Supplementary Information
for
Exploration of Si-N Compounds as High Energy Density Material

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1. Figures

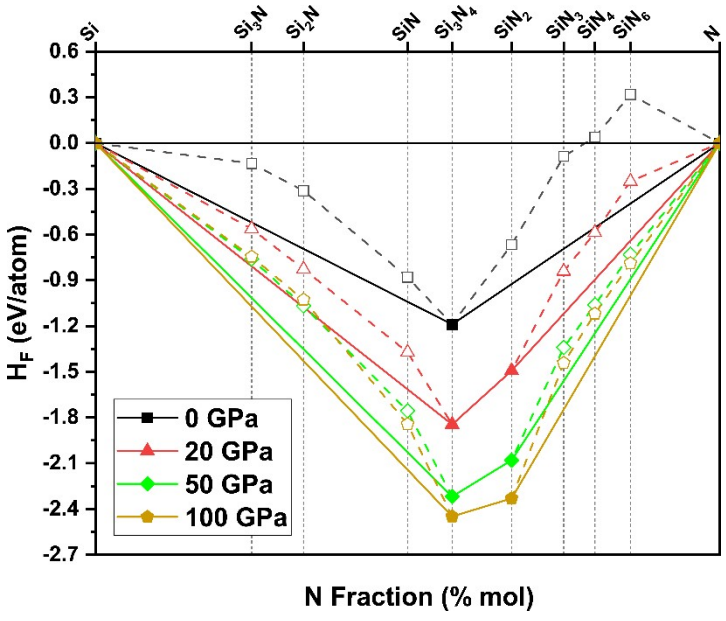

Fig. S1. Convex hull diagram for the Si-N systems at selected pressures by considering stable phases of N_2.

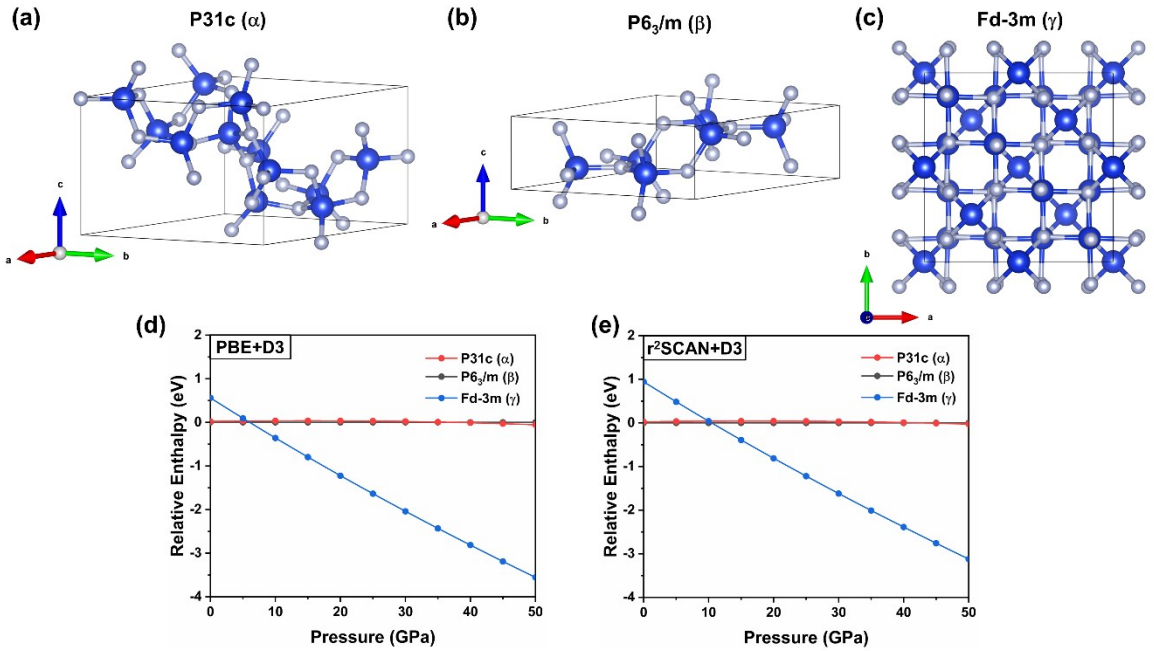

Fig. S2. Structural view of *P31c*-Si_3N_4 at 0 GPa (a), *P6$_3$/m*-Si_3N_4 at 0 GPa (b), *Fd-3m*-Si_3N_4 at 10 GPa (c); pressure dependent relative enthalpy curve using PBE+D3 functional (d) and r^{2}SCAN+D3 functional (e).

