Science Advances
AAAS

Supplementary Materials for

Extending tetrahedral network similarity to carbon: A type-I carbon clathrate stabilized by boron

Timothy A. Strobel *et al.*

Corresponding author: Timothy A. Strobel, tstrobel@carnegiescience.edu

Sci. Adv. **11**, eadv6867 (2025)
DOI: 10.1126/sciadv.adv6867

This PDF file includes:

Description of structural models
Tables S1 to S3
Figs. S1 to S3

Description of crystal structure models

Table S1 contains crystal data and structure refinement parameters for type-I $Ca_8B_xC_{46-x}$ and type-VII CaB_3C_3. The initial crystal structure solution revealed fully occupied Ca atoms located on the 2*a* and 6*d* positions as well as clathrate framework atoms on the 6*c*, 16*i,* and 24*k* positions. Initially, only models with ordered framework atoms were refined (see models **1** and **2a**-**2c** in **Table S2**). It was found that the pure-carbon framework model (**1**) gives the best refinement indicators among the ordered models. However, theoretical computations have shown that Ca_8C_{46} is energetically and dynamically unstable. Hence, refinement of disordered arrangements of C/B atoms was attempted. It was found that the introduction of C/B disorder on the 16*i* leads to unphysical negative boron occupancy in all cases, including two-and three-site disorder, while disorder on 6*c* does not significantly change the boron occupancy from zero (models **3a** and **3c** in **Table S2**). Only the introduction of disorder on the 24*k* position (model **3b** in **Table S2**) leads to significant improvement of refinement indicators and to a boron occupancy significantly different from zero (see **Table S2**). Introduction of B/C disorder on both 24*k* and 6*c* positions (model **3d**) does not lead to improvement of refinement indicators compared with model **3b** and the occupancy of B on the 6*c* position does not differ significantly from zero. Therefore, model **3b** is preferred to model **3d**. Finally, anisotropic displacement parameters for clathrate framework atoms have been refined (model **4** in **Table S2**).

Table S1. Single-crystal refinement parameters for type-I and type-VII Ca–B–C clathrates at 48(2) and 52(2) GPa, respectively.

Empirical formula	$Ca_8B_{8.9\pm1.4}C_{37.1\pm1.4}$	CaB_3C_3
CSD number	2338100	2338099
Formula weight	862.55	108.54
T/K	293(2)	293(2)
Crystal system	cubic	cubic
Space group	$Pm\bar{3}n$	$Pm\bar{3}n$
a /Å	7.0464(12)	4.529(2)
V /Å^3	349.87(18)	92.89(14)
Z	1	2
ρ_{calc} /g·cm^{-3}	4.094	3.881
μ /mm^{-1}	0.299	0.370
F(000)	427.1	106
Crystal size/*mm3*	0.005 × 0.005 × 0.005	0.005 × 0.005 × 0.005
Radiation	Synchrotron (λ = 0.2952 Å)	(λ = 0.3344 Å)
2Θ range for data collection/°	3.40 to 30.2	5.99 to 30.0
Index ranges	$-11 \le h \le 10$, $-12 \le k \le 11$, $-11 \le l \le 11$	$-2 \le h \le 3$, $-6 \le k \le 6$, $-6 \le l \le 6$
Reflections collected	2324	107
Independent reflections	195 [R_{int} = 0.059, R_{sigma} = 0.030]	28 [R_{int} = 0.1815, R_{sigma} = 0.0512]
Data/restraints/parameters	195/0/16	28/0/3
Goodness−of−fit on F^2	1.15	1.26
Final R indexes [I>=2σ(I)]	R_1 = 0.032, wR_2 = 0.066	R_1 = 0.085, wR_2 = 0.221
Final R indexes [all data]	R_1 = 0.046, wR_2 = 0.072	R_1 = 0.096, wR_2 = 0.242
Largest diff. peak/hole / eÅ^{-3}	+0.62/−0.53	+1.8/−1.14

Table S2. Comparison of different structural models for type-I Ca–B–C clathrate.

