Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Pressure-Stabilized Polymerization of Nitrogen in Alkaline-Earth-Metal Strontium Nitrides

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Table S1. Structural parameters of all considered structures for Sr-N.

Str. And S.G.	Lattice parameters (Å, °)	Atomic coordinates (fractional)	Sites
***R*-3*m*-Sr_2N** **P = 0 GPa**	a = 3.862 c = 20.858 γ = 120	N1 (0.0, 0.0, 0.5) Sr1 (0.0, 0.0, 0.0.767)	3*a* 6*c*
***Cc*-Sr_2N** **P = 20 GPa**	a = 7.601 b = 10.775 c = 6.592 β=54.94	N1 (0.281, 0.127, -0.725) N2 (0.723, 0.064, -0.356) Sr1 (0.473, -0.056, -0.984) Sr2 (0.032, 0.005, -0.863) Sr3 (0.718, -0.184, -0.485) Sr4 (0.401, -0.248, -0.593)	4*a* 4*a* 4*a* 4*a* 4*a* 4*a*
***C*2/*m*-SrN** **P = 0 GPa**	a = 13.692 b = 3.797 c = 6.761 β=94.839	N1 (0.977, 0.0 0.906) N2 (0.754, 0.0, 0.251) Sr1 (0.646, 0.0 0.906) Sr2 (0.847, 0.0, 0.611)	4*i* 4*i* 4*i* 4*i*
***P*2$_1$/*c*-SrN** **P = 20 GPa**	a = 4.605 b = 4.576 c = 6.806 β=66.53	N (0.868, 0.593, 0.568) Sr (0.246, 0.0.589, 0.751)	4*e* 4*e*
***P*-62*m*-Sr_2N_3** **P = 20 GPa**	a = 7.001 c = 3.111 γ = 120	N (0.657, 0.889, 0.50) Sr1 (0.558, 0.558, 0.0) Sr2 (0.0, 0.0, 0.0)	6*k* 3*f* 1*a*
***C*2/*c*-Sr_2N_3** **P = 50 GPa**	a = 12.851 b = 6.221 c = 5.642 β=104.679	N1 (0.384, 0.254, 0.470) N2 (0.388, 0.269, 0.901) N3 (0.651, -0.181, 0.333) Sr1 (0.767, -0.035, 0.121) Sr2 (0.50, -0.032, 0.75) Sr3 (0.50, -0.481, 0.75)	8*f* 8*f* 8*f* 8*f* 4*e* 4*e*
***I*4/*mmm*-SrN_2** **P = 0 GPa**	a = 3.848 c = 6.333	N1 (0.5, 0.5, 0.602) Sr1 (0.5, 0.5, 0.0)	4*e* 2*b*
***P*-1-SrN_2** **P = 20 GPa**	a = 3.833 α=76.07 b = 3.408 β=81.29 c = 5.879 γ = 90.12	N1 (0.701, 0.665, 0.199) N2 (0.337, 0.515, 0.565) Sr (0.803, 0.836, 0.776)	2*i* 2*i* 2*i*
***P*2/*m*-SrN_2** **P = 100 GPa**	a = 3.876 b = 2.691 c = 5.152 β=78.01	N1 (0.169, 0.0, 0.427) N2 (0.812, 0.0, 0.831) Sr (0.321, 0.5, 0.779)	2*m* 2*m* 2*n*
***C*2/*m*-SrN_3**	a = 8.579	N1 (0.929, 0.219, 0.700)	8*j*

	b = 5.277 c = 3.342 β=67.25	N2 (0.579, 0.50, 0.054) Sr (0.175, 0.5, 0.688)	4*i* 4*i*
***C*2/*c*-SrN$_4$** **P = 20 GPa**	a = 5.306 b = 5.350 c = 10.136 β=133.54	N1 (0.643, 0.662, 0.934) N2 (0.323, 0.021, 0.435) Sr (0.0, 0.411, 0.25)	8*f* 8*f* 4*e*
***P*2$_1$/*c*-SrN$_4$** **P = 60 GPa**	a = 4.660 b = 5.997 c = 7.246 β=123.36	N1 (0.542, 0.891, 0.509) N2 (0.331, 0.515, 0.421) N3 (0.296, 0.337, 0.777) N4 (0.784, 0.885, 0.258) Sr1 (0.137, 0.730, 0.621)	4*e* 4*e* 4*e* 4*e* 4*e*
***P*-1-SrN$_5$** **P = 60 GPa**	a = 3.402 b = 5.455 c = 5.649 α=78.62 β=93.33 γ = 77.90	N1 (0.738, 0.648, 0.885) N2 (0.073, 0.176, 0.066) N3 (0.142, 0.889, 0.745) N4 (0.906, 0.259, 0.412) N5 (0.151, 0.415, 0.318) Sr1 (0.492, 0.245, 0.737)	2*i* 2*i* 2*i* 2*i* 2*i* 2*i*
***Fm*-3*m*-Sr**	a = 6.032	Sr (0.0, 0.0, 0.0)	4*a*
***P*6$_3$/*mmc*-Sr**	a = 4.251, c = 7.056 γ = 120	Sr (0.667, 0.333, 0.75)	2*c*

Table S2. Calculated Bader charges for *C*2/*m*-SrN$_3$, *C*2/*c*-SrN$_4$, and *P*-1-SrN$_5$, respectively.

