Pressure stabilization of the long-missing bare C_6 hexagonal rings in the Binary Sesquicarbides

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COMPUTATIONAL DETAILS

Our structure prediction is based on a global minimum search of the free energy surfaces obtained by ab initio total energy calculations, through CALYPSO methodology. Structures searches were performed at 0, 30, 50, 100, 200 and 300 GPa with simulation cell sizes of 1 - 4 formula units. The significant feature of this methodology is the capability of predicting the stable structure with the only input knowledge of the chemical composition at given external condition (for example, pressure).

To further analyze the structures, we select a number of structures with lower enthalpies and perform structural optimization with higher accuracy as a function of pressure using DFT (VASP code) calculations. The cut-off energy for the expansion of wavefunctions into plane waves is set to 800 eV in all calculations, and fine Monkhorst-Pack *k* meshes are chosen to ensure that all the enthalpy calculations are well converged to better than 1 meV/atom. Band structures and electronic density of states (DOS) of α-, β- and γ-phases of Y_2C_3 and La_2C_3 compounds are examined. Phonon dispersions are calculated by using finite displacement method[1] as implemented in Phononpy[2] for supercells containing 160 and 80 atoms in the cell for β-Y_2C_3 and γ-Y_2C_3, respectively.

Electron-phonon coupling (EPC) calculations for β-Y_2C_3 and α-Y_2C_3 have been performed using the pseudopotential plane-wave method and density-functional perturbation theory[3,4] as implemented in the QUANTUM ESPRESSO package.[5] A 2

× 2 × 2 MP *q*-point mesh was used and a 6 × 6 × 6 MP *k* mesh is chosen to ensure *k*-point sampling convergence with Gaussians of 0.05 Ry, which approximates the zero-width limit in this calculation.

The calculated EPC parameter λ and the logarithmic average phonon frequency $\omega_{\log}$ of α-Y_2C_3 are 0.74 and 388 K, respectively, at zero pressure. The superconducting critical temperature (T_c) can be estimated from the Allen-Dynes modified McMillan equation[6], $T_c = [\omega_{\log}/1.2]\exp\{[-1.04(1+\lambda)]/[\lambda-\mu^*(1+0.62\lambda)]\}$ where μ^* is the Coulomb pseudopotential. By choice of a typical $\mu^* = 0.13$, the estimated T_c is 12 K, which is in good agreement with the experimental data of 6 K.[8] Instead, the calculated λ of β-Y_2C_3 is rather small at 0.28. With the uses of the calculated $\omega_{\log}$ (523 K) and the $\mu^* = 0.13$, T_c of β-Y_2C_3 is rather small at 0.012 K, which is negligible . We therefore do not suggest the superconductivity of β-Y_2C_3。

We here calculated the all atomic- and molecular-orbital energy levels of the C_2 dimer and C_6 ring through Amsterdam Density Functional (ADF) program, [9] based on Density Functional Theory(DFT). Generalized gradient approximation[10] with Perdew–Burke–Ernzerhof[11] functional for the exchange and correlation interaction was used. Energies have been calculated with standard Slater-type orbitals basis sets and double-zeta-polarized functions for all the atoms. Ignoring Scalar relativistic effect and frozen core approximation is necessary for the light element C. Self-consistent field calculations were carried out with a convergence criterion of 10^{-4} Hartree on the bonding energy. The linear-expansion shooting technique was used to speed up the self-consistent field convergence. A 0.005 Hartree electron smearing was applied to the molecular orbital occupation.

Table S1. Lattice parameters of α - and β -Y_2C_3 structures.

