Supporting Information

Stable calcium nitrides at ambient and high pressures

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Supplementary Figures

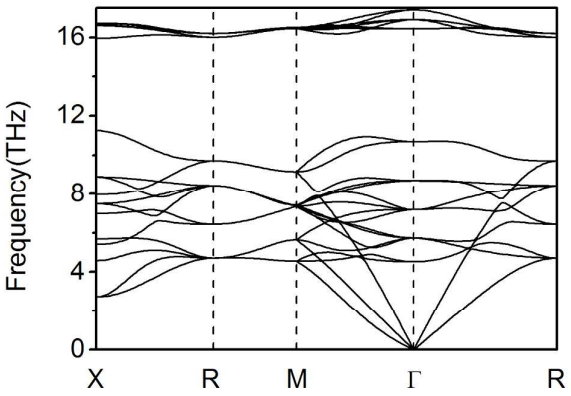

Figure. S1. Phonon dispersion curves of Ca_2N in the *Fm*-3*m* phase at 50 GPa.

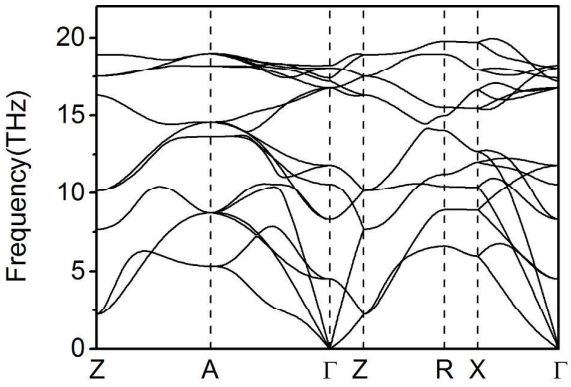

Figure. S2. Phonon dispersion curves of Ca_2N in the *I*4/*mmm* phase at 100 GPa.

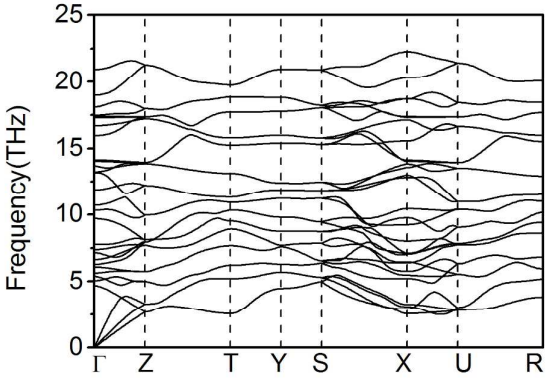

Figure. S3. Phonon dispersion curves of Ca_3N_2 in the *Pm*n2_1 phase at 50 GPa.

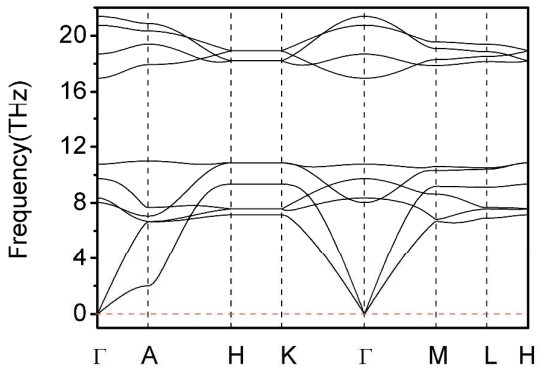

Figure. S4. Phonon dispersion curves of Ca_3N_2 in the *P*-3*m*1 phase at 100 GPa.

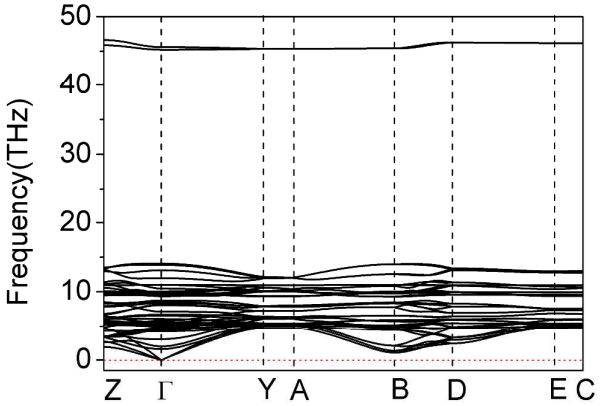

Figure. S5. Phonon dispersion curves of CaN in the *C*2/*m* phase at 0 GPa.