data/model	**1**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**3d**	**4**
Atom positions	Ca (2*a*) Ca (6*d*) C (16*i*) C (24*k*) C (6c)	Ca (2*a*) Ca (6*d*) B (16*i*) C (24*k*) C (6c)	Ca (2*a*) Ca (6*d*) C (16*i*) B (24*k*) C (6c)	Ca (2*a*) Ca (6*d*) C (16*i*) C (24*k*) B (6c)	Ca (2*a*) Ca (6*d*) B/C (16*i*) C (24*k*) C (6c)	Ca (2*a*) Ca (6*d*) C (16*i*) B/C (24*k*) C (6c)	Ca (2*a*) Ca (6*d*) C (16*i*) C (24*k*) B/C (6c)	Ca (2*a*) Ca (6*d*) C (16*i*) B/C (24*k*) B/C (6c)	Ca (2*a*) Ca (6*d*) C (16*i*) B/C (24*k*) C (6c)
Reflections collected	2324 [R_{int} = 0.059, R_{sigma} = 0.030]								
Independent reflections	195								
Data/restraints/parameters	195/0/10					195/0/11		195/0/12	195/0/16
Chemical formula	Ca_8C_{46}	$Ca_8B_{16}C_{30}$	$Ca_8B_{24}C_{22}$	$Ca_8B_6C_{40}$	$Ca_4B_{-0.2}C_{23}$	$Ca_8B_{9.12}C_{36.88}$	$Ca_8B_{0.78}C_{45.22}$	$Ca_8B_{10.92}C_{35.08}$	$Ca_8B_{8.88}C_{37.12}$
$10^3 \cdot U_{11}$ (Ca (2*a*)) /Å^2	3.7(3)	3.4(5)	3.9(3)	3.8(3)	3.8(3)	3.9(3)	3.7(3)	3.9(3)	3.8(3)
$10^3 \cdot U_{11}$ (Ca (6*d*)) /Å^2	4.0(4)	3.6(6)	4.0(4)	4.0(4)	3.9(4)	4.1(4)	4.0(4)	4.1(3)	4.2(3)
$10^3 \cdot U_{33}$ (Ca (6*d*)) /Å^2	6.0(3)	5.9(5)	6.2(3)	6.0(3)	6.1(3)	6.1(2)	6.0(3)	6.1(2)	6.1(2)
$10^3 \cdot U_{iso}$ (C/B (16*i*)) /Å^2	5.7(4)	1.9(7)	6.2(5)	5.8(5)	6.9(5)	5.7(4)	5.7(4)	5.8(4)	5.7(4)†
$10^3 \cdot U_{iso}$ (C/B (24*k*)) /Å^2	6.8(4)	6.6(6)	3.2(4)	6.8(4)	6.7(4)	5.5(4)	6.8(4)	5.4(4)	5.5(4)†
$10^3 \cdot U_{iso}$ (C/B (6*c*)) /Å^2	7.2(7)	7.4(12)	7.2(8)	3.7(8)	7.2(7)	7.2(6)	6.7(8)	6.4(7)	7.6(6)†
B molar fraction*	-	-	-	-	<0‡	0.38(6)	0.13(12)	0.40(6) – 24*k* 0.22(11) – 6*c*	0.37(6)
Goodness-of-fit on F^2	1.12	1.26	1.19	1.19	0.843	1.14	1.14	1.13	1.15
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.035, wR_2 = 0.075	R_1 = 0.045, wR_2 = 0.136	R_1 = 0.037, wR_2 = 0.093	R_1 = 0.038, wR_2 = 0.089	R_1 = 0.036, wR_2 = 0.086	R_1 = 0.033, wR_2 = 0.069	R_1 = 0.035, wR_2 = 0.074	R_1 = 0.033, wR_2 = 0.069	R_1 = 0.032, wR_2 = 0.066
Final *R* indexes [all data]	R_1 = 0.049, wR_2 = 0.082	R_1 = 0.060, wR_2 = 0.147	R_1 = 0.052, wR_2 = 0.103	R_1 = 0.053, wR_2 = 0.096	R_1 = 0.049, wR_2 = 0.098	R_1 = 0.047, wR_2 = 0.075	R_1 = 0.049, wR_2 = 0.080	R_1 = 0.047, wR_2 = 0.076	R_1 = 0.046, wR_2 = 0.072
ρ_{max}/ρ_{min} / eÅ^{-3}	+0.62/−0.65	+1.2/−0.66	+0.79/−0.61	+1.2/−0.77	+0.61/−0.68	+0.62/−0.53	+0.61/−0.66	+0.61/−0.52	+0.62/−0.53

