



Cite this: DOI: 10.1039/d6tc00100a

High-throughput structure searches for ambient-pressure superconductors in boron–carbon clathrates

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Boron–carbon (B–C) clathrates have attracted much attention in recent years due to their excellent sp³ hybridized B–C covalent bonds and distinctive electronic properties. Here, we conduct systematic high-throughput structural searches for ambient-pressure superconductors in B–C clathrates. Twenty-one stable X₂B₈C₄ clathrates are identified, among which superconductivity is found in X₂B₈C₄ (X = Rb, Ca, Sr, Ba, La, and Ce) clathrates with superconducting transition temperatures of 34, 21, 17, 16, 13, and 10 K, respectively. The calculated results indicate that the superconductivities of main-group and transition metal-doped B–C clathrates are influenced by the amount of charge transferred from the metal to the B–C frameworks and the metallicities of the guest metal atoms. The high *T_c* value of the Rb₂B₈C₄ superconductor originates from the strong metallicity and large atomic radius of the Rb atom, which squeezes the B–C cages and strengthens the electron–phonon coupling (EPC) interactions, thereby enhancing superconductivity. The present results enrich the databases of B–C clathrate superconductors and offer a viable strategy for design and synthesis of high-temperature superconductors at ambient pressure.

Received 13th January 2026,
Accepted 30th March 2026

DOI: 10.1039/d6tc00100a

rsc.li/materials-c

1 Introduction

Superconductivity was first discovered by Onnes^{1,2} in 1911 when he observed the sudden drop in resistance of mercury at 4.2 K. For the next 75 years, superconductivity was limited to materials with superconducting transition temperature (*T_c*) below 30 K, as described by the Bardeen–Cooper–Schrieffer (BCS)³ theory, which attributes superconductivity to electron–phonon coupling (EPC) leading to the formation of Cooper pairs. The landscape of superconductivity research changed dramatically in 1986 when Bednorz and Müller^{4–6} discovered superconductivity in La–Ba–Cu–O at 35 K, which was later extended to 95 K in YBa₂Cu₃O_{7–δ}, surpassing the boiling point of liquid nitrogen.⁷ Even higher *T_c* values were subsequently observed in HgBa₂Ca₂Cu₃O_{8+δ}, which exhibits a *T_c* of 135 K at ambient pressure and can be further enhanced to ~164 K under a high pressure of 30 GPa.^{8–10} These discoveries opened the era of high-temperature superconductors. Since then, several other families of high-temperature superconductors have been discovered, such as iron-based,^{11,12} hydrogen-rich,^{13,14}

and nickel-based^{15,16} superconductors. In recent years, B–C clathrates,^{17–19} as a new class of high-temperature superconducting materials,^{20–22} have attracted widespread attention in the scientific community due to their unique structure and excellent superconductivities.

B–C clathrates have unique cage-like structures, mainly composed of B–C frameworks and metal atoms, with three-dimensional (3D) network structures and strong covalent bond characteristics. These compounds not only have potential applications in high-temperature superconductivity but also show broad application prospects in hydrogen storage, ionic conductors, thermoelectric materials, and other fields.^{23–25} In particular, the breakthrough in achieving high-temperature superconductivity at ambient pressure provides new possibilities for the practical applications of superconducting materials. The most common B–C clathrates include XB₃C₃, XB₂C₈, X₂B₈C₄, etc., where X represents different doped metals.^{26,27} These compounds usually show highly symmetric crystal structures, such as cubic and hexagonal structures. Taking SrB₃C₃ as an example, the B–C cage like frameworks form the 3D covalent networks, with Sr atoms located at the center of the cages. This structure not only provides good electron conduction paths but also regulates electronic properties through the interaction between metal atoms and the B–C frameworks, thereby achieving high-temperature superconductivity.

