Supporting Information

Structure Phase Transition and Bonding Properties of High-pressure Polymeric CaN_3

Pugeng Hou[1*], Lili Lian[2], Yongmao Cai[1], Bao Liu[1], Bo Wang[1], Shuli Wei[3], and Da Li[3*]

1. *College of Science, Northeast Electric Power University, No. 169 Changchun Road, Jilin City, 132012, P. R. China *Email: houpugeng@126.com*

2. *The First Hospital of Jilin University, Changchun, 130021, P. R. China.*

3. *State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun, 130012, P. R. China. *Email: dali@jlu.edu.cn*

The detailed computations about crystal structure prediction

Our structural prediction approach is based on a global minimization of free energy surfaces merging ab initio total-energy calculations with CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in the CALYPSO code. In the first step, random structures with certain symmetry are constructed in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the VASP code were done with the conjugate gradients method and stopped when enthalpy changes became smaller than 1×10^{-5} eV per cell. After processing the first generation structures, 60% of them with lower enthalpies are selected to construct the next generation structures by PSO (Particle Swarm Optimization). 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. In most cases, structural searching simulations for each calculation were stopped after generating 1000 ~ 1200 structures (e.g., about 20 ~ 30 generations).

Table S1. Calculated Bader charges for *P*-1-CaN_3 P = 30 GPa and *C*2/*m*-CaN_3 P = 70 GPa.

Str.	Atom	N	Charge	δ(e)
P-1-CaN_3 P = 30 GPa	Ca	2	0.70	-1.30
	N1	2	5.29	0.29
	N2	2	5.31	0.31
	N3	2	5.70	0.70
*C*2/*m*-CaN_3 P = 70 GPa	Ca	4	0.78	-1.22
	N1	4	5.18	0.18
	N2	8	5.52	0.52

Table S2. Structural parameters of *C*2/*m*-CaN_3 and *P*-1-CaN_3.

Str. And S.G.	**Lattice parameters** (Å, º)		**Atomic coordinates (fractional)**	**Sites**
P-1-CaN_3 P = 30 GPa	a = 4.744	α=76.70	N1 (0.307, 0.321, 0.399)	2*i*
	b = 5.307	β=97.94	N2 (0.140, 0.517, 0.507)	2*i*
	c = 3.182	γ=80.80	N3 (0.204, 0.136, 0.262)	2*i*
			Ca (0.696, 0.198, 0.077)	2*i*
*C*2/*m*-CaN_3 P = 70 GPa	a = 8.046	α=90.0	N1 (0.422, 0.275, 0.204)	8*j*
	b = 5.130	β=67.11	N2 (0.085, 0.0, 0.542)	4*i*
	c = 5.183	γ=90.0	Ca (0.673, 0.00, 0.185)	4*i*