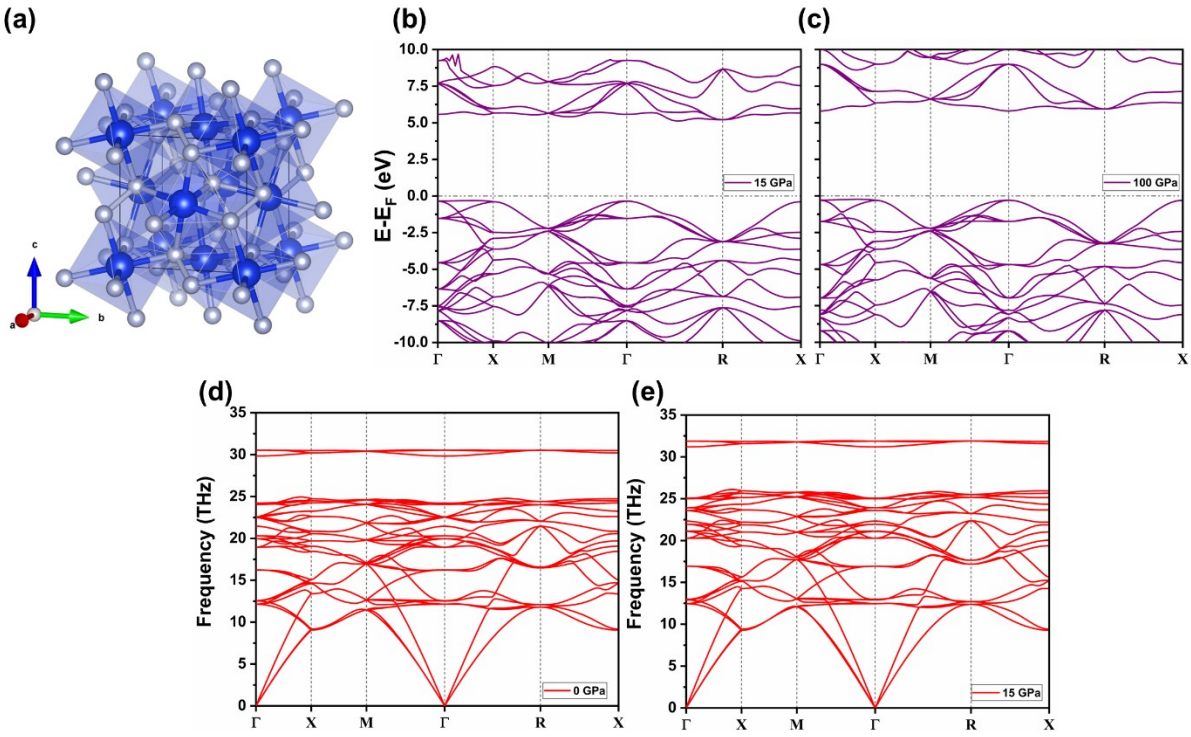

Fig. S3. Structural view at 15 GPa (a); Electronic band structure at 15 GPa (b) and 100 GPa (c); phonon dispersion curves at 0 GPa (d) and 15 GPa (e) of *Pa-3*-SiN_2, respectively.