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A diverse range of B–C clathrates are predicted to be excellent superconductors under ambient pressure,^{18,28,29} including SrB_3C_3 ($T_c = 40\text{--}44\text{ K}$),³⁰ BaB_3C_3 ($T_c = 43\text{ K}$),³¹ *etc.* Zhu *et al.*³² reported the experimental synthesis of SrB_3C_3 in 2020 and subsequently measured its superconducting transition temperature (T_c) in 2023.³³ These studies provide crucial experimental validation of the boron–carbon (BC) clathrate concept and strongly stimulate further theoretical investigations. Importantly, they demonstrate that BC clathrates are not merely theoretical constructs, but experimentally realizable superconducting materials. Typically, Cui *et al.*¹⁸ designed a class of LaH_{10} -type clathrate compounds XB_2C_8 ($\text{X} = \text{K, Rb, Cs, Sr, Ba, Ga, In, Tl, Sn, Pb, and Bi}$) through first-principles calculations and studied their potential superconductivities. They found that when filled with +1 oxidation state metals, the T_c values of XB_2C_8 ($\text{X} = \text{K, Rb, Cs, Ga, In, and Tl}$) compounds all exceed the liquid nitrogen boiling point of 77 K, and the T_c of the TlB_2C_8 compound was expected to reach 96 K at ambient pressure. Another study suggested that $\text{Ca}_4\text{B}_{10}\text{C}_{13}$ exhibited a maximum T_c of 101–109 K in the pressure range of 25–100 GPa.³⁴ This discovery indicates that metal-doped and boron-substituted carbon clathrates are promising high-temperature superconductors under moderate pressure. In addition, two stable 1166-type B–C clathrates, RbYbB_6C_6 and RbBaB_6C_6 , were successfully discovered by our group, with superconducting temperatures up to 70 K.³⁵

Despite significant progress in the research on B–C clathrate superconductors, there are still some critical issues that need to be addressed urgently. Currently, the synthesis of most B–C clathrates requires high-temperature and high-pressure conditions, which not only increases synthesis difficulty and cost but also limits their large-scale application. For example, the synthesis of SrB_3C_3 usually requires pressures of about 5–10 GPa and temperatures of 1500–2000 K.³⁶ How to synthesize high-quality B–C clathrates under mild conditions remains an important challenge in current research. Some B–C clathrates have poor structural stability at ambient pressure and are prone to phase transition or decomposition. How to improve the structural stability of B–C clathrates is also a key issue for their practical application.^{37,38} Although researchers have proposed some hypotheses about the superconducting mechanism of B–C clathrates, a unified understanding has not yet been obtained. How the interactions between metal atoms and the B–C frameworks affect superconducting properties and the specific role of phonon softening and EPC in the superconducting processes remain unclear.^{39,40}

To solve part of the above issues, in this work, we carried out high-throughput structure searches for B–C clathrate superconductors under ambient pressure. The high-throughput calculations were performed for 64 metallic elements (covering all main-group metals and most transition metals), all non-metallic elements, and noble gases. The calculated results demonstrate that doping with non-metallic elements or noble gases fails to stabilize the B_8C_4 caged frameworks. Only metal atom doping exhibits the capability to induce structural stabilization of the B_8C_4 cages. Twenty-one B–C clathrates with the

space group $P4/mmm$ symmetry (denoted as $P4/mmm\text{-X}_2\text{B}_8\text{C}_4$, where X represents the main-group and transition metals) were identified to be stable. It is worth noting that Yan *et al.*⁴¹ previously reported a related clathrate structure involving thorium (Th) filling, namely, ThB_4C_2 , whose structure is similar to the $\text{X}_2\text{B}_8\text{C}_4$ structure investigated in this work. The space groups of the two structures are $I4/mmm$ and $P4/mmm$, respectively. In their study, they reported that ThB_4C_2 ($I4/mmm$) exhibits a superconducting transition temperature (T_c) of 0.3 K. For comparison, we also performed calculations involving the Th element. Our results indicate that $\text{Th}_2\text{B}_8\text{C}_4$ ($P4/mmm$) is a metallic phase with an extremely low superconducting transition temperature, with a T_c of 1.3 K. This result further supports the reliability of our computational approach. Therefore, we conducted a detailed investigation of the crystal structural characteristics, lattice dynamical stability, and the potential superconducting behavior at ambient pressure of the $P4/mmm\text{-X}_2\text{B}_8\text{C}_4$ structures.

