

## **Supplemental Material for Prediction of Novel Boron-carbon Based Clathrates**

Zhi Cui<sup>1</sup>, Xiaohua Zhang<sup>1,2</sup>, Yuanhui Sun<sup>3,\*</sup>, Yong Liu<sup>1</sup>, and Guochun Yang<sup>1,2,\*</sup>

*<sup>1</sup>State Key Laboratory of Metastable Materials Science & Technology and Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao 066004, China*

*<sup>2</sup>Centre for Advanced Optoelectronic Functional Materials Research and Key Laboratory for UV Light-Emitting Materials and Technology of Northeast Normal University, Changchun 130024, China*

*<sup>3</sup>Department of Chemistry and Biochemistry, California State University Northridge, Northridge 91330, United States*

\*Corresponding Author Email: [yuanhui.sun@csun.edu](mailto:yuanhui.sun@csun.edu), [yanggc468@nenu.edu.cn](mailto:yanggc468@nenu.edu.cn), [yanggc@ysu.edu.cn](mailto:yanggc@ysu.edu.cn)

## Table of Contents

Computational Details .....	S3
Structure parameters of the predicted $\text{SrB}_2\text{C}_4$ and $\text{LaB}_4\text{C}_2$ .....	S5
Possible synthesis pathway of $\text{SrB}_2\text{C}_4$ and $\text{LaB}_4\text{C}_2$ .....	S6
Stability of the predicted structures .....	S7
Electronic property of the predicted structures .....	S9
Superconductivity and Vickers hardness of the predicted structures .....	S12
References.....	S13

## Computational Details

Evolutionary search by the crystal structure analysis by particle swarm optimization (CALYPSO) code,<sup>1,2</sup> was employed to find the possibly stable  $\text{SrB}_x\text{C}_y$ , and  $\text{LaB}_x\text{C}_y$  structures. We focus on the structure identification with  $\text{SrB}_x\text{C}_y$ , and  $\text{LaB}_x\text{C}_y$  ( $x : y = 1 : 5, 5 : 1, 2 : 4, 4 : 2, 2 : 3, 3 : 2, 2 : 5, 5 : 2$ ) stoichiometries at 50 GPa. Unit cells containing 1 and 2 formula units are considered. Firstly, random structures are constructed with atomic coordinates generated by the crystallographic symmetry operations. Local optimizations are performed by the Vienna ab-initio simulation package (VASP)<sup>3,4</sup> using the conjugate gradient method and the electronic total energy convergence threshold is set at  $10^{-5}$  eV. Then the 60% of the first generation structures with lowest Gibbs free energy are selected to construct the next generation structures by particle swarm optimization. 40% of the next generation structures are generated randomly. A fingerprinting technique based on bond characterization is applied to strictly avoid identical structures. This procedure significantly enhances the diversity of the structures, which is crucial for the efficiency of the global structure search. In most cases, 800-1200 structures (20-30 generations) are generated.

Local optimizations and electronic property calculations are performed in the framework of the projected augmented wave pseudopotentials<sup>5,6</sup> as implemented in VASP. To obtain a better energy convergence, we have chosen a plane-wave cutoff energy of 800 eV and Monkhorst-Pack  $k$  meshes of  $2\pi \times 0.03 \text{ \AA}^{-1}$ . The electronic total energy convergence threshold is set at  $10^{-6}$  eV. The Heyd-Scuseria-Ernzerhof hybrid functional is used to for the calculation of electronic properties. The finite-temperature smearing of the occupations is not considered here. Based on the supercell approach of the Phonopy code,<sup>7</sup> the phonon dispersions of  $\text{SrB}_x\text{C}_y$ , and  $\text{LaB}_x\text{C}_y$  are calculated in  $2 \times 2 \times 2$  supercell. Ab initio molecular dynamics simulations were performed at 300 K using the NVT ensemble and the temperature was controlled by using Nosé–Hoover method and last 8  $ps$  with 1  $fs$  step.<sup>8</sup>