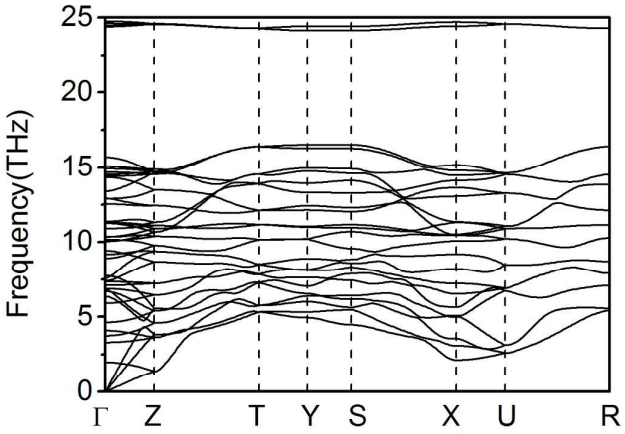

Figure. S6. Phonon dispersion curves of CaN in the $Cmc2_1$ phase at 20 GPa.

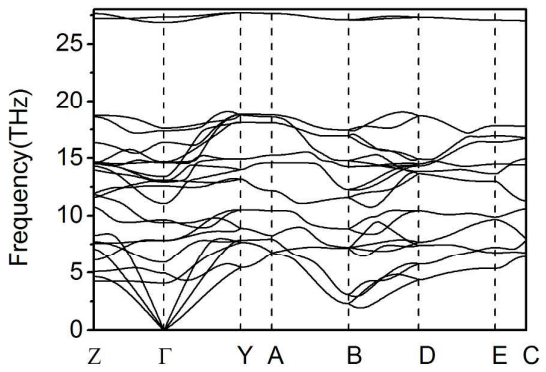

Figure. S7. Phonon dispersion curves of CaN in the *C*2/*m* phase at 50 GPa.

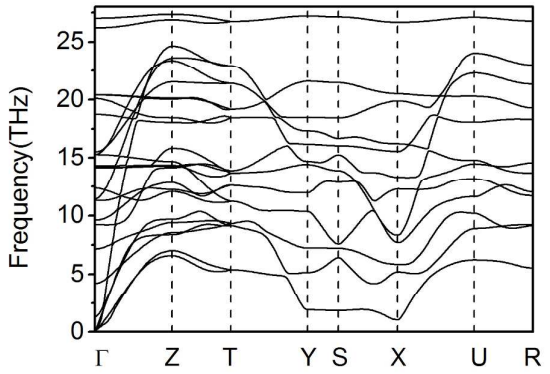

Figure. S8. Phonon dispersion curves of CaN in the *Pbam* phase at 100 GPa.

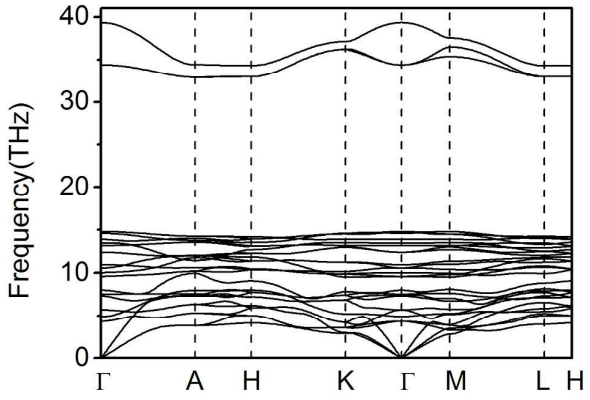

Figure. S9. Phonon dispersion curves of Ca_2N_3 in the *P*-62*m* phase at 20 GPa.

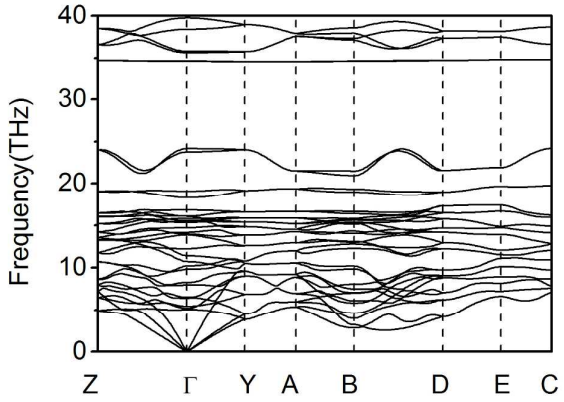

Figure. S10. Phonon dispersion curves of CaN_2 in the *P*21/*c* phase at 50 GPa.