2 Theoretical methods

The high-throughput structure searches for B–C clathrate superconductors under ambient pressure were performed using the Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) method^{42–44} and Vienna *Ab initio* Simulation Package (VASP).^{45,46} The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional (PBE-GGA)⁴⁷ was adopted to describe the exchange–correlation interactions. The projector augmented wave (PAW) method was used to treat the core valence electron interactions. A plane-wave cutoff energy of 800 eV was set to ensure the convergence of electronic structure calculations.^{47,48} During the structural optimization process, strict convergence criteria were imposed. The energy convergence threshold was set to 10^{-6} eV, and the force convergence threshold for each atom was set to 10^{-4} eV $\text{\AA}^{-1}$, to obtain the ground-state crystal structures. *Ab initio* molecular dynamics (AIMD) simulations were performed using the VASP package for 10 ps at 500 K and 2000 K to characterize the dynamical and thermodynamic stability of the $\text{Rb}_2\text{B}_8\text{C}_4$ structure.

To analyze the chemical bonding characteristics of $\text{X}_2\text{B}_8\text{C}_4$ superconductors, Crystal Orbital Hamilton Population (COHP) calculations were performed using the LOBSTER package.⁴⁹ For the evaluation of structural stabilities and related superconductivities of $\text{X}_2\text{B}_8\text{C}_4$, phonon dispersion curves, EPC strengths, and superconducting transition temperatures (T_c) were calculated by using the QUANTUM ESPRESSO (QE) package.^{50,51} The PAW-type pseudopotentials were employed to represent the ion–electron interactions for boron (B), carbon (C), and the doped atoms.⁵² The plane-wave kinetic energy cutoff is set to 100 Ry and a charge density cutoff of 1000 Ry is employed. An $8 \times 8 \times 8$ k -point mesh was used for charge density calculations to ensure sufficient sampling of the Brillouin zone. For the calculations of dynamical matrices and EPC, an $8 \times 8 \times 8$ k -point mesh and a $4 \times 4 \times 4$ q -point mesh were adopted, respectively, to balance computational accuracy and efficiency.

The T_c values of the B–C clathrate superconductors were estimated using the McMillan equation, which is expressed as follows:

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

where μ^* represents the Coulomb pseudopotential and $\omega_{\log}$ is the logarithmic mean of phonons, which is expressed as

$$\omega_{\log} = \exp \left[\frac{2}{\lambda} \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \right] \quad (2)$$

The EPC constant λ is expressed as

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad (3)$$

3 Results and discussion

To explore the structural stabilities and superconductivities of $X_2B_8C_4$ B–C clathrates under ambient pressure, high-throughput calculations are performed. Detailed results are summarized in Fig. 1, where yellow shading denotes stable structures; after verification, all these materials possess metallic properties, but the electron–phonon coupling is extremely weak ($\lambda < 0.4$), and thus the estimated superconducting critical temperature T_c is lower than approximately 3 K. Their energy bands and phonon spectra are all provided in the SI, Fig. S1–S8.⁵³ Apricot shading represents unstable structures, and red shading indicates structures with superconducting behavior. It is worth noting that, for $X_2B_8C_4$ systems containing transition-metal guest atoms, we carefully examined the possible emergence of magnetic ordering within the structures and performed spin-polarized calculations to assess potential magnetic effects.^{54,55} The calculated results indicate that doping with non-metallic atoms or noble gases is incapable of stabilizing the B_8C_4 frameworks (see Fig. 2(a)). Thus, these B–C clathrates are not discussed. Further analysis revealed that six of these stable $X_2B_8C_4$ structures (with $X = Rb$,