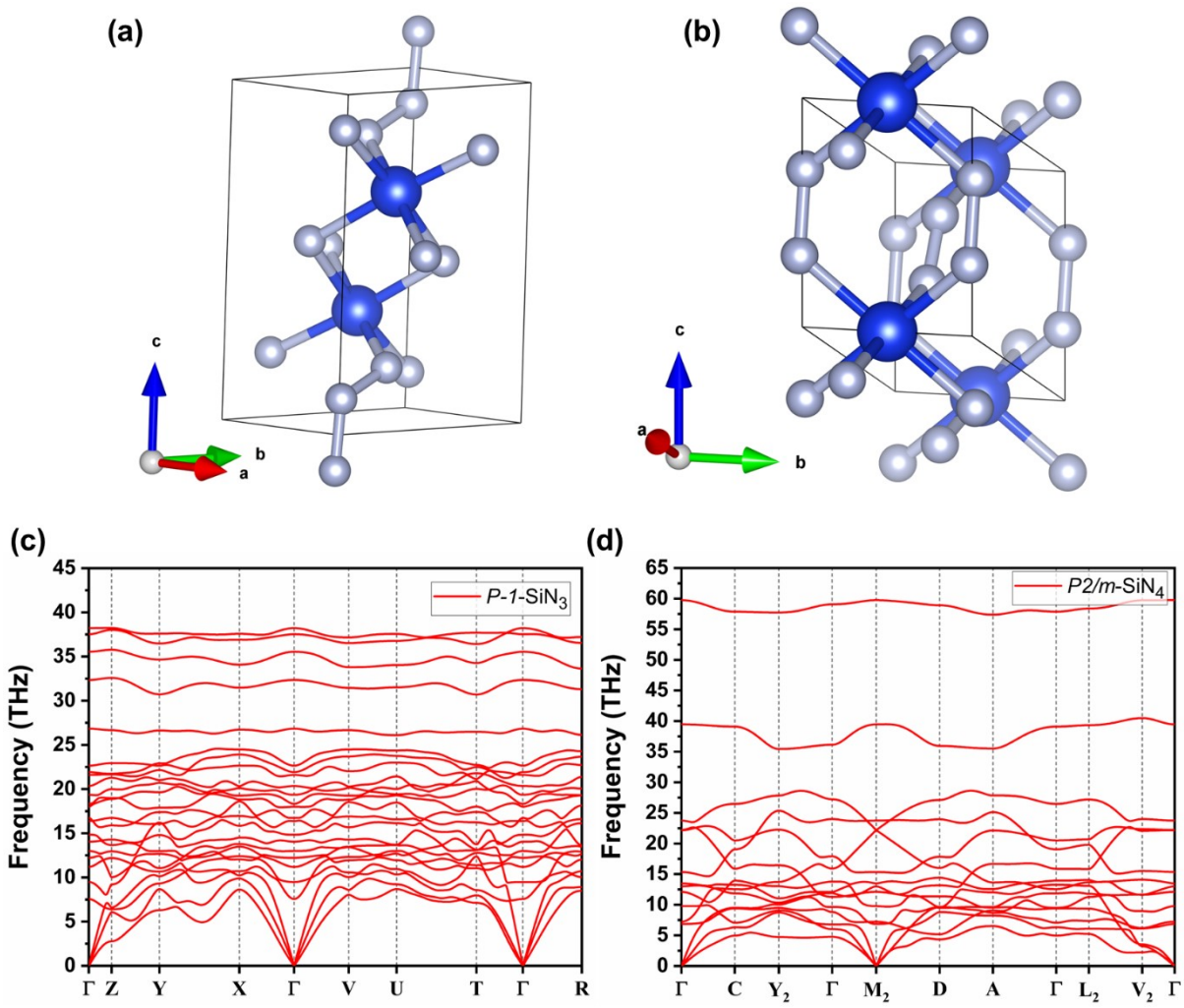

Fig. S4. Structural view (a and b); phonon dispersion curves (c and d) of *P-1*-SiN_3 and *P2/m*-SiN_4 at ambient pressure, respectively.