Str.	Atom	N	Charge value(e)	δ(e)
*C*2/*m*-SrN$_3$	N1	8	5.58	0.58
	N2	4	5.22	0.22
	Sr	4	8.62	-1.38
*C*2/*c*-SrN$_4$	N1	8	5.37	0.37
	N2	8	5.39	0.39
	Sr	4	8.49	-1.51
P-1-SrN$_5$	N1	2	5.19	0.19
	N2	2	5.33	0.33
	N3	2	5.28	0.28

	N4	2	5.33	0.33
	N5	2	5.35	0.35
	Sr	2	8.52	-1.48

Table S3. Calculated integrated crystal orbital Hamiltonian populations of N−N pairs without inclusion of spin polarization in *C*2/*m*-SrN_3, *C*2/*c*-SrN_4 and *P*-1-SrN_5.

Str. And S.G.	**Pressure**	**Atom**	**Atom**	**Distance (Å)**	**ICOHP(E_f)**
*C*2/*m*-SrN_3	60	**N1**	**N1**	**1.42**	**-2.09**
		N 2s	N 2s		0.06
		N 2s	N 2p		-0.78
		N 2p	N 2p		-1.37
		N1	**N2**	**1.40**	**-3.22**
		N 2s	N 2s		0.46
		N 2s	N 2p		-1.29
		N 2p	N 2p		-2.39
		N2	**N2**	**1.53**	**-3.13**
		N 2s	N 2s		0.11
		N 2s	N 2p		-0.66
		N 2p	N 2p		-2.58
*C*2/*c*-SrN_4	20	**N1**	**N1**	**1.37**	**-2.33**
		N 2s	N 2s		0.40
		N 2s	N 2p		0.45
		N 2p	N 2p		-3.18
		N1	**N2**	**1.36**	**0.60**
		N 2s	N 2s		1.49
		N 2s	N 2p		0.21
		N 2p	N 2p		-1.10
		N2	**N2**	**1.38**	**-3.79**
		N 2s	N 2s		0.07
		N 2s	N 2p		-0.07
		N 2p	N 2p		-3.79
P-1-SrN_5	60	**N1**	**N2**	**1.33**	**-4.43**

		N 2s	N 2s		1.36
		N 2s	N 2p		-2.48
		N 2p	N 2p		-3.31
		N2	**N3**	**1.36**	**-3.57**
		N 2s	N 2s		0.69
		N 2s	N 2p		-1.49
		N 2p	N 2p		-2.77
		N3	**N4**	**1.34**	**-4.38**
		N 2s	N 2s		0.98
		N 2s	N 2p		-2.72
		N 2p	N 2p		-2.64
		N4	**N5**	**1.37**	**-4.55**
		N 2s	N 2s		0.66
		N 2s	N 2p		-2.23
		N 2p	N 2p		-2.97
		N5	**N1**	**1.31**	**-3.80**
		N 2s	N 2s		1.12
		N 2s	N 2p		-2.06
		N 2p	N 2p		-2.86

Table S4. Vickers hardness(H_v) of $P2_1/c$-SrN , P-62m-Sr_2N_3 , $C2/c$-Sr_2N_3 , P-1-SrN_2 , $P2/m$-SrN_2 , $C2/m$-SrN_3 , $C2/c$-SrN_4 , $P2_1/c$-SrN_4 , P-1- SrN_5.

Str.	$P2_1/c$-SrN	P-62m-Sr_2N_3	$C2/c$-Sr_2N_3	P-1-SrN_2	$P2/m$-SrN_2	$C2/m$-SrN_3	$C2/c$-SrN_4	$P2_1/c$-SrN_4	P-1- SrN_5
H_v (GPa)	8.7	14.5	17.9	15.9	21.8	29.1	25.7	28.4	32.5

Table S5. The enthalpy of $C2/m$-SrN_3, $C2/c$-SrN_4 and P-1- SrN_5 under different pressures, considering SOC or not.

Enthalpy(eV/f.u.)	P = 0 GPa	P =10 GPa	P =20 GPa	P =30 GPa	P =40 GPa	P =50 GPa	P =60 GPa	P =70 GPa	P =80 GPa	P =90 GPa	P =100 GPa
$C2/m$-SrN_3	-26.66806	-23.74975	-21.03437	-18.48055	-16.04878	-13.71575	-11.46595	-9.39854	-7.31601	-5.28422	-3.29775
$C2/m$-SrN_3 with SOC	-26.66807	-23.74975	-21.03437	-18.48054	-16.04878	-13.71575	-11.46595	-9.39857	-7.31599	-5.28422	-3.29775
$C2/c$-SrN_4	-35.47447	-31.88885	-28.55612	-25.41302	-22.41567	-19.53634	-16.75607	-14.06085	-11.44007	-8.88541	-6.3901
$C2/c$-SrN_4 with SOC	-35.49005	-31.88896	-28.55611	-25.41304	-22.41567	-19.53634	-16.75607	-14.06085	-11.44007	-8.88541	-6.3901
P-1- SrN_5	-43.29589	-38.87962	-34.98612	-31.36552	-27.93648	-24.65795	-21.50308	-18.45313	-15.49428	-12.61554	-9.80825
P-1- SrN_5 with SOC	-43.47356	-38.88499	-34.98768	-31.36648	-27.93703	-24.65828	-21.50341	-18.45357	-15.49479	-12.61613	-9.80873

The enthalpy difference curves of the strontium nitrides under high pressures.