Ca, Ba, Sr, La, and Ce) possess superconducting properties, with $Rb_2B_8C_4$ achieving the highest T_c value of 34 K. The crystal structure of the $Rb_2B_8C_4$ B–C clathrate is shown in Fig. 2(b). Rb atoms occupy the central 1d (0.50, 0.50, 0.50) and corner 1a (0.00, 0.00, 0.00) Wyckoff positions, while B and C atoms form the covalent networks that encapsulate the central Rb atoms. Specifically, B atoms are located at the 4i (0.00, 0.50, 0.21) and 4m (0.27, 0.00, 0.50) Wyckoff sites, and C atoms occupy the 4n (0.73, 0.50, 0.00) Wyckoff site. Eight B atoms and four C atoms constitute the B–C clathrate cage. To evaluate the mechanical stability of $Rb_2B_8C_4$, we calculated its elastic constants. The results show that the elastic constants satisfy the Born mechanical stability criteria ($C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, and $C_{44} > 0$), confirming its mechanical stability. Furthermore, to investigate whether $Rb_2B_8C_4$ can maintain dynamical stability, we performed *ab initio* molecular dynamics (AIMD) simulations. A $2 \times 2 \times 2$ supercell was employed, and AIMD simulations were carried out for 10 ps at 500 K and 2000 K, respectively. The corresponding results are shown in Fig. S9,⁵³ where the dark blue curve represents the simulation at 500 K, while the green curve corresponds to the simulation at 2000 K. As can be clearly observed from the figure, within the 10 ps simulation time window, $Rb_2B_8C_4$ exhibits no significant energy fluctuations or structural instabilities at either 500 K or 2000 K. Throughout the entire AIMD simulation process, the structure remains intact without any signs of structural collapse or phase transition. These results indicate that the structure maintains excellent dynamical stability even under thermal perturbations.

As shown in Fig. 2(c), the phonon spectrum of the intrinsic B_8C_4 cage under ambient pressure exhibits dynamical instability, characterized by the presence of imaginary frequencies. In contrast, the $Rb_2B_8C_4$ B–C clathrate is stable under ambient pressure, and as shown in Fig. 2(d), no imaginary frequencies are present. The lattice constants of $Rb_2B_8C_4$ are $a = b = 4.977$ Å and $c = 5.116$ Å. All B–C bonds in $Rb_2B_8C_4$ are equivalent, with bond lengths of 1.729 Å, which are markedly longer than B–C bond lengths (1.603 Å) in the intrinsic B_8C_4 cage. This visible elongation of B–C bonds induced by Rb doping is consistent

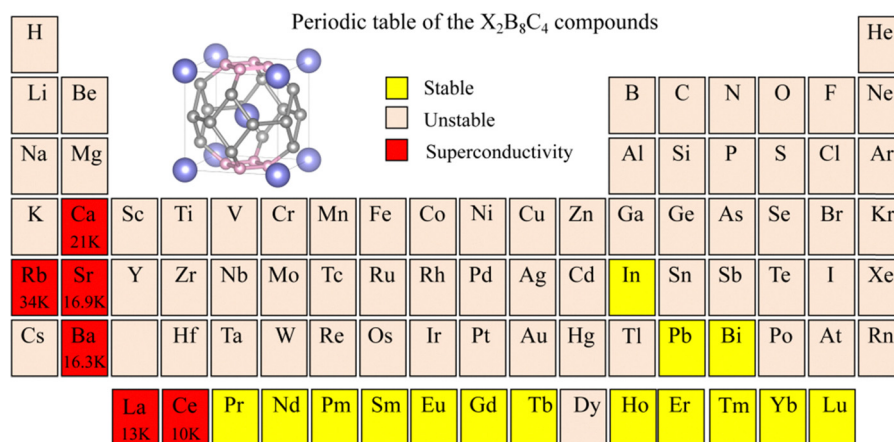


Fig. 1 The $X_2B_8C_4$ boron–carbon clathrates under ambient pressure. Yellow fillings are the stable structures, apricot fillings represent unstable structures, red fillings denote structures with superconducting properties, and white fillings correspond to the structures that have not been calculated.