* B molar fraction on the disordered site only; † U_{eq} since C and B atoms were refined anisotropically. ‡All refinements of B on 16*i* produce unphysical parameters.

Table S3. Rietveld refinement parameters for type-I Ca–B–C clathrate at ambient pressure.

Atom	Site	*x*	*y*	*z*	*Fractn*	*Uiso*×100
Ca1	2*a*	0	0	0	1	1.71(6)
Ca2	6*d*	0.25	0.5	0	1	1.71(6)
C1	6*c*	0.5	0.25	0	1	1.1(1)
C2	16*i*	0.1871(5)	0.1871(5)	0.1871(5)	1	1.1(1)
C3	24*k*	0.3058(9)	0.1274(6)	0	0.62(3)*	1.1(1)
B3	24*k*	0.3058(9)	0.1274(6)	0	0.38(3)*	1.1(1)
Space group	$Pm\bar{3}n$					
a /Å	7.4040(2)					
Radiation	Synchrotron (λ = 0.3344 Å)					
R_{wp}–Bknd	0.022					

**Initialized composition from high-pressure SXRD data*

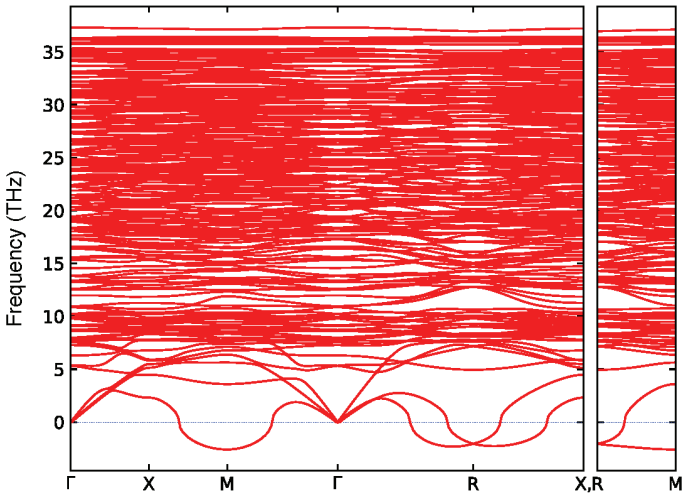

Fig. S1. Phonon dispersion relations for type-I Ca_8C_{46} at 50 GPa showing that the structure is dynamically unstable without boron. The calculated convex hull distance is >700 meV/atom at 50 GPa.