The electron-phonon coupling calculations are carried out with the density functional perturbation (linear response) theory as implemented in the QUANTUM ESPRESSO package.<sup>9</sup> We employ ultrasoft pseudopotentials with Mg.pbe-spnl-rrkjus\_psl.1.0.0.UPF, B.pbe-n-rrkjus\_psl.1.0.0.UPF and C.pbe-rrkjus.UPF for  $\text{MgB}_2\text{C}_4$ , Ca.pbe-mt\_fhi.UPF, B.pbe-mt\_fhi.UPF and C.pbe-mt\_fhi.UPF for  $\text{CaB}_2\text{C}_4$  and  $\text{CaB}_4\text{C}_2$ , Sr.pbe-sp-van.UPF, B.pbe-n-rrkjus\_psl.1.0.0.UPF

and C.pbe-van\_ak.UPF for SrB<sub>4</sub>C<sub>2</sub>, Sc.pbe-spn-rrkjus\_psl.1.0.0.UPF, B.pbe-n-van\_ak.UPF and C.pbe-rrkjus.UPF for ScB<sub>2</sub>C<sub>4</sub>, Ti.pbe-spn-rrkjus\_psl.1.0.0.UPF, B.pbe-n-rrkjus\_psl.0.1.1.UPF and C.pbe-rrkjus.UPF for TiB<sub>2</sub>C<sub>4</sub>, and La.pbe-spfm-rrkjus\_psl.1.0.0.UPF, B.pbe-n-van\_ak.UPF and C.pbe-van\_ak.UPF for LaB<sub>4</sub>C<sub>2</sub>. The considered kinetic energy cutoff and Gaussians of width are 100 Ry and 0.05 Ry, respectively. To reliably calculate EPC in metallic systems, we need to sample dense k-meshes for electronic Brillouin zone integration and enough q-meshes for evaluating average contributions from the phonon modes. Dependent on specific structures of stable compounds, we use 12×12×12 *k*-meshes and 4 × 4 × 4 *q*-meshes for MB<sub>2</sub>C<sub>4</sub> and MB<sub>4</sub>C<sub>2</sub>. We have calculated the superconducting  $T_c$  of MB<sub>2</sub>C<sub>4</sub> and MB<sub>4</sub>C<sub>2</sub> as estimated from the McMillan-Allen-Dynes formula:<sup>10-12</sup>

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \quad (1)$$

where  $\mu^*$ , the Coulomb pseudopotential, was assumed to be 0.1. The electron-phonon coupling constant,  $\lambda$ , and the logarithmic average phonon frequency,  $\omega_{\log}$ , are calculated from the Eliashberg spectral function for the electron-phonon interaction:

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)} \sum_{kq,v} |g_{k,k+q,v}|^2 \delta(\epsilon_k) \delta(\epsilon_{k+q}) \delta(\omega - \omega_{q,v}) \quad (2)$$

where  $\lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega}$ ;  $\omega_{\log} = \exp \left[ \frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega) \right]$ . Herein,  $N(E_F)$  is the electronic density of states at the Fermi level,  $\omega_{q,v}$  is the phonon frequency of mode  $v$  and wave vector  $q$ , and  $|g_{k,k+q,v}|$  is the electron-phonon matrix element between two electronic states with momenta  $k$  and  $k+q$  at the Fermi level.<sup>13</sup>

## Structure parameters of the predicted SrB<sub>2</sub>C<sub>4</sub> and LaB<sub>4</sub>C<sub>2</sub>

Table S1 Structural information of the predicted SrB<sub>2</sub>C<sub>4</sub> and LaB<sub>4</sub>C<sub>2</sub> at 50 GPa.