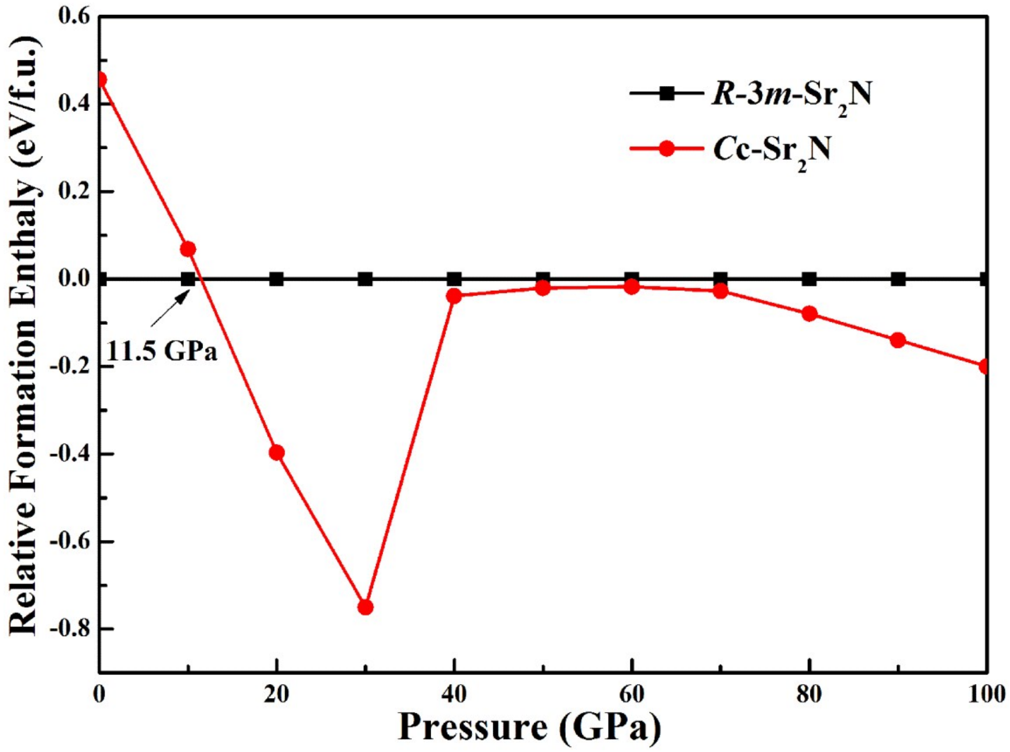

Fig. S1 Calculated enthalpies per formula unit (f.u.) of the high-pressure Sr_2N phases with respect to *R*-3*m*-Sr_2N structure.

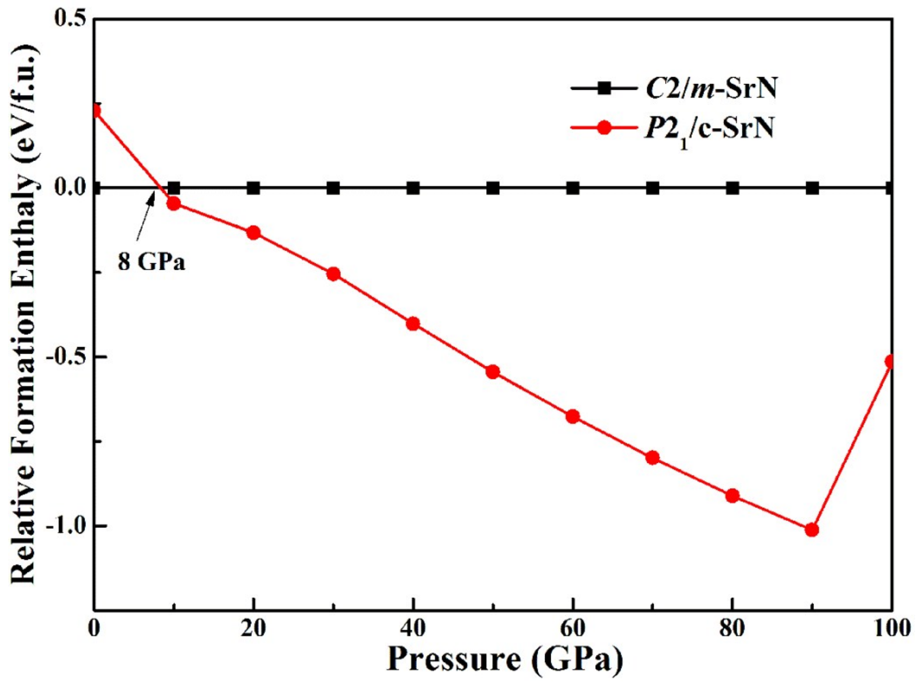

Fig. S2 Calculated enthalpies per formula unit (f.u.) of the high-pressure SrN phases with respect to *C*2/*m*-SrN structure.