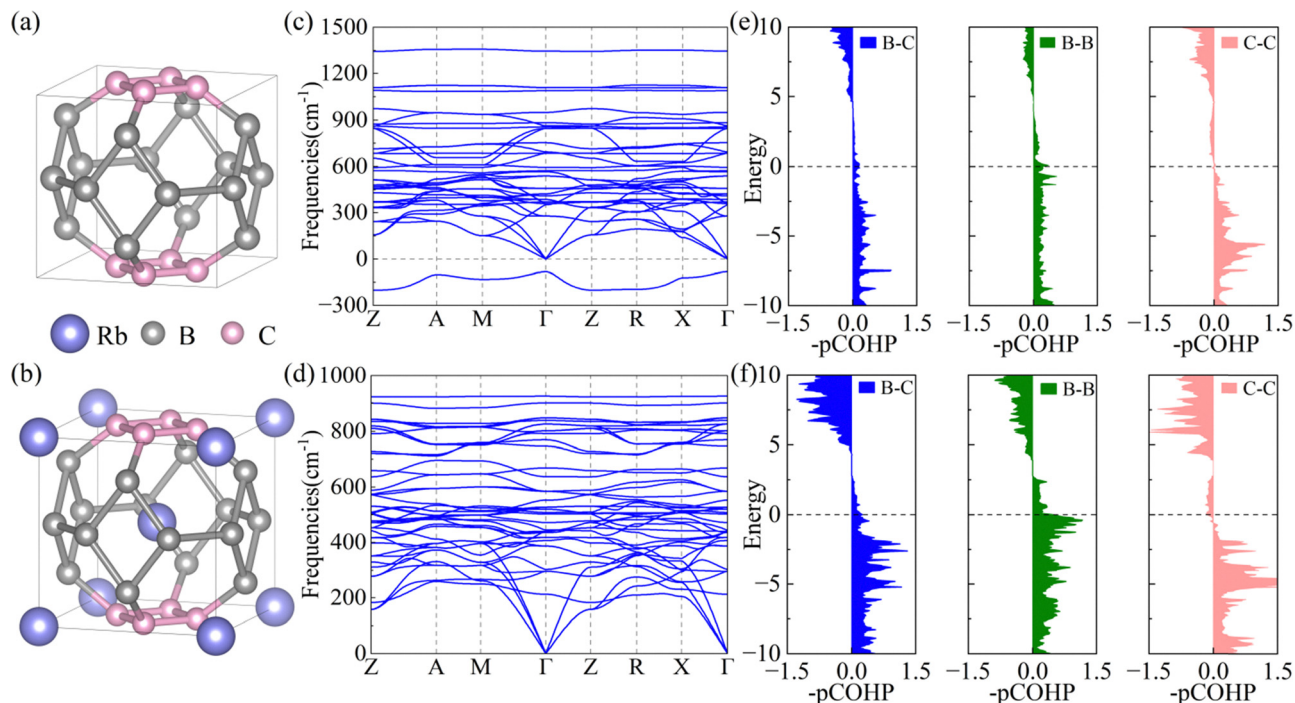


Fig. 2 Structures, stabilities, and COHP calculations of boron-carbon clathrates under ambient pressure. (a) Crystal structure of the B₈C₄ cage; (b) crystal structure of the Rb₂B₈C₄ superconductor; (c) phonon spectrum of the B₈C₄ cage; (d) phonon spectrum of the Rb₂B₈C₄ superconductor; (e) pCOHP for B-C, B-B, and C-C bonds in the B₈C₄ cage; and (f) pCOHP for B-C, B-B, and C-C bonds in the Rb₂B₈C₄ superconductor.

with trends reported by Duan *et al.*,⁵⁶ confirming the regulatory effect of metal dopants on the B-C frameworks.