Phases	Pressure (GPa)	Lattice Parameters (Å, °)	Atoms	Wyckoff Positions (fractional)		
				<i>x</i>	<i>y</i>	<i>z</i>
<i>I4/mmm</i> SrB <sub>2</sub> C <sub>4</sub>	50	<i>a</i> = 4.6188	Sr(2a)	0.50000	0.50000	0.50000
		<i>b</i> = 4.6188	B (4d)	0.00000	0.50000	0.25000
		<i>c</i> = 4.5218	C (8j)	0.73953	0.50000	0.00000
		<i>α</i> = 90.0000				
		<i>β</i> = 90.0000				
		<i>γ</i> = 90.0000				
<i>I4/mmm</i> LaB <sub>4</sub> C <sub>2</sub>	50	<i>a</i> = 4.6629	La (2a)	0.00000	0.00000	0.00000
		<i>b</i> = 4.6629	B (8j)	0.23032	0.50000	0.00000
		<i>c</i> = 4.8194	C (4d)	0.50000	0.00000	0.25000
		<i>α</i> = 90.0000				
		<i>β</i> = 90.0000				
		<i>γ</i> = 90.0000				

## Possible synthesis pathways of SrB<sub>2</sub>C<sub>4</sub> and LaB<sub>4</sub>C<sub>2</sub>

**Table S2** Formation enthalpy of SrB<sub>2</sub>C<sub>4</sub> within different synthesis pathways at 50 GPa. The *P6<sub>3</sub>/mmc* Sr,  $\gamma$ -B<sub>28</sub>, graphite or diamond C, *Imma* SrB, *C2/m* SrB<sub>2</sub>, *R-3m* SrB<sub>4</sub>, *Cmmm* SrB<sub>6</sub>, *P6<sub>3</sub>/mmc* SrBC, *Pm-3n* SrB<sub>3</sub>C<sub>3</sub>, and *C2/m* SrC<sub>2</sub> are adopted for the calculation, respectively.

Synthesis pathways		$\Delta H$ with respect to graphite carbon (meV)/atom	$\Delta H$ with respect to diamond carbon (meV)/atom
SrB <sub>2</sub> C <sub>4</sub>	Sr+2B+4C	-567.189	-309.449
	SrB <sub>2</sub> +4C	-289.230	-31.559
	SrC <sub>2</sub> +2B+2C	-238.444	-109.573
	SrBC+B+3C	-176.779	16.526
2SrB <sub>2</sub> C <sub>4</sub>	SrB <sub>4</sub> +SrC <sub>2</sub> +6C	-184.244	9.062
	SrB+SrB <sub>3</sub> C <sub>3</sub> +5C	-155.954	5.134
	SrB <sub>2</sub> +SrC <sub>2</sub> +2B+6C	-263.872	-70.566
	SrB+SrC <sub>2</sub> +3B+6C	-313.488	-120.183
	SrB <sub>3</sub> C <sub>3</sub> +SrC <sub>2</sub> +B+3C	-80.909	15.744
	2SrBC+2B+6C	-176.779	16.526
3SrB <sub>2</sub> C <sub>4</sub>	SrB <sub>6</sub> +2SrC <sub>2</sub> +8C	-162.636	9.191
	2SrB <sub>3</sub> C <sub>3</sub> +SrC <sub>2</sub> +4C	-28.397	57.516
	2SrB <sub>3</sub> C <sub>3</sub> +6C+Sr	-137.979	-9.109
	SrB <sub>3</sub> C <sub>3</sub> +2SrBC+B+7C	-92.311	58.038