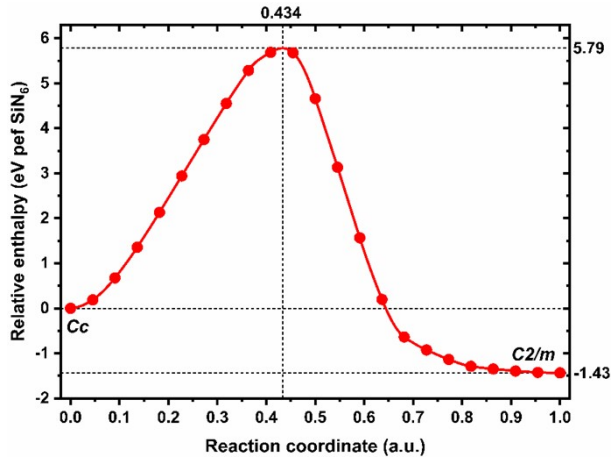

Fig. S5. The energy barrier for the *Cc* to *C2/m*-SiN_6 structural phase transition at ambient pressure.

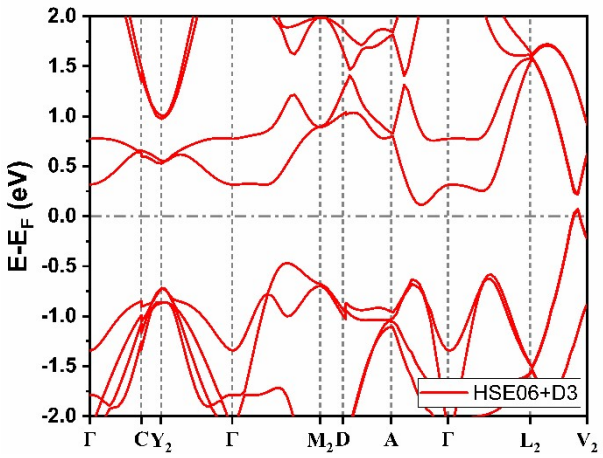

Fig. S6. Electronic band structure of *Cc*-SiN_6 at and 100 GPa using HSE06+D3.

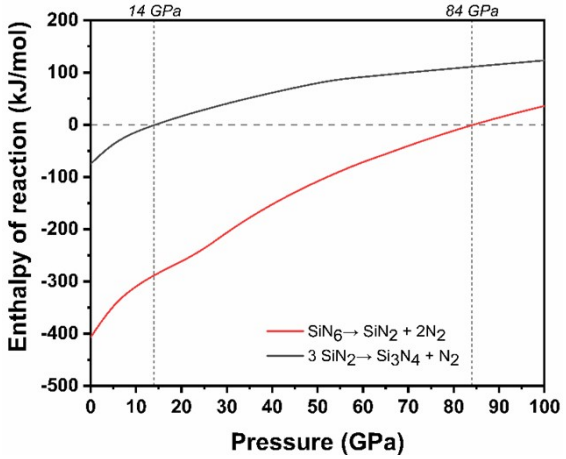

Fig. S7. Enthalpy of reaction for SiN_6 and SiN_2 as function of pressure.