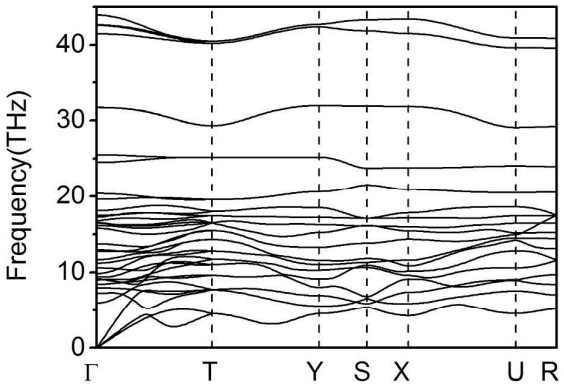

Figure. S11. Phonon dispersion curves of CaN_2 in the *Pbam* phase at 100 GPa.

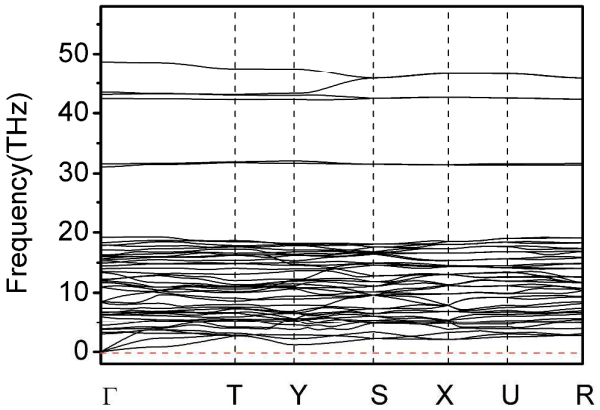

Figure. S12. Phonon dispersion curves of CaN_3 in the *Pmma* phase at 20 GPa.

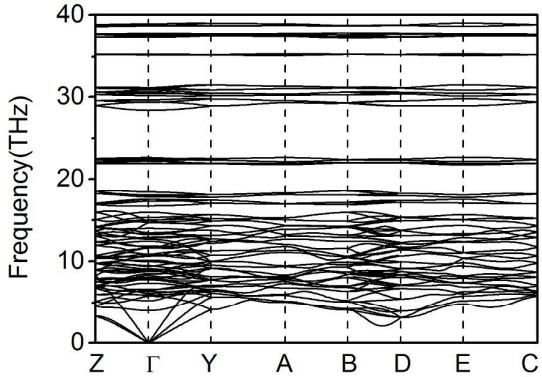

Figure. S13. Phonon dispersion curves of CaN_3 in the *C*2/*c* phase at 50 GPa.

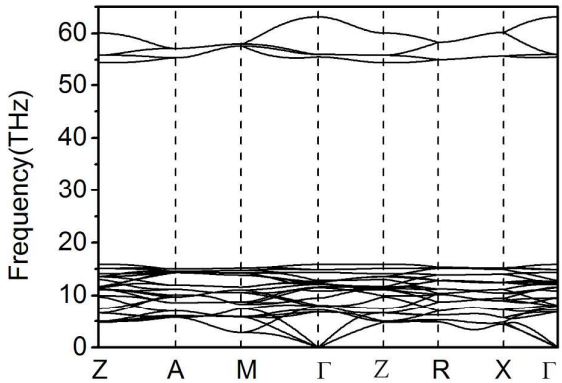

Figure. S14. Phonon dispersion curves of CaN_4 in the *P*4/*mbm* phase at 15 GPa.

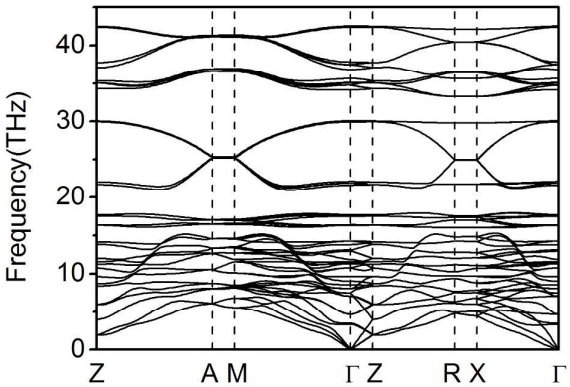

Figure. S15. Phonon dispersion curves of CaN_4 in the $P4_12_12$ phase at 50 GPa.

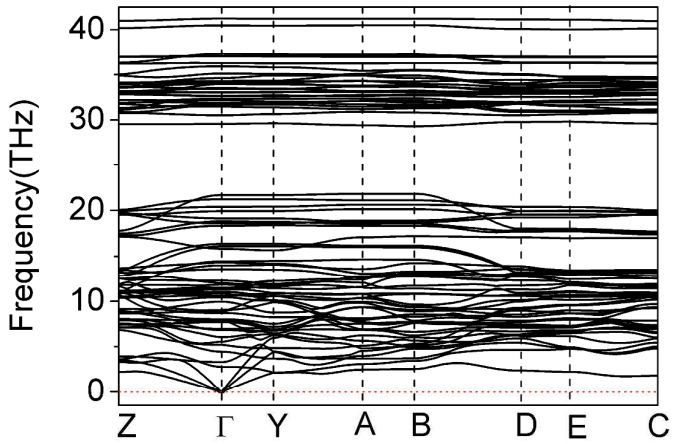

Figure. S16. Phonon dispersion curves of CaN_5 in the *Pm* phase at 50 GPa.