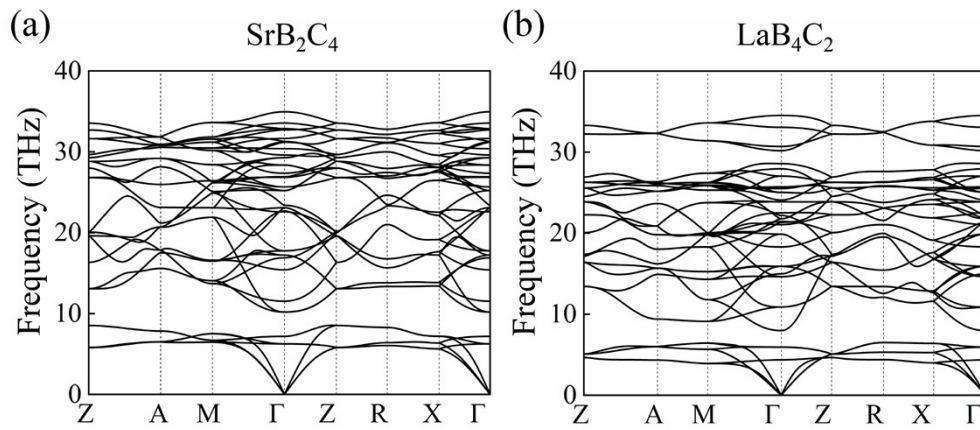
**Table S3** Formation enthalpy of LaB<sub>4</sub>C<sub>2</sub> within different synthesis pathways at 50 GPa. The *dfcc* La,  $\gamma$ -B<sub>28</sub>, graphite or diamond C, *R-3m* LaB, *P4/mbm* LaB<sub>4</sub>, *Pm-3m* LaB<sub>6</sub>, and *Pm-3n* LaB<sub>3</sub>C<sub>3</sub> are adopted for the calculation, respectively.

Synthesis pathways		$\Delta H$ with respect to graphite carbon (meV)/atom	$\Delta H$ with respect to diamond carbon (meV)/atom
LaB <sub>4</sub> C <sub>2</sub>	La+4B+2C	-513.540	-384.669
	LaB <sub>4</sub> +2C	-112.054	16.816
2LaB <sub>4</sub> C <sub>2</sub>	LaB+LaB <sub>4</sub> +3B+4C	-252.655	-123.785
	LaB+LaB <sub>6</sub> +B+4C	-204.512	-75.642
	LaB <sub>3</sub> C <sub>3</sub> +LaB <sub>4</sub> +B+C	-24.780	7.437
3LaB <sub>4</sub> C <sub>2</sub>	2LaB <sub>3</sub> C <sub>3</sub> +LaB <sub>6</sub>	36.407	36.407
	2LaB <sub>6</sub> +La+6C	-181.692	-52.821
	LaB <sub>3</sub> C <sub>3</sub> +2LaB <sub>4</sub> +B+3C	-53.872	10.563