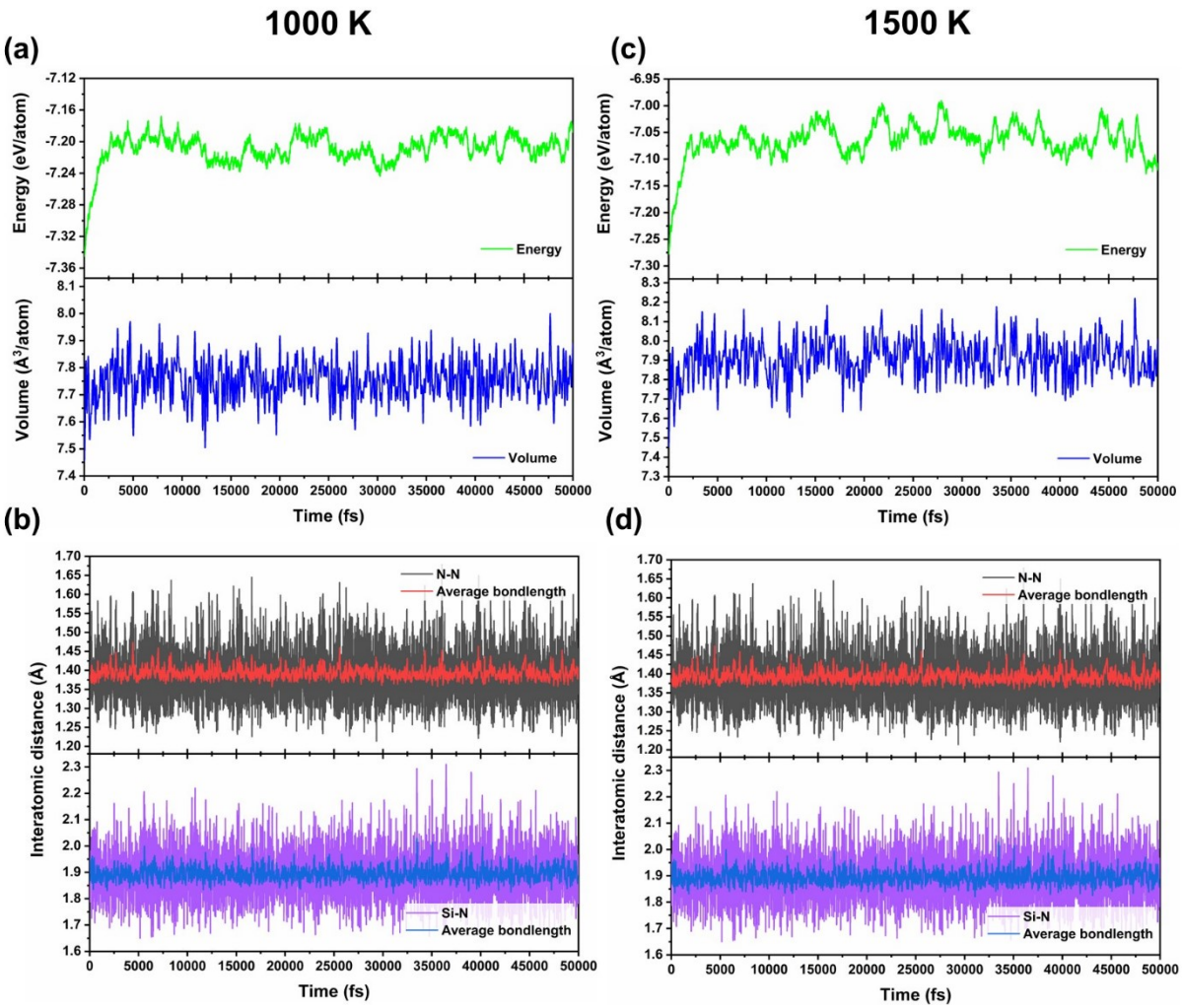

Fig. S8. Fluctuations in Energy, volume, and interatomic distances (N-N, Si-N) of *Cc*-SiN_6 with respect to MD steps for 1000 K (a, b) and 1500 K (c, d), respectively.