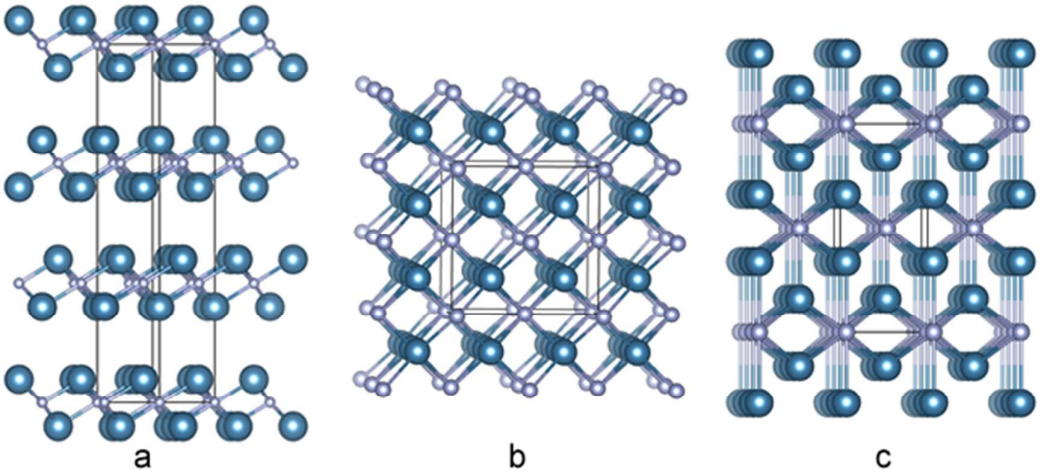

Figure. 17. Crystal structures of Ca_2N. a, b, and c represent *R*-3*m, Fm*-3*m, I*4/*mmm* Phase of Ca_2N, respectively.

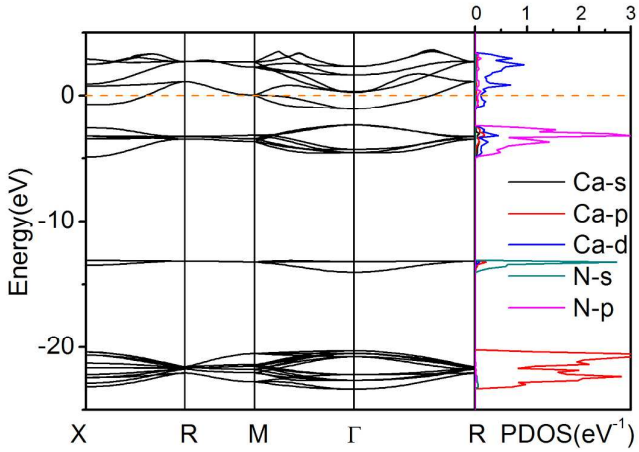

Figure. S18. Electronic band structure and projected DOS of the *Fm*-3*m*

structure of Ca_2N at 50 GPa.

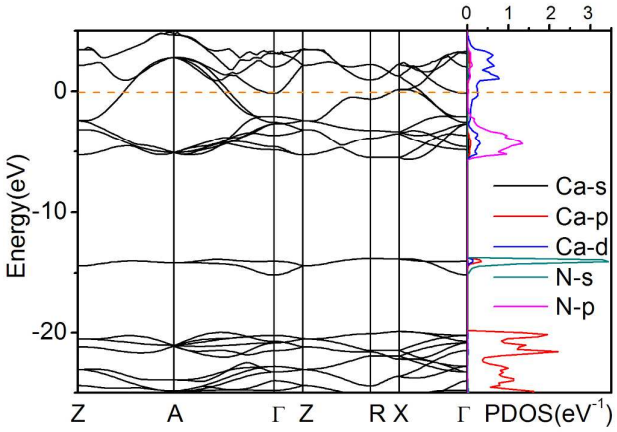

Figure. S19. Electronic band structure and projected DOS of the *I*4/*mmm* structure of Ca_2N at 100 GPa.