Structure	**Pressure（GPa）**	**Lattice Parameters（Å）**	**Atomic Position**			
			Atoms	**x**	**y**	**z**
Fmmm	50	a= 6.2473 b= 10.3098 c= 6.4011	Y1(8i)	0.00000	0.00000	0.28629
			Y3(8f)	0.25000	0.75000	0.75000
			C1(16m)	0.79443	0.92652	0.00000
			C5(8h)	0.00000	0.14813	0.00000
Cmcm	160	a= 3.5200 b= 16.8590 c= 2.6015	Y1(4c)	0.00000	-0.06765	0.25000
			Y3(4c)	0.00000	-0.20369	-0.25000
			C5(4c)	0.00000	-0.38840	0.25000
			C7(4c)	0.00000	-0.52239	-0.25000
			C9(4c)	0.00000	-0.65728	0.25000

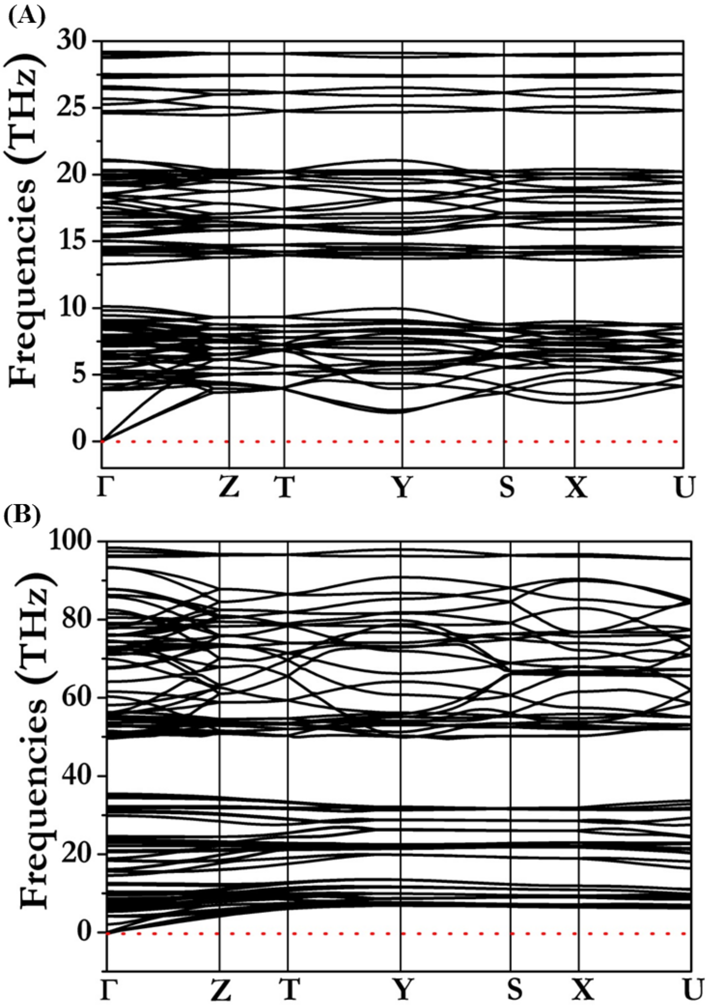

Figure S1. (A) Phonon dispersion curves for β-Y_2C_3 at 50 GPa. (B) Phonon dispersion curves for γ-Y_2C_3 at 160 GPa. These phonon calculations demonstrated the structural stabilities of the predicted β and γ-Y_2C_3 in view of the absence of any imaginary phonons.