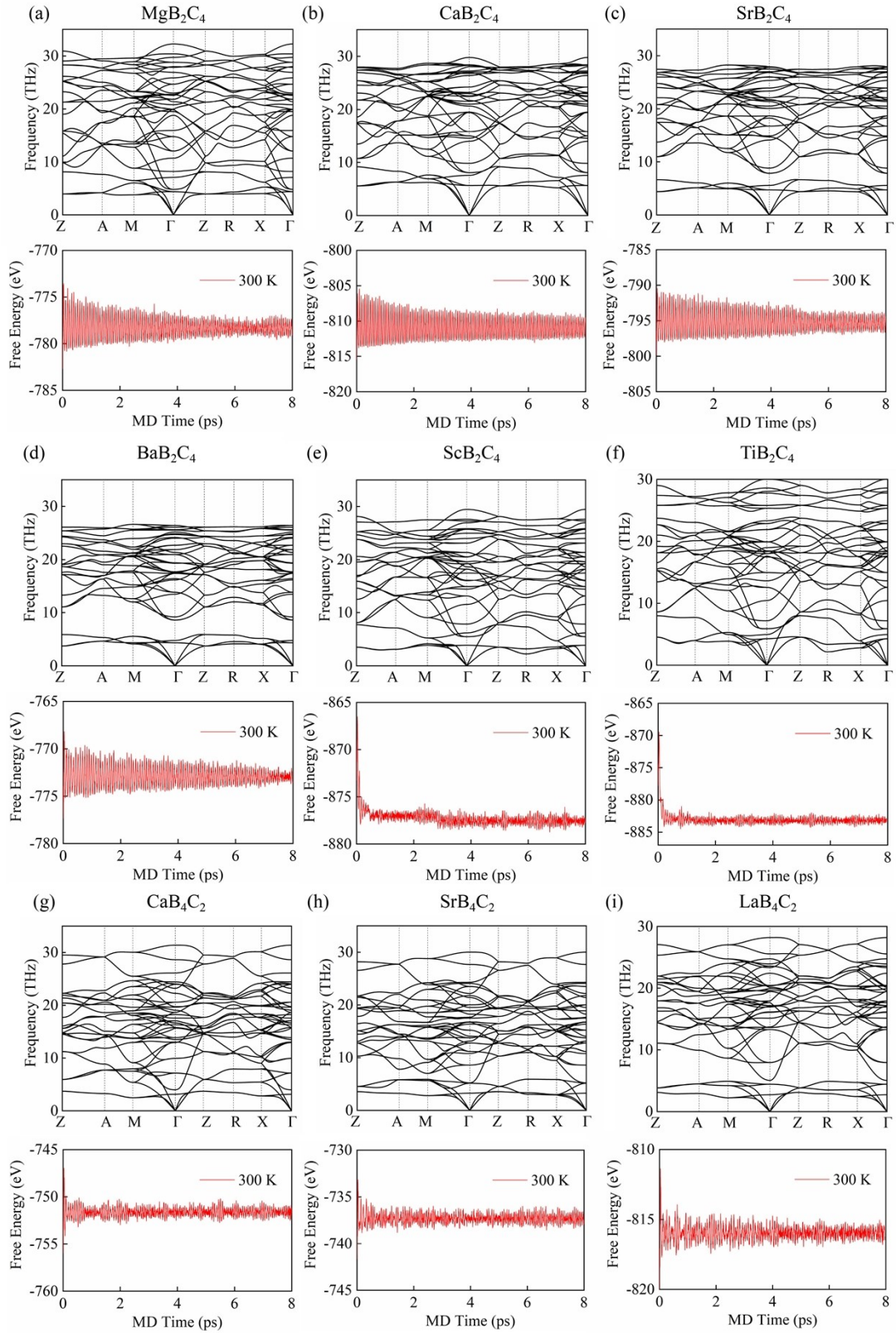
## Stability of the predicted structures

**Table S4** The  $k$ -space coordinates of selected high symmetry points in the first Brillouin zone for the calculation of band structures and phonon dispersions.

High symmetry points	Coordinates		
Z	0.000	0.000	0.500
A	0.500	0.500	0.500
M	0.500	0.500	0.000
G	0.000	0.000	0.000
Z	0.000	0.000	0.500
R	0.000	0.500	0.500
X	0.000	0.500	0.500
G	0.000	0.000	0.000



