Supplemental Material

for

Lanthanium Nitride LaN_9 Featuring Azide Units: the First Metal Nine-nitride as High-energy Density Material

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A New High-Pressure Phase for LaN_4

In addition to the known La-N compounds, and newly predicted LaN_9, a notable monoclinic phase for LaN_4 (denoted as *P*-1 LaN_4), in the pressure range from 39 to 83 GPa is predicted. Combined with previous reports[1], LaN_4 is energetically stable above 14 GPa, then undergoes a structural transition from *C*2/*c* to *P*-1 structure at 39 GPa, and finally it decomposes into *C*2/*c* LaN_3 *and Cm* LaN_8 at 83 GPa. As shown in Fig. S4(b), *P*-1 LaN_4 possesses N_4 chair-type polymeric nitrogen units with an average N-N bond length of 1.33 Å at 50 GPa. Figure S4 (c) suggests that the N-N bonding states are fully occupied, while the antibonding states are partially occupied, indicating the covalent bonding between neighboring N atoms. The ICOHP value for N-N in *P*-1 LaN_4 is -4.2, which is smaller in absolute magnitude compared to that of N-N in both LaN_9 and *Cm* LaN_8, indicating the relatively weaker N-N covalent bonding in *P*-1 LaN_4. Phonon spectra calculations and AIMD simulations demonstrate the dynamical and thermal stability of *P*-1 LaN_4 at 50 GPa [Figs. S5(a) and S5(b)]. Band structure calculation reveals the metallic property of *P*-1 LaN_4 [Fig. S5(c)]. After the structure optimization, N_4 chair-type polymeric nitrogen units will turn into nitrogen molecules at ambient pressure[Fig. S4(d)], attributed to the weak N-N covalent interactions.

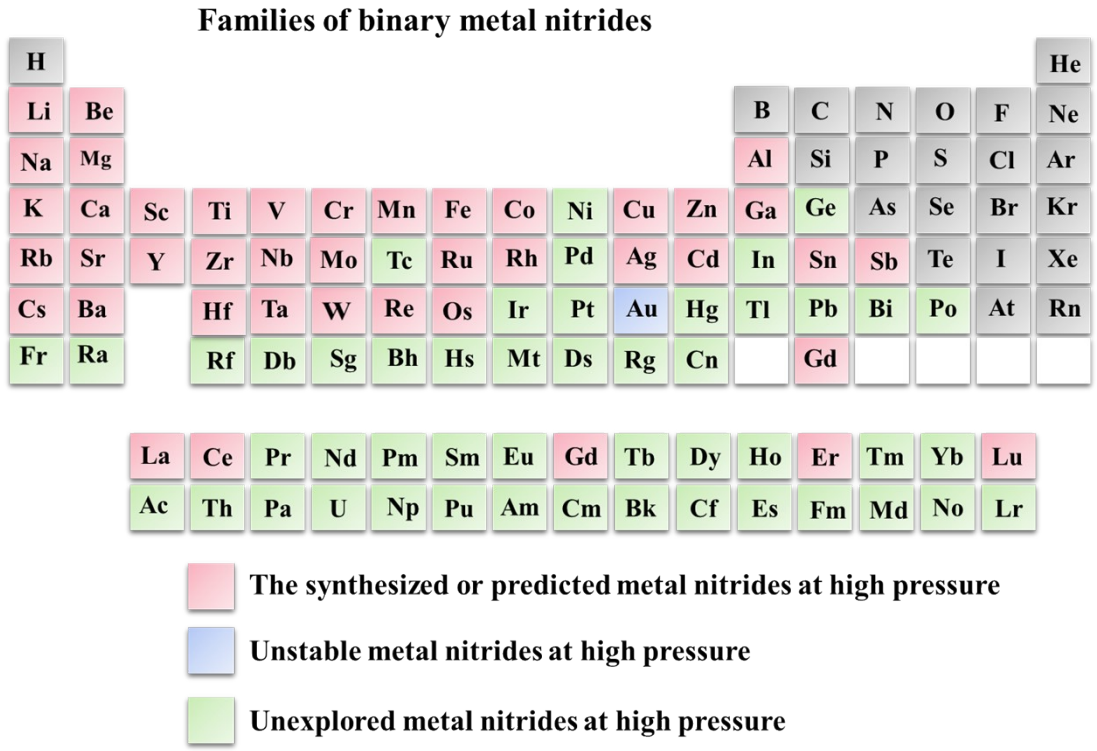


Figure. S01. The families of binary metal nitrides at high pressure. Lanthanum, a member of the lanthanide series, tends to have higher production costs compared to other metals such as lithium, sodium, potassium, calcium, magnesium, iron, nickel, and copper. This is primarily attributed to the relative scarcity of lanthanides and the complexity involved in their extraction processes. Despite these higher production costs, it is noteworthy that a high level of purity, specifically 99.99%, can be obtained for lanthanum at a cost of $3.5 per gram. Therefore, lanthanum can be considered relatively affordable.