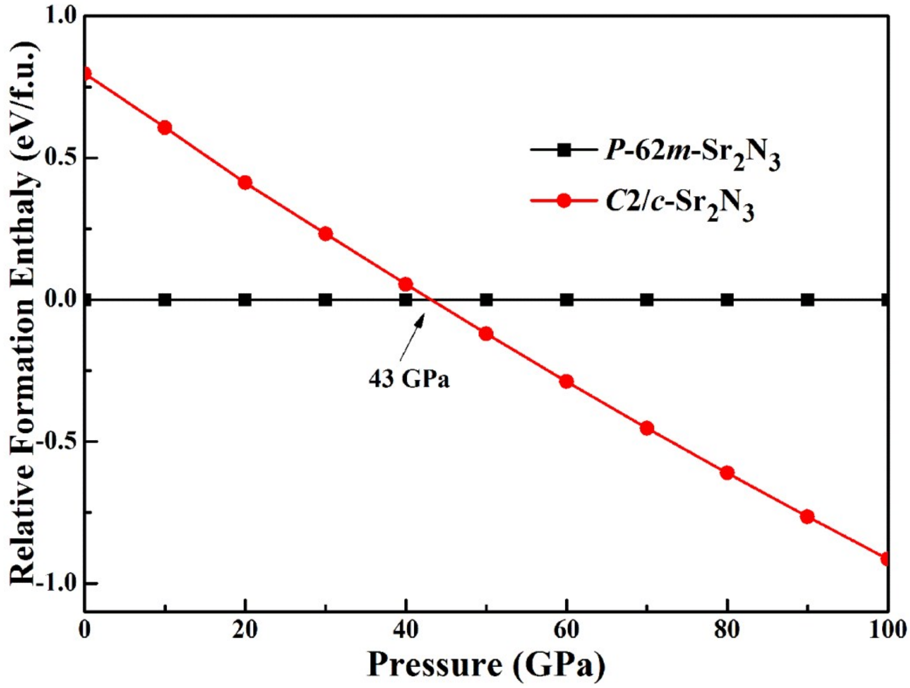

Fig. S3 Calculated enthalpies per formula unit (f.u.) of the high-pressure Sr_2N_3 phases with respect to *P*-62*m*-Sr_2N_3 structure.

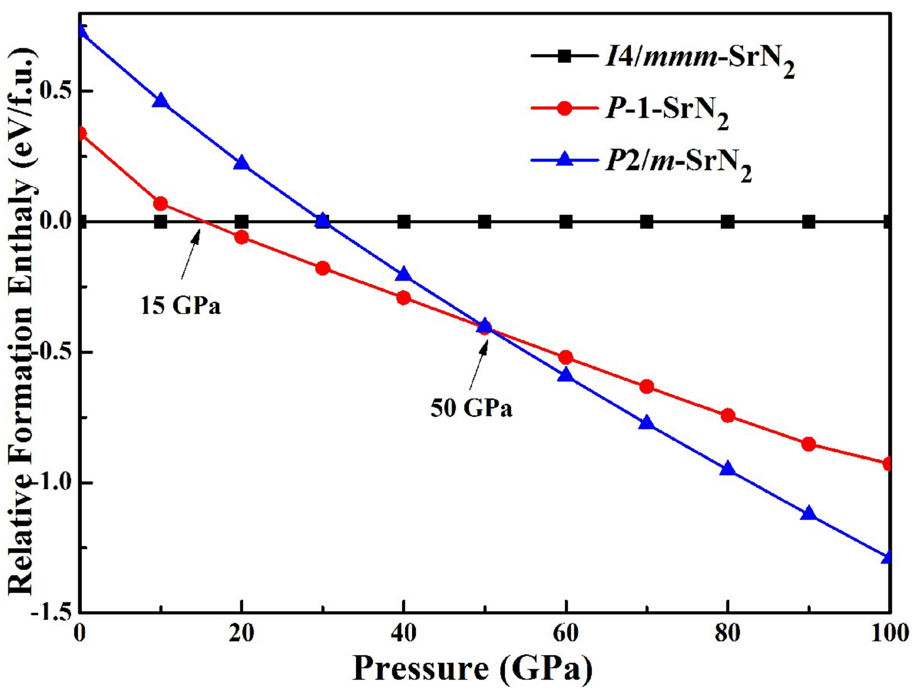

Fig. S4 Calculated enthalpies per formula unit (f.u.) of the high-pressure SrN_2 phases with respect to ambient-pressure *I*4/*mmm*-SrN_2 structure.

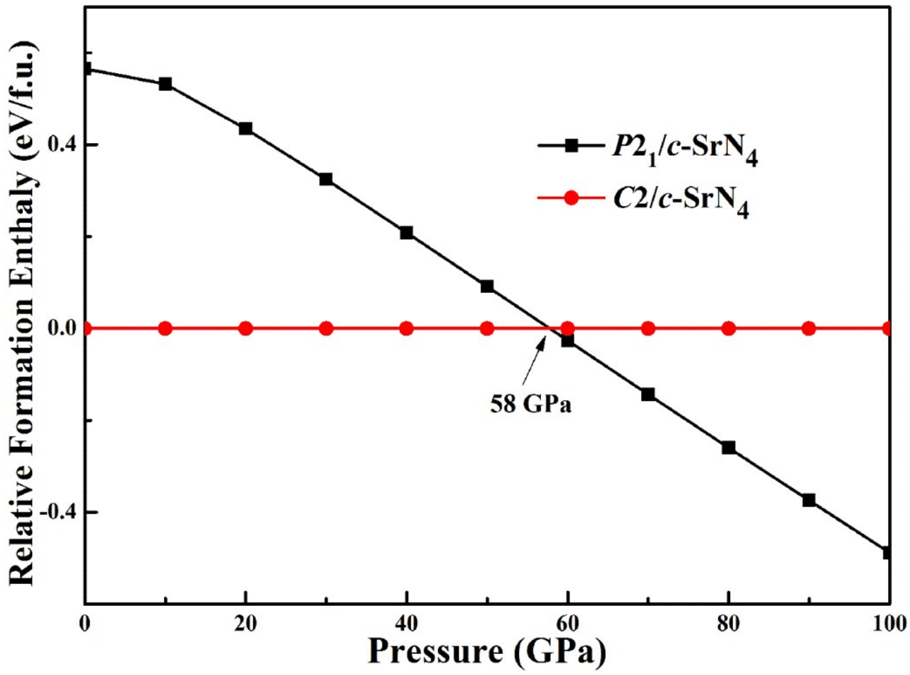

Fig. S5 Calculated enthalpies per formula unit (f.u.) of the high-pressure SrN_4 phases with respect to *C*2/*c*-SrN_4 structure.