To gain deeper insight into the chemical bonding and stabilization mechanism of X₂B₈C₄ superconductors, additional calculations were performed, including the Bader charge analysis, the electron localization function (ELF), and the crystal orbital Hamiltonian population (COHP) analysis. Bader charge analysis of Rb₂B₈C₄ reveals that 0.80 electrons are transferred from each Rb atom to the B-C framework, indicating ionic character, that is the formation of ionic bonds between the Rb atoms and the B-C skeleton. Similarly, other guest metal atoms, such as Ca, Sr, and Ba atoms, also transfer electrons to the B-C frameworks and each metal atom transfers 1.50, 1.40, and 1.40 electrons, respectively. The strong cation-anion ionic interactions in X₂B₈C₄ superconductors enhance the binding energy, thereby improving the structural stabilities.

This stabilization effect after Rb doping is further supported by electron localization function (ELF) analysis. The ELF map of Rb₂B₈C₄ shows that regions with high ELF values are primarily concentrated in the B-C network and around the corner Rb atoms, suggesting the presence of strong covalent bonds in the B-C network or localized closed-shell electron clouds around Rb atoms. The high ELF values near corner Rb atoms arise from the low electronegativity (~ 0.82) of metal Rb. Rb is an alkali metal. It readily loses its outermost 5s electrons to form the Rb⁺ cation. The remaining electrons of the Rb⁺ cation occupy tightly bound atomic orbitals. These core electrons are strongly attracted by the Coulomb potential of the nucleus, resulting in a highly compact and localized spatial distribution, with

minimal participation in or diffusion into bonding with the surrounding anionic B-C framework. This leads to electron density characteristics in this region that resemble those of a localized closed-shell electron cloud. The charge transfer between metal Rb and the B-C cage further promotes interionic interactions and ionic bond formation. As shown in Fig. S10⁵³, 3D electron density isosurfaces of Rb₂B₈C₄ under ambient pressure visually confirm the localized charge around Rb atoms and the shared electrons between B and C atoms, validating both the ionic bonding between Rb and the B₈C₄ cage and the strong covalent bonding within the B-C network. Notably, delocalized electron channels are observed in the interstices of the B-C network. These channels may serve as transport pathways for Cooper pairs, which are critical for superconductivity.

To explore the strength of covalent bonds in the B-C frameworks of the Rb₂B₈C₄ B-C clathrate, COHP and integrated COHP (ICOHP) calculations are performed for B-C, B-B, and C-C bonds in both the intrinsic B₈C₄ cage and the Rb₂B₈C₄ clathrate. The calculated results are shown in Fig. 2(e) and (f). The pCOHP curves for other X₂B₈C₄ (X = Ca, Sr, Ba, and La) clathrates are presented in Fig. S11.⁵³ A direct comparison of Fig. 2(e) and (f) reveals that Rb doping obviously enhances the bond strengths of B-C, B-B, and C-C bonds. For the Rb₂B₈C₄ clathrate, the pCOHP curve shows that B-C and B-B bonds exhibit strong bonding states. These bonds are the primary contributors to structural stabilization. While the C-C bonds are also present, their contributions to stability are relatively weaker. The bonding states near the Fermi level (E_F) influence the stability of the Rb₂B₈C₄ clathrate. The C-C bond shows

almost no bonding state at the E_F , whereas the B–C and B–B bonds exhibit pronounced bonding states at the E_F . This observation indicates that the formed B–C framework is electronically stable. This observation also reflects that sp^3 hybridization of B and C atoms strongly promotes the stability of the $Rb_2B_8C_4$ clathrate under ambient pressure, which is consistent with the above Bader charge and ELF analyses.