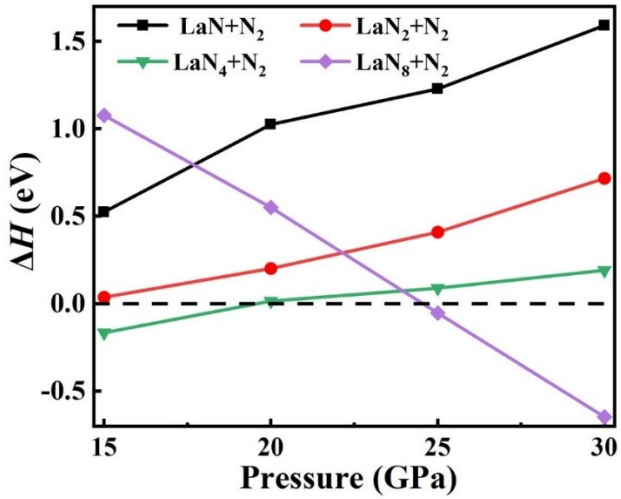


Fig. S1. (a) The formation enthalpy of LaN_9 with respect to discomposition into stable binary comounds and nitrogen at given pressure.

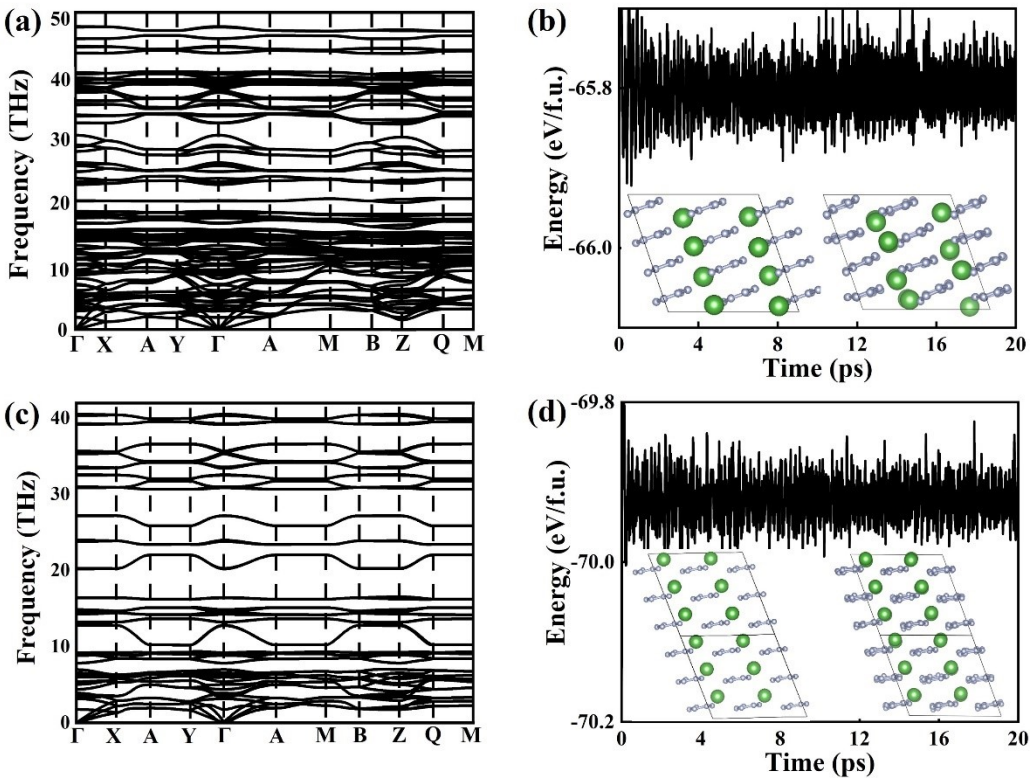


Figure S2. Phonon dispersion curves of LaN_8 at (a) 60 and (c) 0 GPa. Energy fluctuations during MD simulations (300 K) of LaN_8 at (b) 60 and (d) 0 GPa.