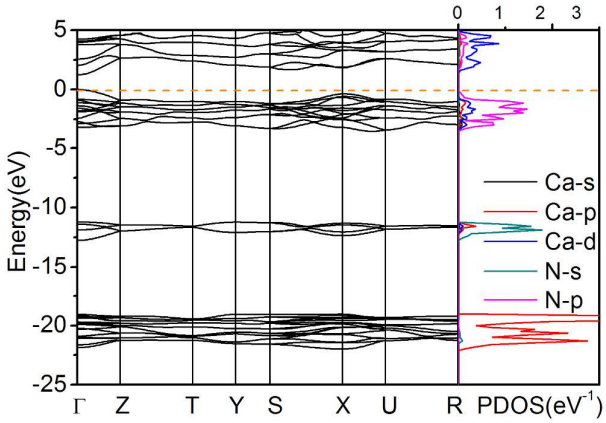

Figure. S20. Electronic band structure and projected DOS of the *Pmn*2$_1$ structure of Ca_3N_2 at 50 GPa.

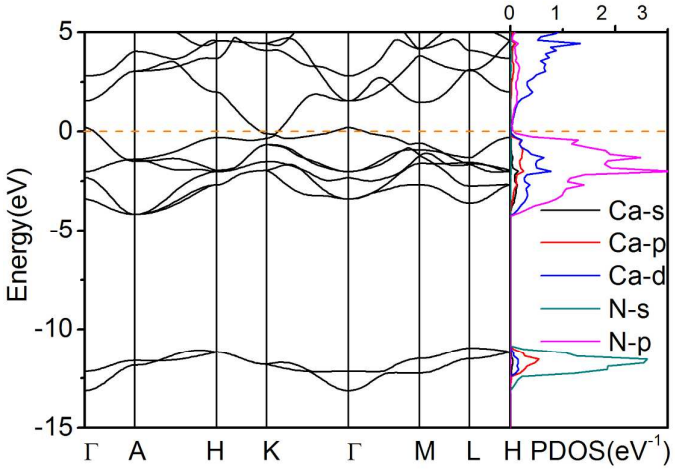

Figure. S21. Electronic band structure and projected DOS of the *P*-3*m*1 structure of Ca_3N_2 at 100 GPa.

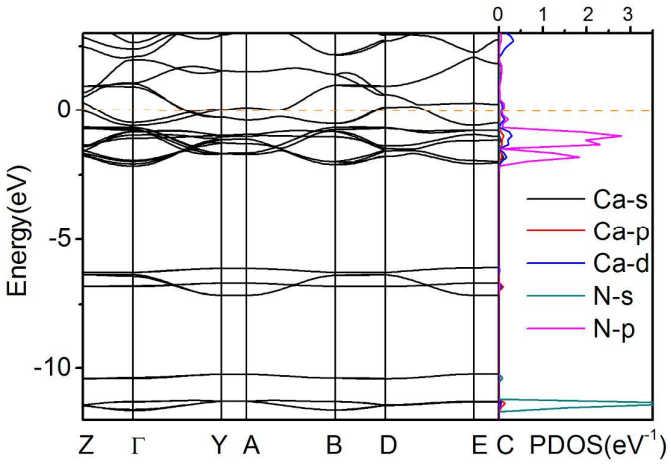

Figure. S22. Electronic band structure and projected DOS of the *C*2/*m* structure of CaN at 0 GPa.

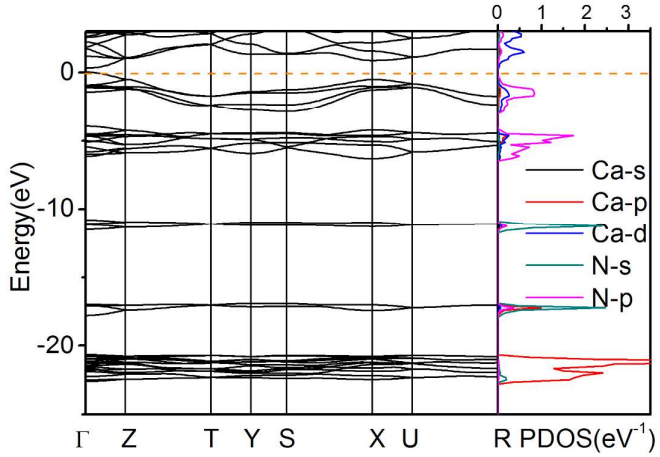

Figure. S23. Electronic band structure and projected DOS of the *Cmc*2$_1$ structure of CaN at 20 GPa.