Phonon dispersion curves for the strontium nitrides

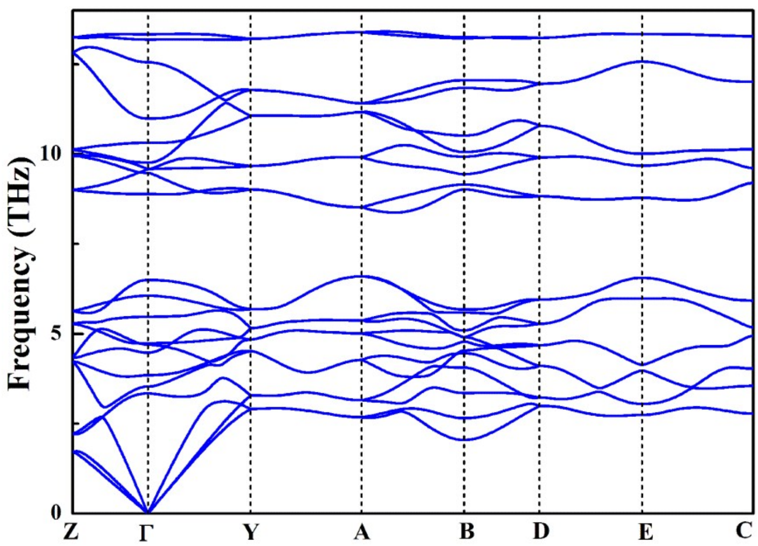

Fig. S6 Phonon dispersion curves for the $P2_1/c$-SrN at P = 20 GPa

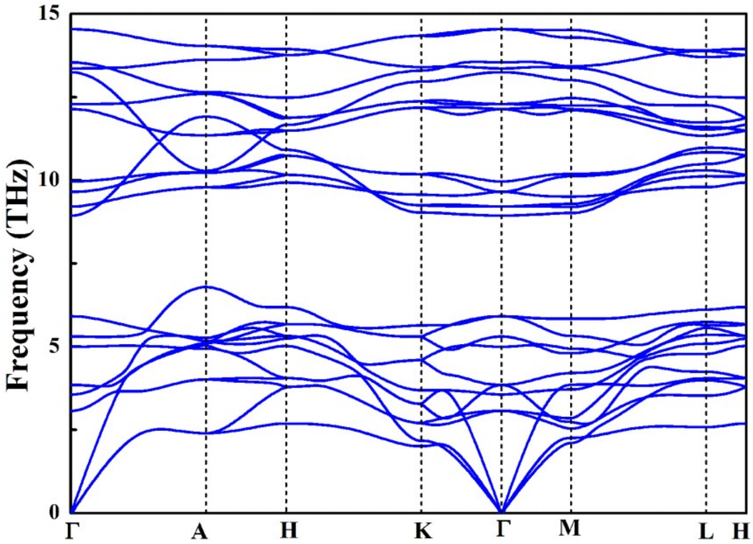

Fig. S7 Phonon dispersion curves for the *P*-62*m*-Sr_2N_3 at P = 20 GPa

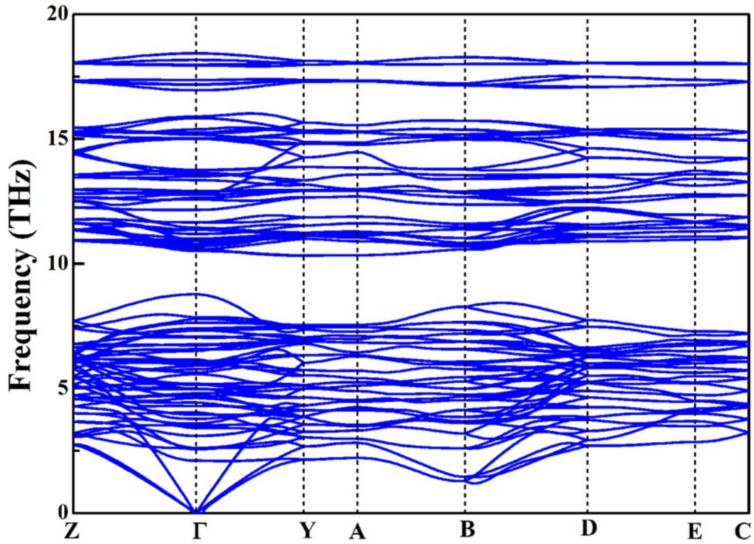

Fig. S8 Phonon dispersion curves for the *C*2/*c*-Sr_2N_3 at P = 50 GPa

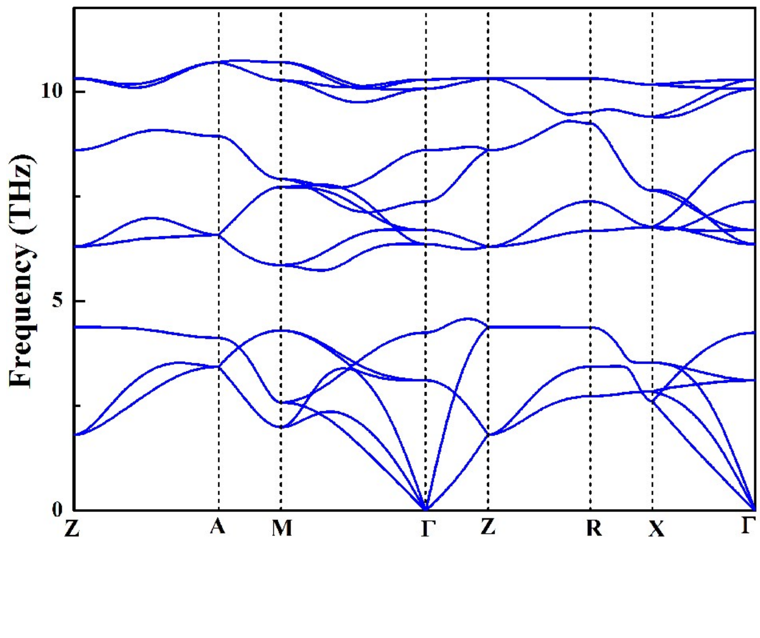

Fig. S9 Phonon dispersion curves for the *I*4/*mmm*-SrN_2 at P = 0 GPa.