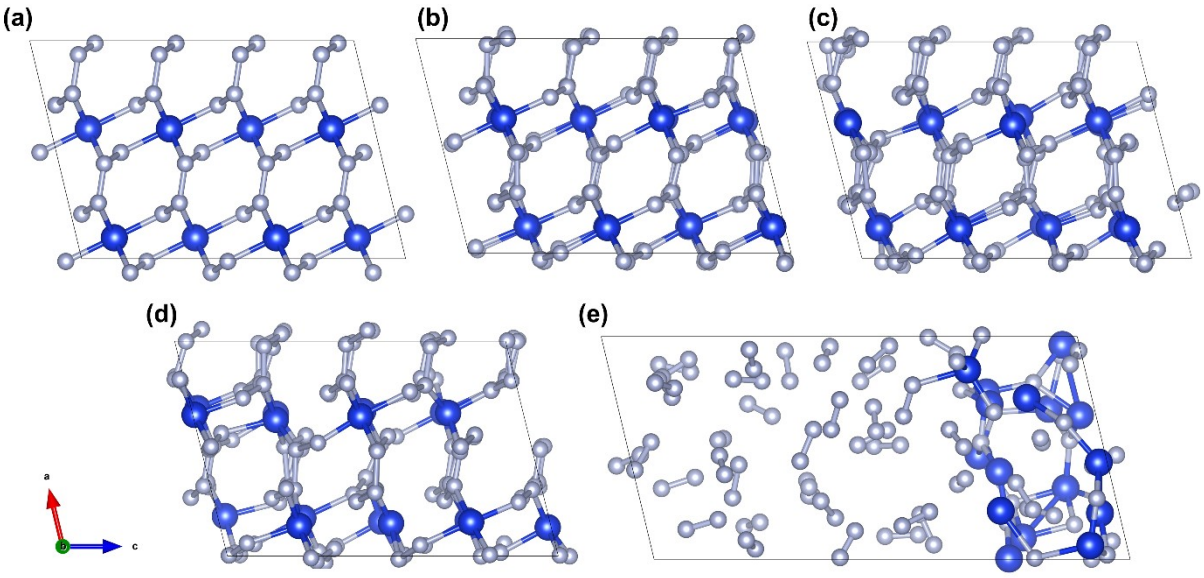

Fig. S9. Structural snapshot of *Cc*-SiN_6 after 50 ps of MD run at 0 (a), 300 (b), 1000 (c), 1500 (d) and 2000 K temperature, respectively.

2. Tables

Table S1. Comparison of structural parameters of Si_3N_4.

Phase	**Pressure (GPa)**	**Lattice parameters**	**Reference**
β-Si_3N_4 $P6_3/m$	0	*a = b = 7.595 Å* *c = 2.902 Å*	Experimental[1]
		a = b = 7.615 Å ***c = 2.909 Å***	**This work (PBE+D3)**
		a = b = 7.585 Å *c = 2.898 Å*	This work (r2SCAN+D3)
		a = b = 7.657 Å *c = 2.925 Å*	This work (PBE)
		a = b = 7.632 Å *c = 2.915 Å*	Theory[2]
α-Si_3N_4 *P31c*	0	*a = b = 7.754Å* *c = 5.621 Å*	Experimental[3]
		a = b = 7.760 Å ***c = 5.627 Å***	**This work (PBE+D3)**
		a = b = 7.731 Å *c = 5.604 Å*	This work (r2SCAN+D3)
		a = b = 7.807Å *c = 5.658 Å*	This work (PBE)
		a = b = 7.781Å *c = 5.641 Å*	Theory[2]
γ-Si_3N_4 *Fd-3m*	0	*a=7.736 Å*	Experimental[4]
		a=7.732Å	**This work (PBE+D3)**
		a=7.708 Å	This work (r2SCAN+D3)
		a= 7.785 Å	This work (PBE)
		a=7.773 Å	Theory[2]

Table S2. Comparison of structural parameter of SiN_2.

Phase	**Pressure (GPa)**	**Lattice parameters**	**Reference**
$Pa\bar{3}$-SiN_2	0	*a=4.437 Å*	Experimental[5]
		a=4.439 Å	**This work (PBE+D3)**
		a=4.428 Å	This work (r2SCAN+D3)
		a=4.469 Å	This work (PBE)

Table 3. Charge analysis and interatomic distance between Si-N and N-N at 20 GPa using r2SCAN+D3 functionals at in Si_3N_4, SiN_2 and SiN_6.

Properties	**Si_3N_4 (*Fd-3m*)**	**SiN_2 (*$Pa\bar{3}$*)**	**SiN_6 (*C2/m*)**	**SiN_6 (*Cc*)**
q(Si)	1.42, 1.54	1.38 (x1)	1.23	1.40
q(N)	-1.09	-0.69 (x2)	-0.21 (x6)	-0.22(x4), -0.25(x2)
R(Si-N)	1.731(x4), 1.840(x6)	1.855	1.843(x6), 1.820(x4)	1.822(x6), 1.814(x4)
ICOBI (Si-N)	0.76, 0.51	0.54	0.54, 0.55	0.53, 0.54
R(N-N)	-	1.455	1.174	1.343, 1.358
ICOBI (N-N)	-	0.95	1.91	1.05, 1.06

References:

1 R. Grün, The crystal structure of β-Si_3N_4: structural and stability considerations between α- and β-Si_3N_4, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.*, 1979, **35**, 800–804.

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