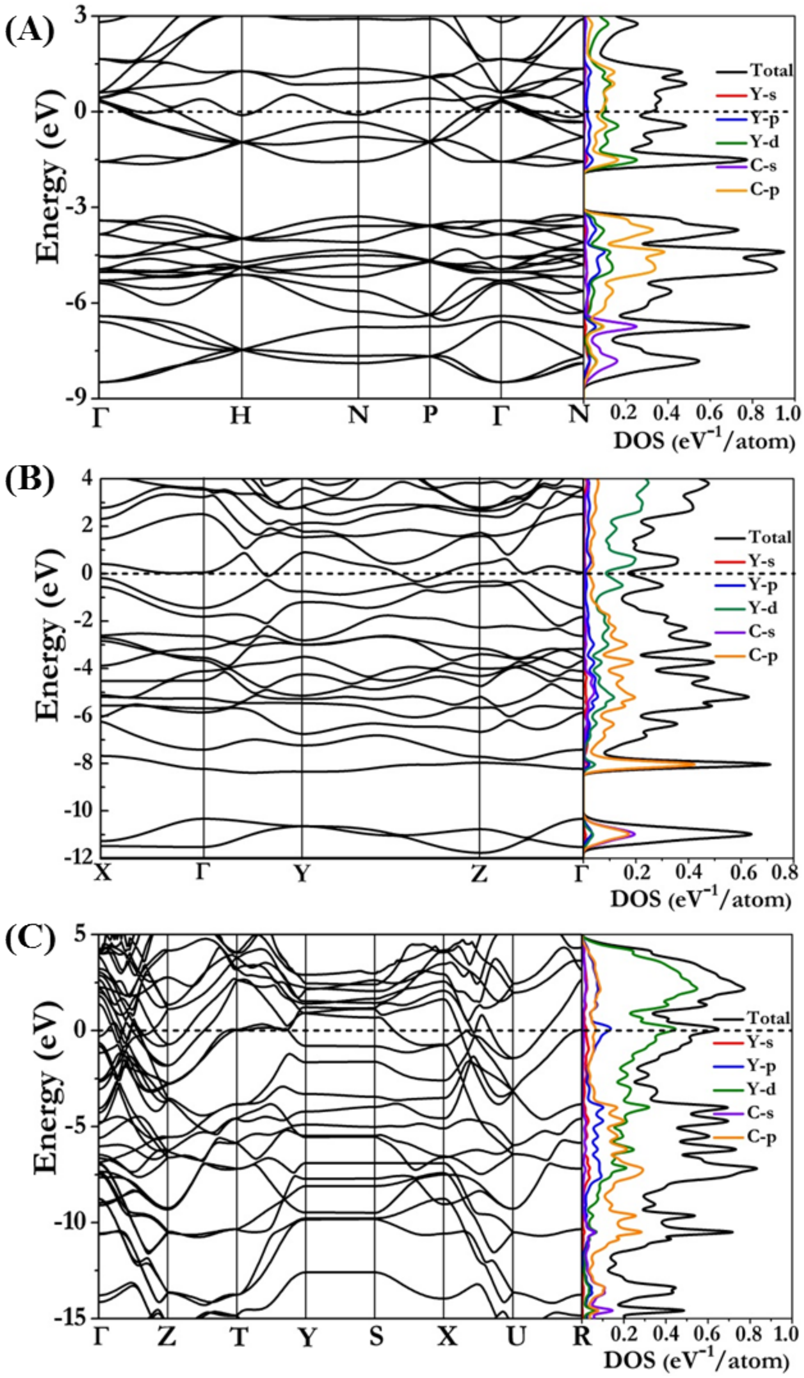

Figure S2. (A), (B), and (C) Electronic band structures (left panel) and partial electronic density of states (DOS，right panel) of α-Y_2C_3 at 50 GPa, β-Y_2C_3 at 50 GPa, and γ-Y_2C_3 at 160 GPa respectively. The dashed line is an indication of Fermi energy, which is set to zero.