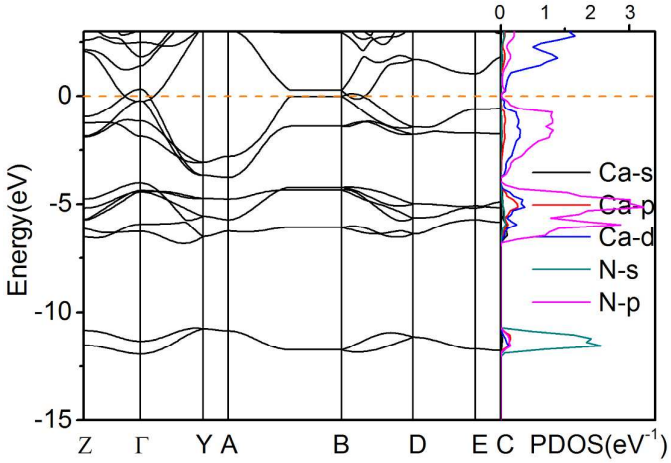

Figure. S24. Electronic band structure and projected DOS of the *C*2/*m* structure of CaN at 50 GPa.

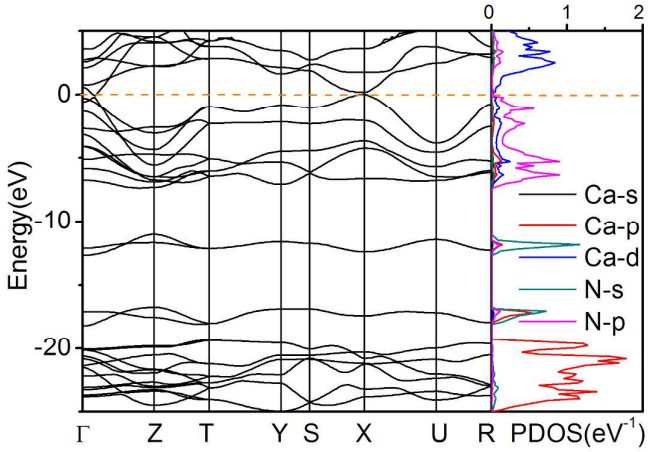

Figure. S25. Electronic band structure and projected DOS of the *Pbam* structure of CaN at 100 GPa.

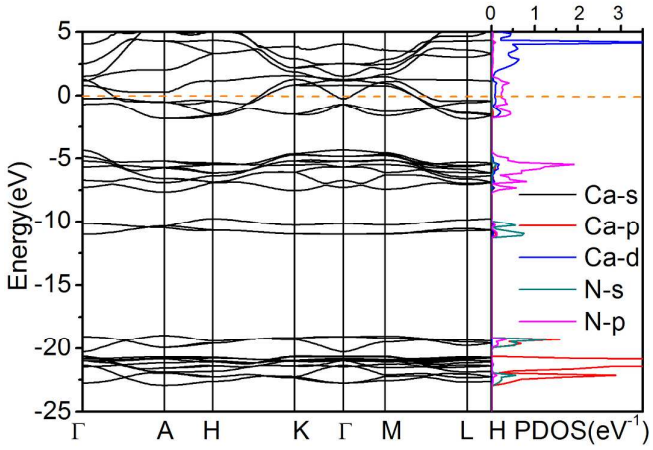

Figure. S26. Electronic band structure and projected DOS of the *P*-62*m* structure of Ca_2N_3 at 20 GPa.

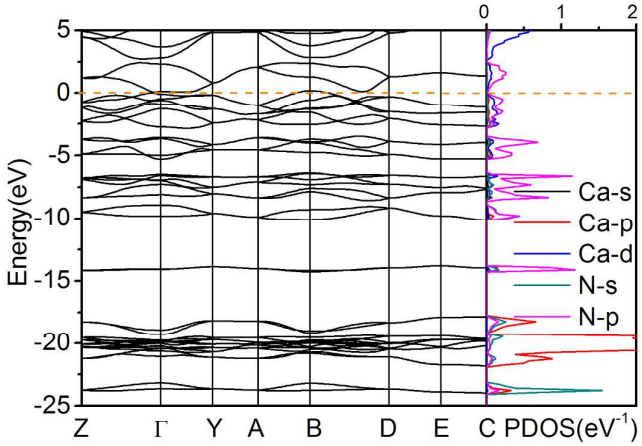

Figure. S27. Electronic band structure and projected DOS of the $P2_1/c$ structure of CaN_2 at 50 GPa.