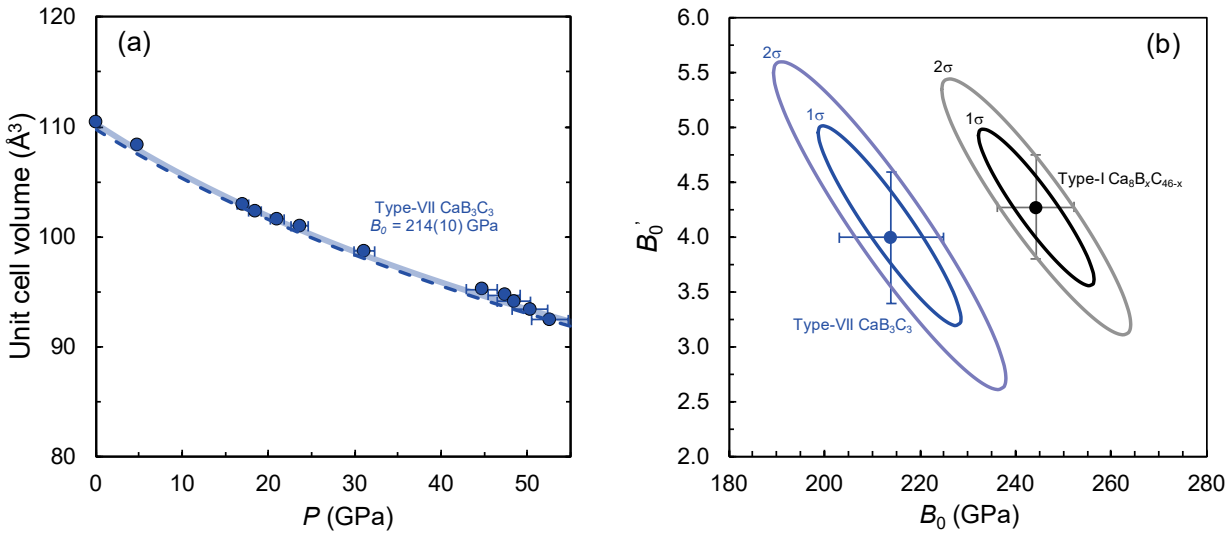

Fig. S2. Experimental *PV* data were modelled using a third-order Birch–Murnaghan equation of state (EOS) to obtain the zero-pressure volume, V_0, bulk modulus, B_0, and its pressure derivative, B_0'. Refined experimental parameters are V_0 = 405.9(3), B_0 = 244(8) and B_0' = 4.2(4) for type-I $Ca_8B_xC_{46-x}$ and V_0 = 110.5(1), B_0 = 214(10) and B_0' = 4.1(6) for type-VII CaB_3C_3, which compare favorably with DFT (PBE) calculations that yield B_0 = 256 and B_0' = 3.8 for type-I $Ca_8B_xC_{46-x}$ and B_0 = 224 and B_0' = 3.7 for type-VII CaB_3C_3. (a) Experimental unit cell volume as a function of pressure for type-I clathrate (points) and refined EOS (solid line) compared with theoretical equation of state for ordered type-I $Ca_8B_{16}C_{30}$ (dashed line). (b) Experimental uncertainty in B_0 and B_0' as confidence ellipses drawn at one and two standard deviations for type-I $Ca_8B_xC_{46-x}$ (black) and type-VII CaB_3C_3 (blue).

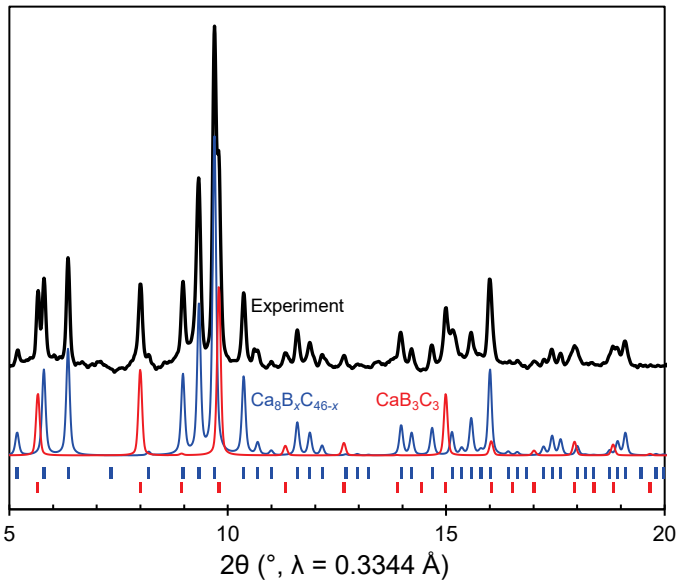

Fig. S3. Experimental powder XRD pattern (black) collected at ambient pressure (recovered from ~50 GPa) compared with calculated profiles for $Ca_8B_xC_{46-x}$ (red) and CaB_3C_3 (blue).