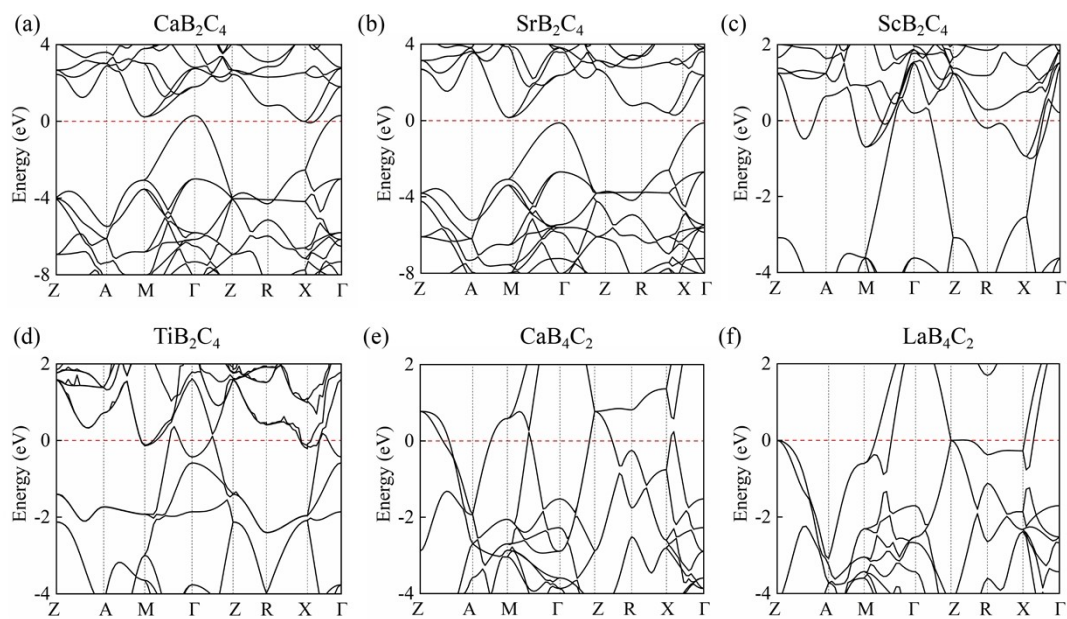
**Fig. S1** Phonon dispersion curves of the predicted SrB<sub>2</sub>C<sub>4</sub> and LaB<sub>4</sub>C<sub>2</sub> at 50 GPa, which are demonstrated as dynamically stable compounds by the absence of imaginary frequency mode.



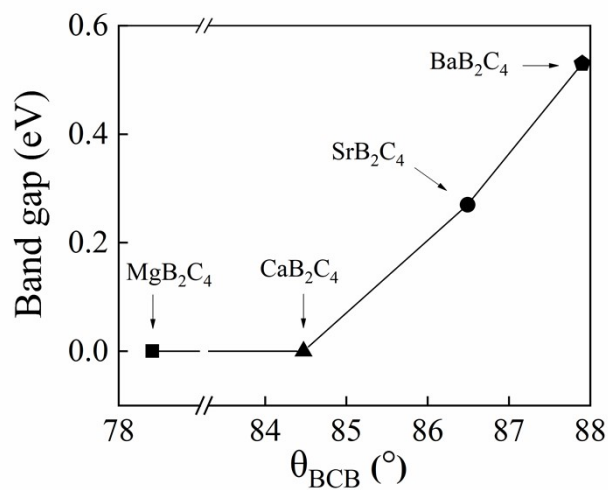
**Fig. S2** Phonon dispersion curves (upper) of B-C clathrates at 0 GPa and the corresponding fluctuation of the total potential energy (lower) at 300 K.



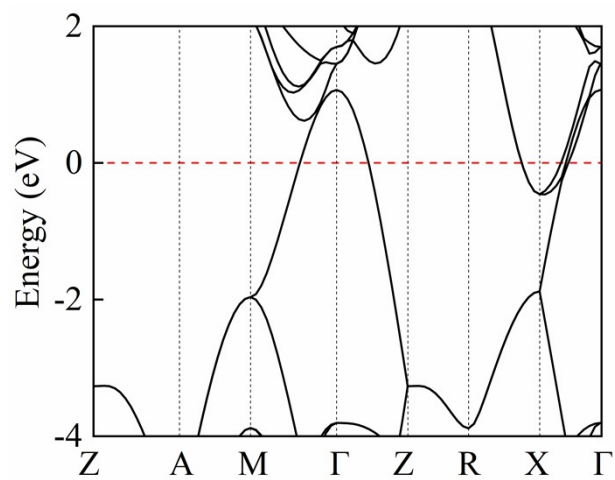
## Electronic property of the predicted structures