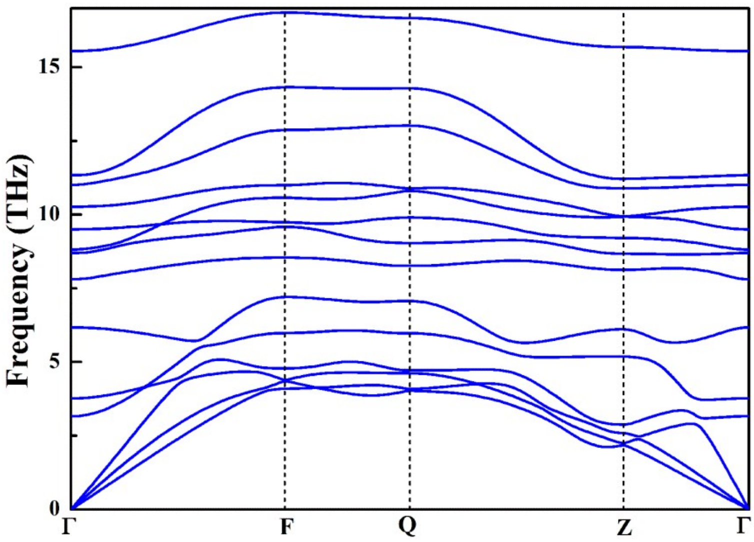

Fig. S10 Phonon dispersion curves for the *P*-1-SrN_2 at P = 20 GPa.

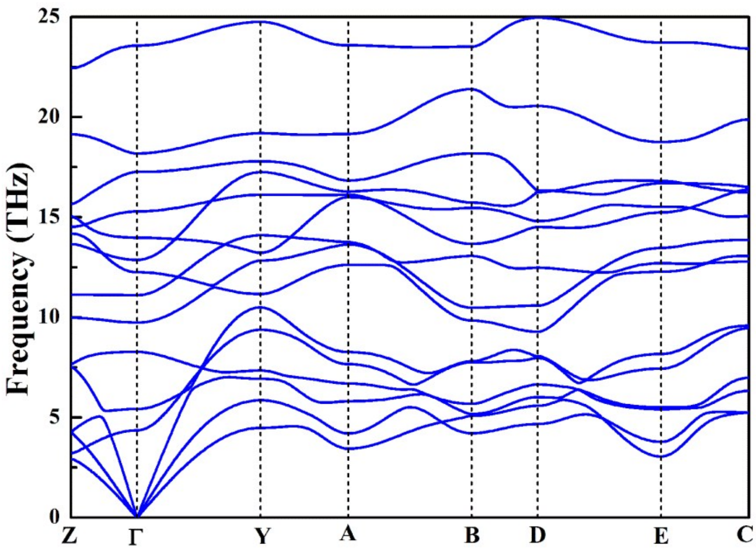

Fig. S11 Phonon dispersion curves for the *P*2/*m*-SrN_2 at P = 100 GPa.

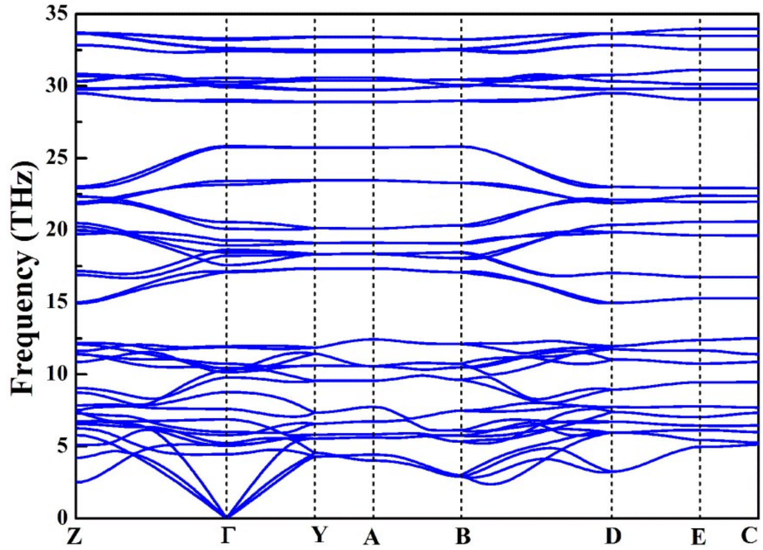

Fig. S12 Phonon dispersion curves for the *C*2/*m*-SrN_3 at P = 60 GPa.