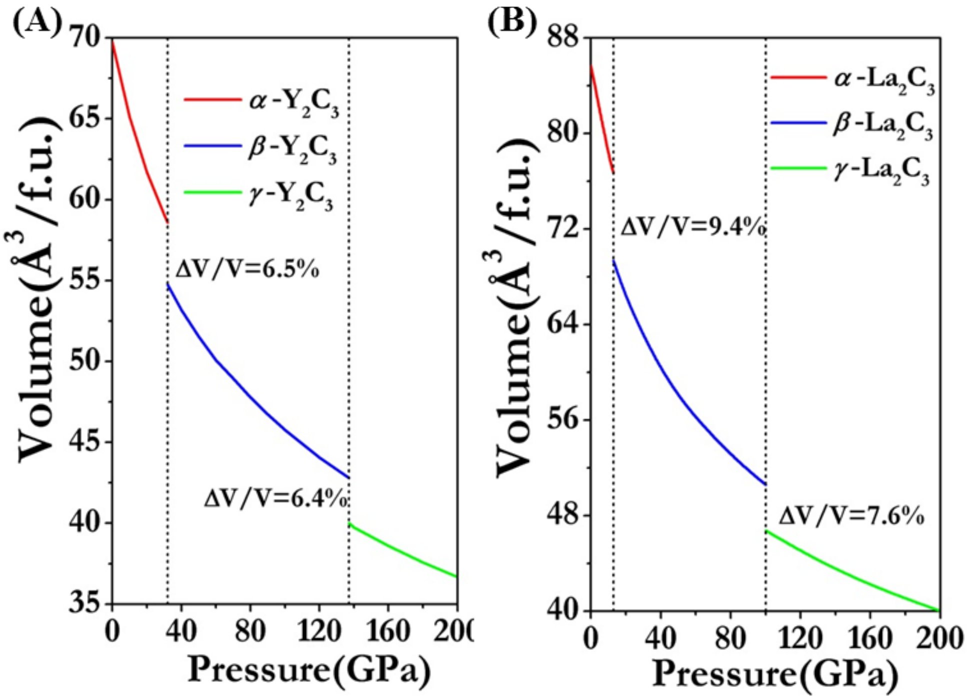

Figure S3. (A) and (B) volume vs. pressure data for α-, β-, and γ-phases of Y_2C_3 and La_2C_3, respectively.

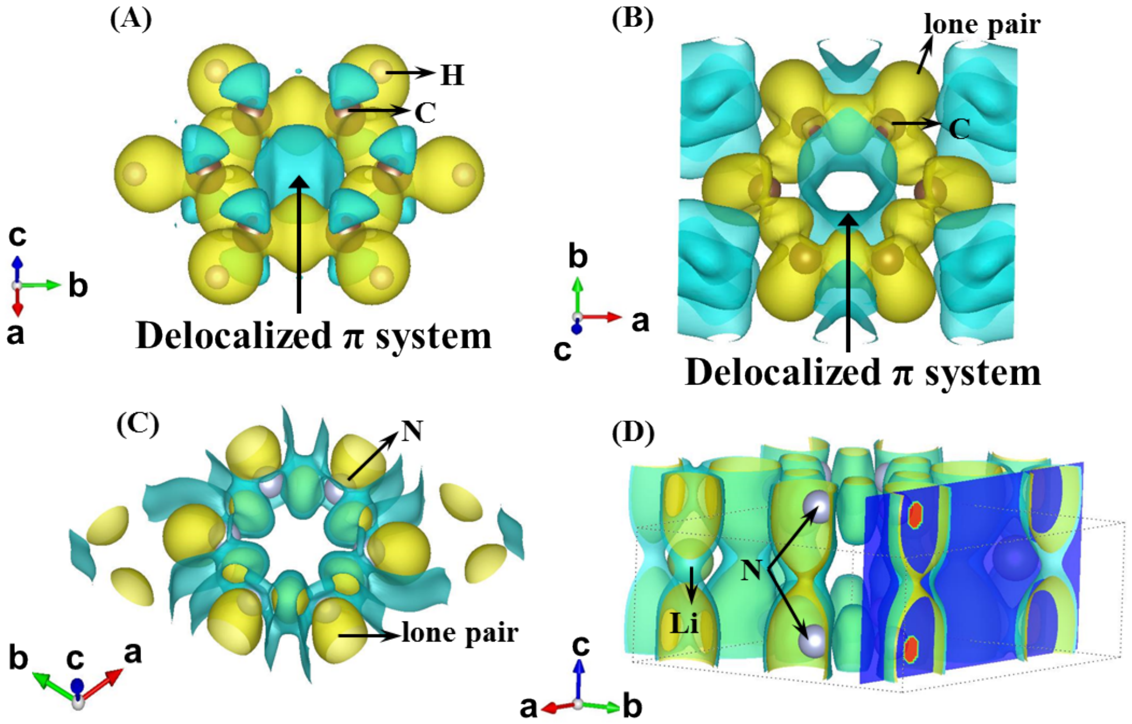

Figure S4. The three-dimensional difference charge density plots at 50 GPa for benzene C_6H_6 (A), β-Y_2C_3 (B), and *P*6/*m*-structured LiN_3 taken from Ref. 7 (C) and (D). The brown and blue colors indicate the electron gain and loss, respectively. The two-dimensional plane shown in (D) is a cut for (0 1 0) plane, where an inter-layer N-N covalent bonding between N_6 rings is evident. From (C), it is seen that there is no electron gain of N and delocalized π system is absent in N_6 ring, in contrast to that in (A) and (B).