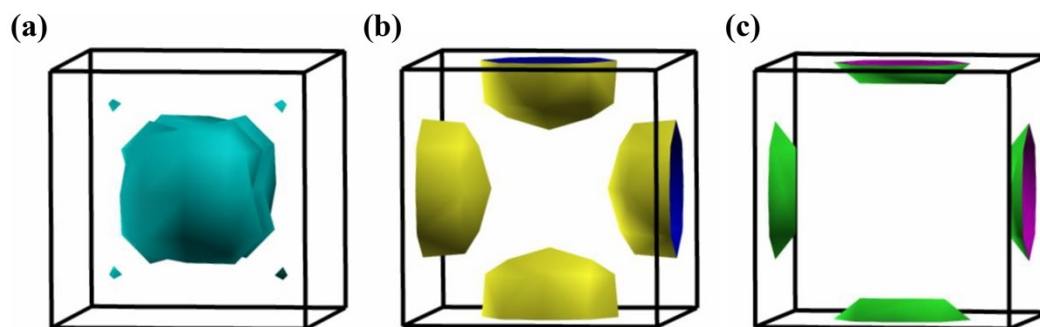
**Fig. S3** Electronic band structures of  $\text{XB}_2\text{C}_4$  and  $\text{XB}_4\text{C}_2$  compounds by using HSE06 level of theory.



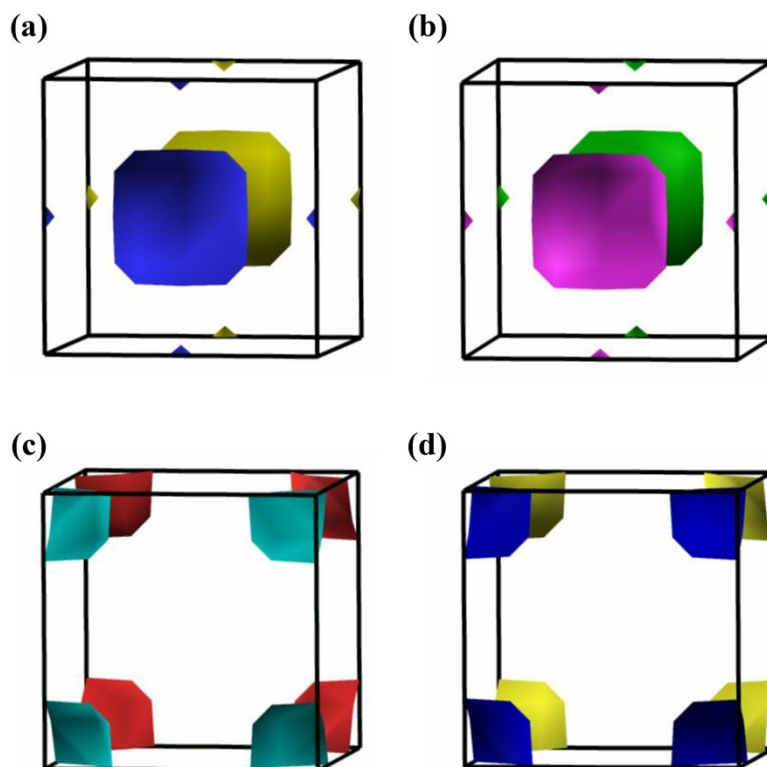
**Fig. S4** Evolution of band gap as a function of  $\theta_{\text{BCB}}$  of  $\text{XB}_2\text{C}_4$  ( $X = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ).



**Fig. S5** Electronic band structures of  $[\text{Ba}_0\text{B}_2\text{C}_4]^{2-}$  with the same  $\theta_{\text{BCB}}$  of  $[\text{Mg}_0\text{B}_2\text{C}_4]^{2-}$ .



**Fig. S6** The separated Fermi surfaces of the three bands cross the Fermi level in the band structure of  $\text{MgB}_2\text{C}_4$  at ambient pressure.



**Fig. S7** The separated Fermi surfaces of the four bands cross the Fermi level in the band structure of  $\text{SrB}_4\text{C}_2$  at ambient pressure.