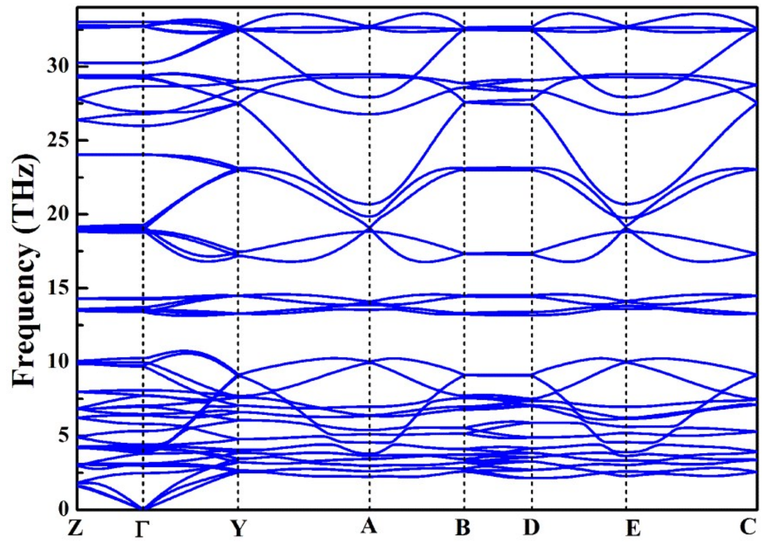

Fig. S13 Phonon dispersion curves for the *C*2/*c*-SrN_4 at ambient pressure.

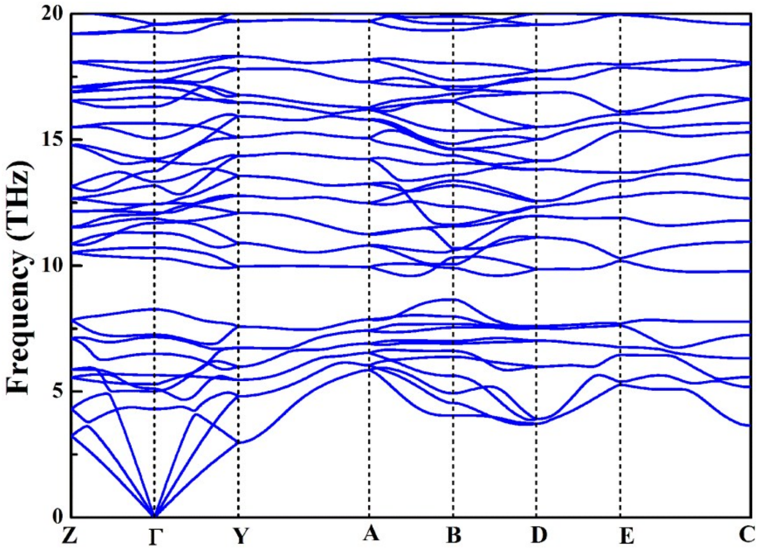

Fig. S14 Phonon dispersion curves for the $P2_1/c$-SrN_4 at P = 60 GPa.

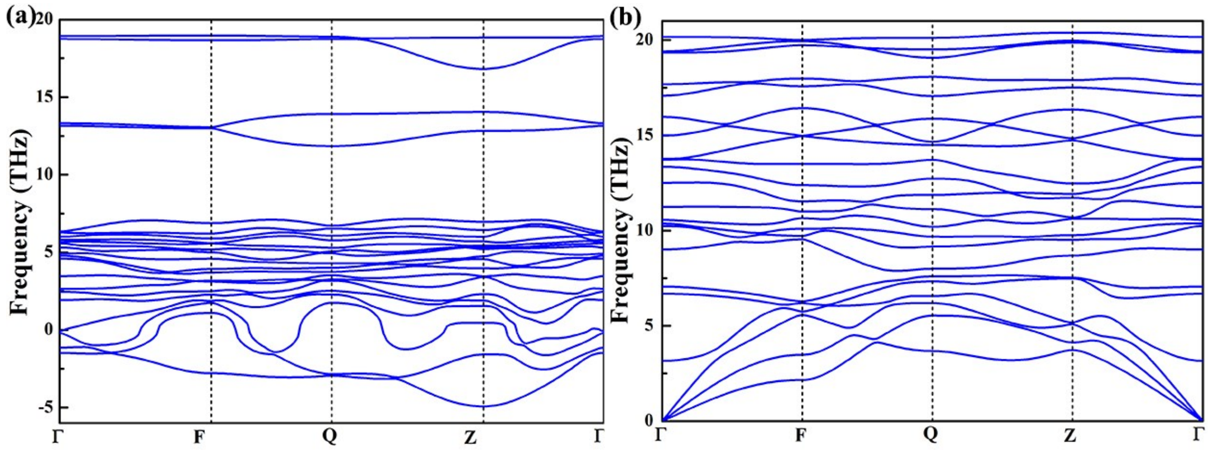

Fig. S15 Phonon dispersion curves for the *P*-1-SrN_5 at P = 0 GPa(a) and P = 60 GPa(b).

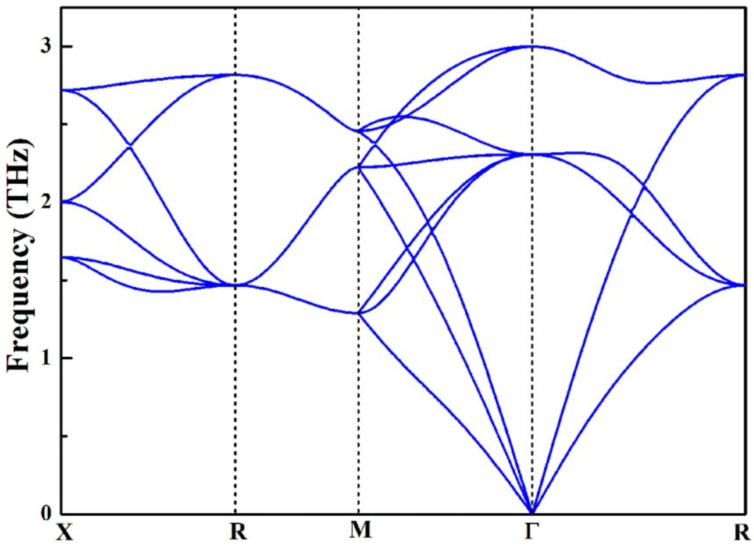

Fig. S16 Phonon dispersion curves for the *Fm*-3*m*-Sr at P = 0 GPa.