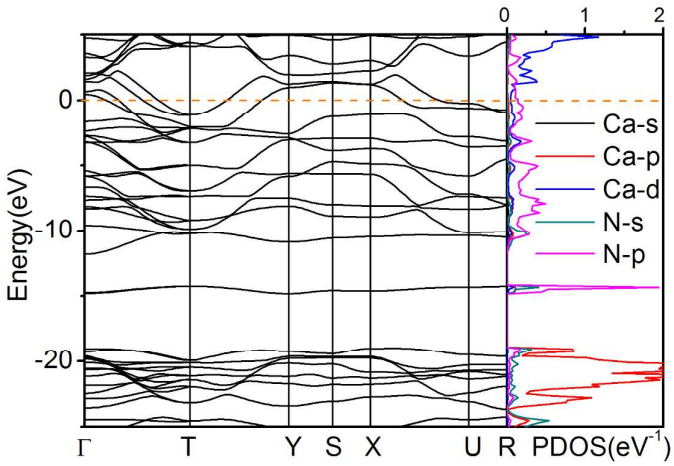

Figure. S28. Electronic band structure and projected DOS of the *Pbam* structure of CaN_2 at 100 GPa.

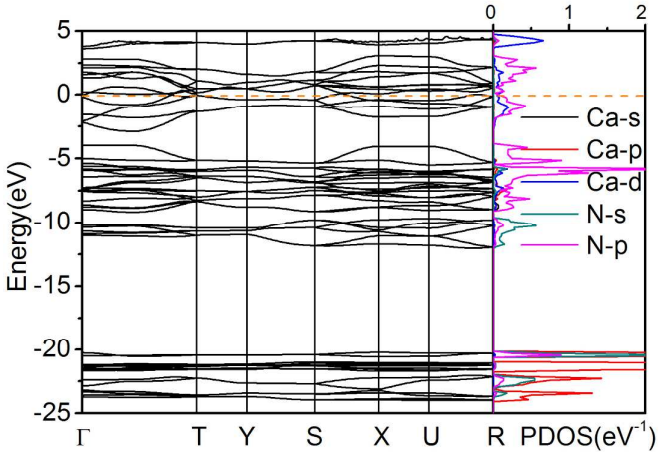

Figure. S29. Electronic band structure and projected DOS of the *Pmma* structure of CaN_3 at 20 GPa.

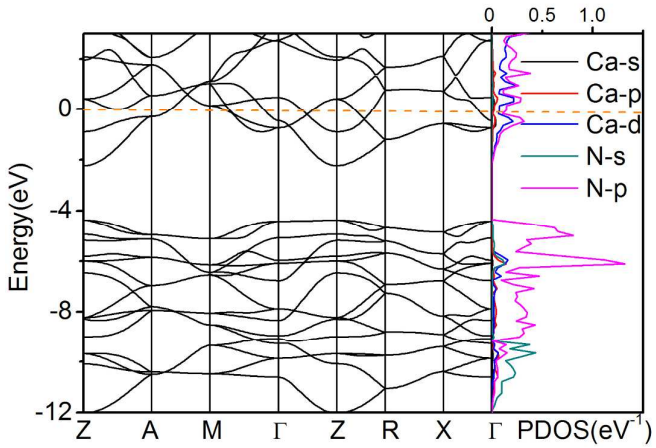

Figure. S30. Electronic band structure and projected DOS of the *P*4/*mbm* structure of CaN_4 at 15 GPa.

Supplementary Table

Table S1. Calculated structural parameters of various Ca-N compounds.

	Space group	Lattice Parameters (Å, °)	Atoms	Atomic coordinates (fractional) X	Y	Z
Ca_2N	*Fm*-3*m*	*a*=*b*=*c* = 5.3187	Ca(8c)	0.25000	0.25000	0.25000
(50 GPa)		*α*=*γ*=*β*=90.0000°	N(4b)	0.00000	0.00000	0.50000
Ca_2N	*I*4/*mmm*	*a* = *b* =2.8703	Ca(4e)	0.00000	0.00000	0.33818
(100 GPa)		*c* = 6.8385	N(2a)	0.00000	0.00000	0.00000
		α=*β*=*γ*= 90.0000°				
Ca_3N_2	$Pmn2_1$	*a* = 3.2169	Ca(2a)	0.00000	-0.33944	0.89565
(20 GPa)		*b* = 6.7772	Ca(2a)	0.00000	-0.93351	0.18708
		c = 5.4518	Ca(2a)	0.50000	-0.68528	0.84652
		α=*β*=*γ*= 90.0000°	N(2a)	0.50000	-0.39528	0.61973
			N(2a)	0.50000	-0.13609	0.10469
Ca_3N_2	*P*-3*m*1	*a* = *b* = 3.6349	Ca(2d)	0.66667	0.33333	0.30385
(100 GPa)		*c* = 4.4464	Ca(1a)	0.00000	0.00000	0.00000
		α=*β*= 90.0000°	N(2d)	0.66667	0.33333	0.78427
		γ=120.0000°				
CaN	*C*2/*m*	*a* =12.7626	Ca(4i)	0.14827	0.50000	0.40762
(0 GPa)		*b* = 3.5534	Ca(4i)	0.84454	0.00000	0.11016
		c = 6.311	N(4i)	0.97579	0.00000	0.41143
		α=*γ*= 90.0000°	N(4i)	0.75661	0.00000	0.75224
		β= 94.9644°				
CaN	$Cmc2_1$	*a* = 3.356	Ca(4a)	0.00000	-0.27151	-0.29429
(20 GPa)		*b* = 8.0533	Ca(4a)	0.00000	-0.98924	-0.03104
		c = 7.2251	N(4a)	0.00000	-0.55985	-0.26118
		α=*β*=*γ*= 90.0000°	N(4a)	0.00000	-0.31592	-0.60377
CaN	*C*2/*m*	*a* =7.7222	Ca(4i)	0.13552	0.50000	0.70991
(50 GPa)		*b* = 3.1153	N(4i)	0.07896	0.00000	0.14545
		c = 3.4349				
		α=*γ*= 90.0000°				
		β= 97.1753°				
CaN	*Pbam*	*a* = 3.5865	Ca(4g)	0.33932	0.85762	0.00000
(100 GPa)		*b* = 6.898	N(4h)	0.87233	0.91483	0.50000
		c = 2.7525				
		α=*β*=*γ*= 90.0000°				
Ca_2N_3	*P*-62*m*	*a* = *b* = 6.6162	Ca(3f)	0.44264	0.44264	0.00000
(20 GPa)		*c* = 2.9409	Ca(1a)	0.00000	0.00000	0.00000