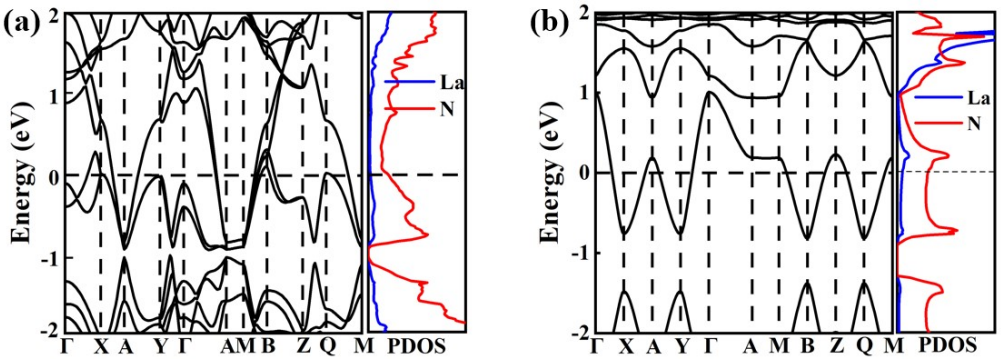


Figure S3. Band structures and PDOS for LaN_8 at (a) 60 GPa and (b) 0 GPa.

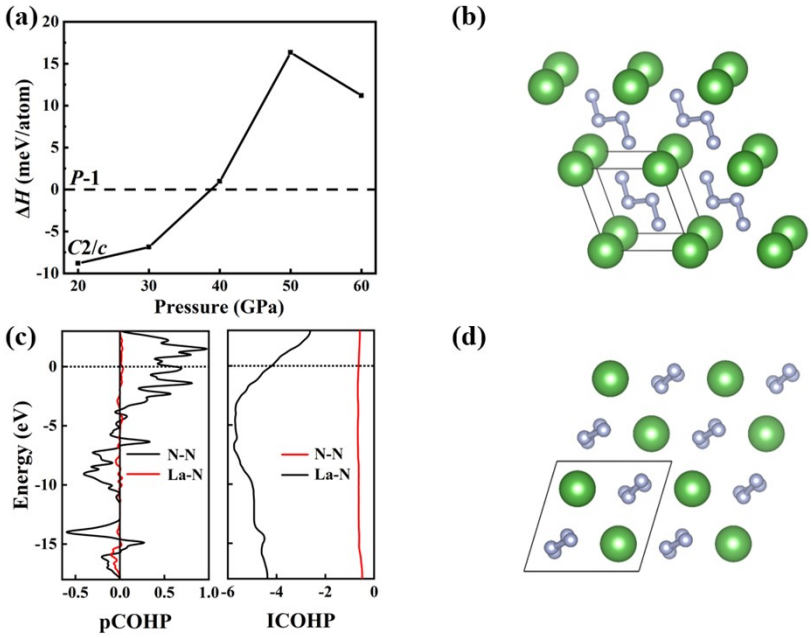


Figure S4. (a) The enthalpy difference curves of LaN_4 in the *C*2/*c* phase with respect to the *P*-1 phase. (b) Crystal structure of LaN_4 at 50 GPa. (c) Plots of pCOHP and ICOHP for LaN_4 at 50 GPa. (d) Crystal structure of LaN_4 at 0 GPa.

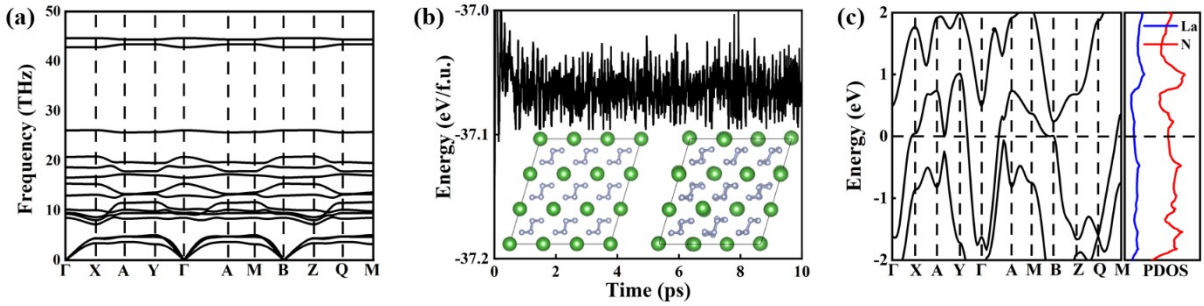
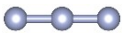
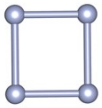
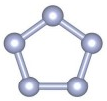
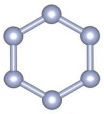


Figure S5. (a)Phonon dispersion curves, (b) energy fluctuations during MD simulations at 300 K, and (c) band structures and PDOS of LaN_4 at 50 GPa.