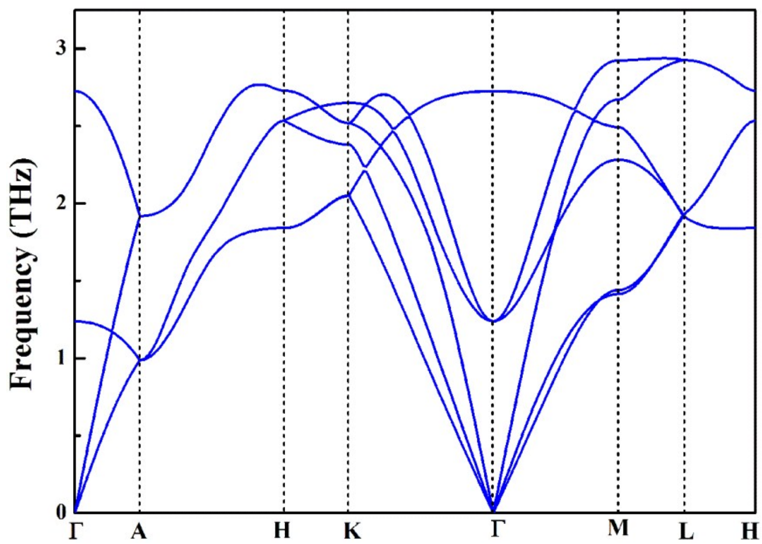

Fig. S17 Phonon dispersion curves for the $P6_3/mmc$-Sr at P = 5 GPa.

Crystal orbital Hamilton population (COHP) curves

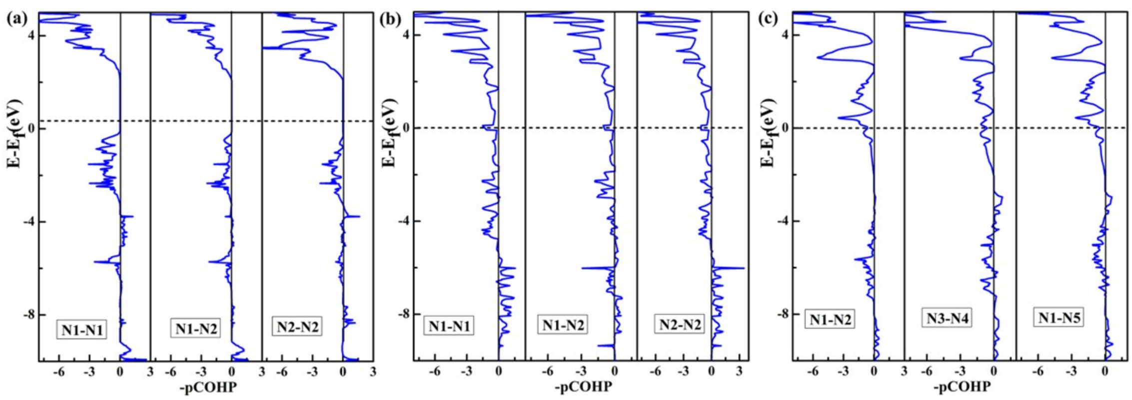

Fig. S18 Crystal orbital Hamilton population (COHP) analyses for C2/m-SrN_3 at P = 60 GPa(a), C2/c-SrN_4 at P = 20 GPa(b), and P-1-SrN_5 at P = 60 GPa(c). The horizontal line at zero is the Fermi level.

Total density of states considering spin of the electron

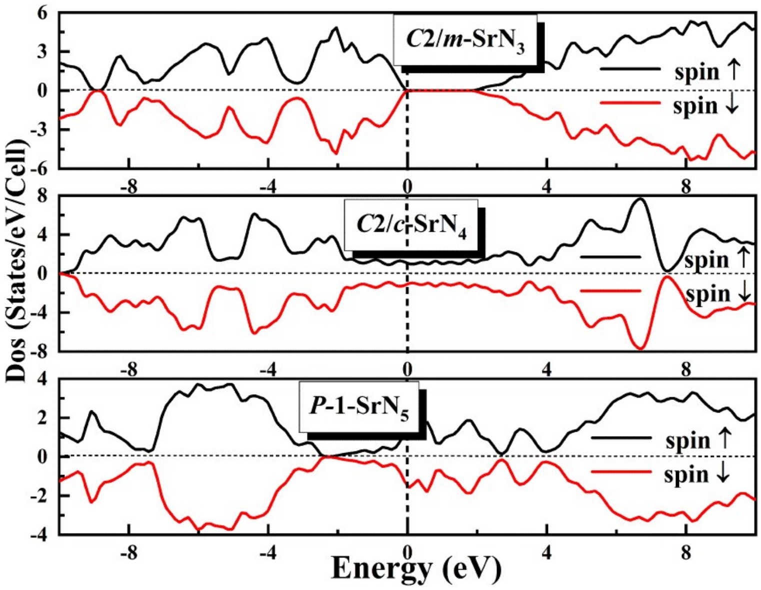

Fig. S19. Total density of states considering spin of the electron for *C*2/*m*-SrN_3 at P = 60GPa (a), *C*2/*c*-SrN_4 at P = 20 GPa (b), and *P*-1-SrN_5 at P = 60 GPa (c).