.20	0.20
	N$_2$	2	5.22	0.22
	N$_3$	2	5.37	0.37
	N$_4$	2	5.39	0.39
P4/mmm-MnN$_4$	Mn$_1$	1	11.76	-1.24
	N$_1$	4	5.31	0.31
P $\bar{1}$-MnN$_5$	Mn$_1$	2	11.90	-1.10
	N$_1$	2	5.34	0.34

	N_2	2	5.34	0.34
	N_3	2	5.25	0.25
	N_4	2	5.19	0.19
	N_5	2	4.99	-0.01
C2/m-MnN$_6$	Mn_1	2	11.70	-1.30
	N_1	8	5.23	0.23
	N_2	4	5.19	0.19
P $\bar{1}$-MnN$_8$	Mn_1	1	11.72	-1.28
	N_1	2	5.22	0.22
	N_2	2	5.04	0.04
	N_3	2	5.16	0.16
	N_4	2	5.18	0.18