Table S0I. Common polymerization forms of nitrogen in metal nitrides.

Compounds	Structure type	Nitrogen net
MN_3(M=Li, Na, K, Rb, Cs), BaN_6, Ba_2N_{11}	N_3 units	
MnN_4, Al_2N_7, Na_2N_8, Li_2N_4, MgN_4	N_4 rings	
MN_5(M=Li, Na, K, Rb, Cs, Ca, Sr, Ba, Cu, Ta), MN_{10}(M=Be, Mg, Ba), MN_{15}(M=Al, Ga, Sc, Y),HfN_{20}	N_5 rings	
WN_6, SnN_6, MN_3(M=Cs, Ca, Sr, K, Mg)	N_6 rings	

MN_4 (M = Be, Cd, Fe, Gd, Re, Os, W, Ru, Zn, Sn),GdN_6, ReN_8, HfN_{10}, ScN_5, SnN_8, FeN_6, FeN_4, FeN_8, Fe_3N_8	N-chains	

Table SI. The optimized structural parameters of LaN_4, LaN_8 and LaN_9.

Compound	Pressure (GPa)	Space group	*a*, *b*, *c* (Å) *α*, *β*, *γ* (deg)	Atomic position
LaN_4	50	*P*-1	*a*=6.366 *b*=7.034 *c*=5.116 *α*=*γ*=90 *β*=110.410	La (2a) (0.000, 0.000, 0.000) N1 (2i) (0.279, 0.739, 0.670) N2 (2i) (0.551, 0.526, 0.342)
LaN_8	0	*Cm*	*a*=6.366 *b*=7.034 *c*=9.456 *α*=*γ*=90 *β*=149.532	La(2a) (1.179, 0.000, 0.283) N1(4b) (1.257, 0.154, 0.583) N2(4b) (1.198, -0.171, 0.972) N3(4b) (0.878, -0.178, 0.696) N4(2a) (0.326, 0.000, 0.094) N5(2a) (1.462, 0.000, 0.751)
LaN_8	50	*Cm*	*a*=9.274 *b*=6.629 *c*=4.605 *α*=*γ*=90 *β*=80.883	La1(2a) (-0.384, 0.000, 0.207) La2(2a) (-0.846, 0.000, 0.817) N1(4b) (-0.191, -0.162, -0.172) N2(4b) (-0.742, -0.161, 0.324) N3(4b) (-0.034, -0.825, -0.705) N4(4b) (-0.481, -0.823, -0.240) N5(4b) (-0.124, -0.327, -0.195) N6(4b) (-0.674, -0.329, 0.329) N7(2a) (-0.414, 0.000, -0.285) N8(2a) (-0.970, 0.000, 0.325) N9(2a) (-0.108, 0.000, -0.183) N10(2a) (-0.657, 0.000, 0.304)
LaN_9	20	*Pm*-3	*a*=*b*=*c*=4.732 *α*=*β*=*γ*=90	La (1b) (0.500, 0.500, 0.500) N1(3d) (0.000, 0.000, 0.500) N2(6g) (0.753, 0.500, 0.000)

Table SII. The calculated elastic constants C_{ij} (GPa) of LaN_8 and LaN_9 at ambient pressure.

Compounds	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
LaN_8	55	37	41	-5	317	32	-12	184	-1	31	-2	23	12
LaN_9	155	25	/	/	/	/	/	/		15			

Table SIII. Bader charges analysis of *P*-1 LaN_4, *cm* LaN_8, and LaN_9 at high pressure.

Compounds	Pressure	La(e)	N(e)
LaN_4	50	-1.88	+0.47
LaN_8	60	-1.98	+0.25
LaN_9	20	-2.10	+0.23

REFERENCES

1 X. Li, X. Zhang, Z. Yang, Y. Liu and G. Yang, Pressure-stabilized graphene-like P layer in superconducting LaP_2, *Phys. Chem. Chem. Phys.*, 2022, **24**, 6469–6475.