## Superconductivity and Vickers hardness of the predicted structures

**Table S5** Superconducting properties of the metallic M-B-C phases.

phases	Pressure (GPa)	$T_c$ (K) $\mu^*=0.1$	$N(E_f)$ (states/Ry)	$\lambda$	$\omega_{\log}$ (K)
MgB <sub>2</sub> C <sub>4</sub>	0	4.6	5.59	0.43	712.39
CaB <sub>2</sub> C <sub>4</sub>	0	1.7	5.95	0.36	731.03
ScB <sub>2</sub> C <sub>4</sub>	0	9.6	10.33	0.68	299.67
TiB <sub>2</sub> C <sub>4</sub>	0	5.4	13.23	0.53	365.75
CaB <sub>4</sub> C <sub>2</sub>	0	15.0	8.06	0.62	604.84
SrB <sub>4</sub> C <sub>2</sub>	0	19.6	8.20	0.79	431.61
LaB <sub>4</sub> C <sub>2</sub>	0	5.0	9.44	0.46	603.51

**Table S6** Calculated elastic constant  $C_{ij}$  (GPa), bulk modulus  $B$  (GPa), shear modulus  $G$  (GPa) and Vickers hardness  $H_v$  (GPa) of M-B-C phases.

	$C_{11}$	$C_{33}$	$C_{44}$	$C_{66}$	$C_{12}$	$C_{13}$	$B$	$G$	$G/B$	$H_v$
MgB <sub>2</sub> C <sub>4</sub>	652	355	175	230	32	160	258.4	193.7	0.75	28.1
CaB <sub>2</sub> C <sub>4</sub>	630	468	229	203	29	132	257.0	224.5	0.87	37.5
SrB <sub>2</sub> C <sub>4</sub>	616	504	229	219	38	96	243.4	234.4	0.96	43.6
BaB <sub>2</sub> C <sub>4</sub>	578	532	188	233	67	64	230.8	219.5	0.95	41.2
ScB <sub>2</sub> C <sub>4</sub>	637	478	95	84	56	162	278.8	132.1	0.47	11.5
TiB <sub>2</sub> C <sub>4</sub>	642	522	121	145	83	165	292.2	162.1	0.56	16.7
CaB <sub>4</sub> C <sub>2</sub>	359	670	175	159	153	39	203.1	170.2	0.84	29.8
SrB <sub>4</sub> C <sub>2</sub>	350	638	183	54	105	40	186.2	141.8	0.76	23.1
LaB <sub>4</sub> C <sub>2</sub>	422	622	204	220	143	58	219.4	201.9	0.92	37.5

## References

1. Y. Wang, J. Lv, L. Zhu and Y. Ma, *Phys. Rev. B*, 2010, **82**, 094116.
2. Y. Wang, J. Lv, L. Zhu and Y. Ma, *Comput. Phys. Commun.*, 2012, **183**, 2063-2070.
3. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.
4. G. G. Kresse and J. J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
5. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
6. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.
7. A. Togo, F. Oba and I. Tanaka, *Phys. Rev. B*, 2008, **78**, 134106.
8. G. J. Martyna, M. L. Klein and M. Tuckerman, *J. Chem. Phys.*, 1992, **97**, 2635-2643.
9. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovitch, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.
10. L. N. Oliveira, E. K. U. Gross and W. Kohn, *Phys. Rev. Lett.*, 1988, **60**, 2430-2433.
11. M. Lüders, M. A. L. Marques, N. N. Lathiotakis, A. Floris, G. Profeta, L. Fast, A. Continenza, S. Massidda and E. K. U. Gross, *Phys. Rev. B*, 2005, **72**, 024545.
12. P. B. Allen and R. C. Dynes, *Phys. Rev. B*, 1975, **12**, 905-922.
13. J. P. Carbotte, *Rev. Mod. Phys.*, 1990, **62**, 1027-1157.