		$\alpha=\beta=$ 90.0000°	N(6k)	0.11499	0.34747	0.50000
		γ=120.0000°				
CaN_2	$P2_1/c$	a = 5.4169	Ca(4e)	0.77731	0.03015	0.18464
(50 GPa)		b = 4.622	N(4e)	0.18834	0.03269	0.30373
		c = 4.5534	N(4e)	0.56816	0.59928	0.09167
		$\alpha=\gamma=$ 90.0000°				
		β= 104.4639°				
CaN_2	$Pbam$	a = 6.509	Ca(4g)	0.30162	0.91086	0.00000
(100 GPa)		b = 5.6328	N(4h)	0.92886	0.28523	0.50000
		c = 2.4987	N(4h)	0.44775	0.60573	0.50000
		$\alpha=\beta=\gamma=$ 90.0000°				
CaN_3	$Pmma$	a = 5.1785	Ca(2f)	0.25000	0.50000	0.28875
(20 GPa)		b = 4.9009	Ca(2e)	-0.25000	0.00000	0.13703
		c = 6.5496	N(4k)	-0.25000	0.37878	0.35212
		$\alpha=\beta=\gamma=$ 90.0000°	N(4g)	0.00000	0.62555	0.00000
			N(4i)	0.13709	0.00000	0.31998
CaN_3	$C2/c$	a = 8.4571	Ca(8f)	0.69560	-0.29172	0.76750
(50 GPa)		b = 5.1055	N(8f)	0.29838	0.00578	0.49593
		c = 11.8724	N(8f)	0.72439	-0.20145	0.59500
		$\alpha=\gamma=$ 90.0000°	N(8f)	0.29511	-0.55106	0.45445
		β= 149.4620°				
CaN_4	$P4/mbm$	$a = b$ =5.0401	Ca(2a)	0.50000	0.50000	0.00000
(20 GPa)		c = 4.1756	N(8k)	0.32135	0.17865	0.36078
		$\alpha=\beta=\gamma=$ 90.0000°				
CaN_4	$P4_12_12$	$a = b$ =3.5543	N(8b)	0.62664	0.84104	0.59026
(50 GPa)		c = 13.0156	N(8b)	0.97025	0.87451	0.34127
		$\alpha=\beta=\gamma=$ 90.0000°	Ca(4a)	0.83657	0.83657	0.00000
CaN_5	Pm	a = 5.02520	Ca(2c)	0.75565	0.25438	0.74925
(50 GPa)		b = 8.54030	Ca(2c)	0.24413	0.74651	0.24730
		c = 4.32800	N(2c)	0.10647	0.07688	0.72510
		$\alpha=\gamma=$ 90.0000°	N(2c)	0.89317	0.92315	0.22432
		β=90.5438°	N(2c)	0.59784	0.57464	0.30725
			N(2c)	0.40231	0.42558	0.80341
			N(2c)	0.84392	0.62628	0.23642
			N(2c)	0.15272	0.37318	0.75423
			N(2c)	0.35851	0.12440	0.74240
			N(2c)	0.64178	0.87554	0.24370
			N(1a)	0.49084	0.00000	0.24821
			N(1a)	0.50950	0.00000	0.74761
			N(1b)	0.00300	0.50000	0.69128

	N(1b)	0.00302	0.50000	0.27222