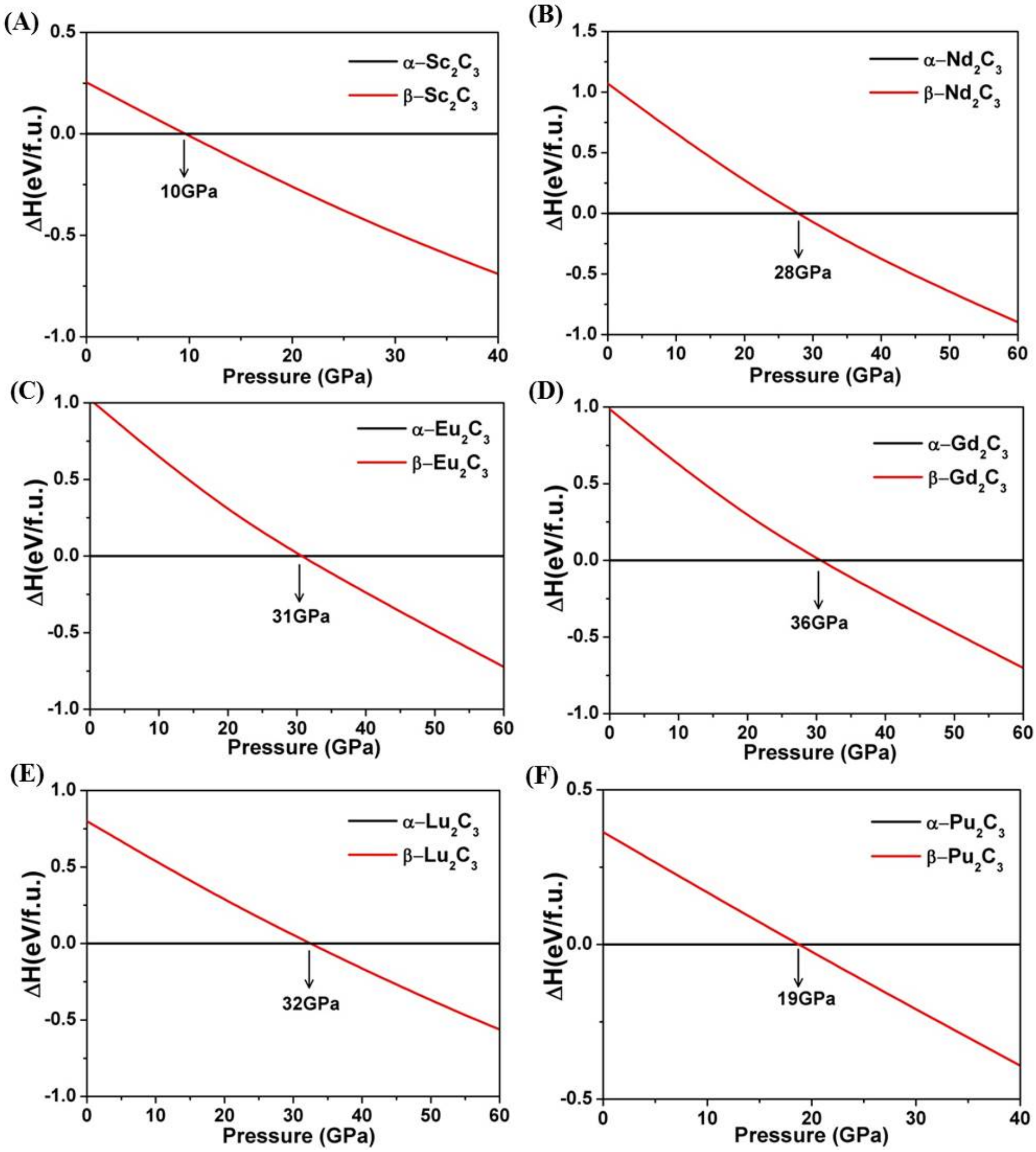

Figure S5. Enthalpy curves as a function of pressure for various rare-earth metal carbides and actinide carbides within α- and β-phase structures: (A) Sc_2C_3, (B) Nd_2C_3, (C) Eu_2C_3, (D) Gd_2C_3, (E) Lu_2C_3, and (F) Pu_2C_3.

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