The band structures and corresponding projected density of states (PDOS) for B–C clathrates under ambient pressure are presented in Fig. 3. As shown in Fig. 3(a), for the intrinsic B_8C_4

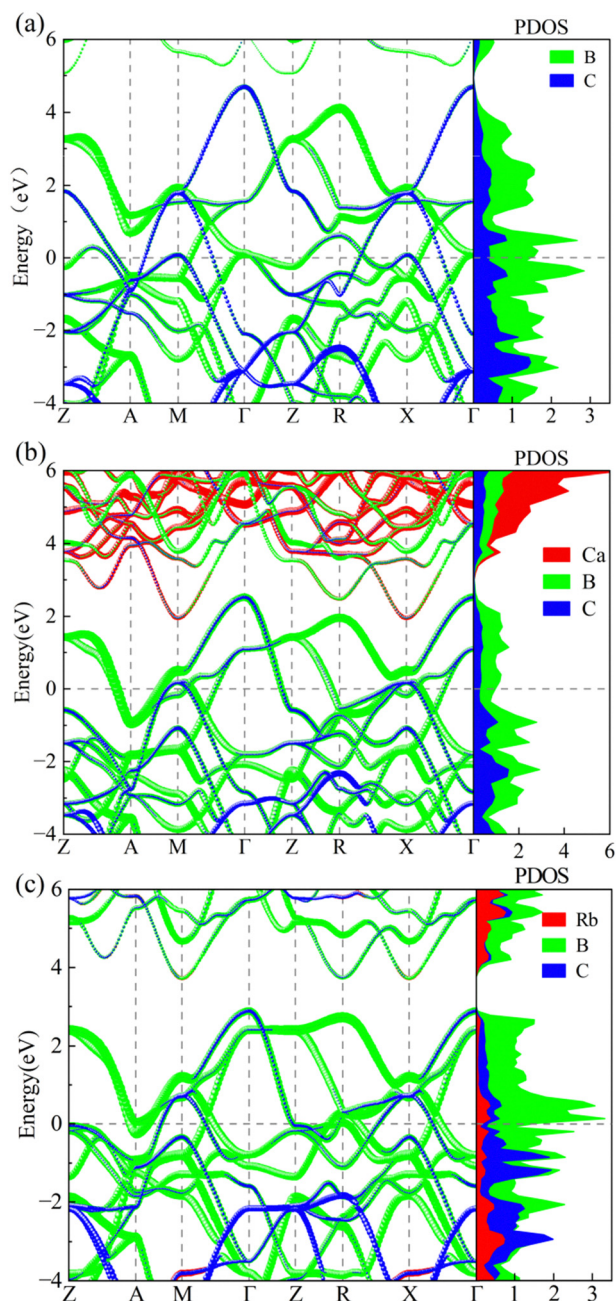


Fig. 3 Band structure and PDOS of boron-carbon clathrates under ambient pressure: (a) Intrinsic B_8C_4 cage, (b) $Ca_2B_8C_4$, and (c) $Rb_2B_8C_4$. The E_F is indicated by a gray horizontal dashed line.

cage without metal doping, the PDOS at the E_F is found to be relatively low. No prominent PDOS peak is observed near E_F . It is generally known that high electronic density of states at the E_F is favorable for the formation of Cooper pairs and plays a critical role in achieving high superconducting transition temperature (T_c). Thus, we introduce the dopant to upshift the E_F , thereby positioning the peak of the density of states near the E_F . As shown in Fig. 3(b), the band structure of the Ca-doped $Ca_2B_8C_4$ clathrate clearly shows that metal Ca atom doping modifies the electronic density of states profile of the B_8C_4 cage. Although the Ca atom contributes the high density of states, it is solely located in the conduction bands, contributing minimally near the E_F . The sharp peak of density of states at the E_F is absent in the $Ca_2B_8C_4$ clathrate. As a result, the superconducting transition temperature of the $Ca_2B_8C_4$ clathrate is just 21 K. In contrast, the band structure of the Rb-doped $Rb_2B_8C_4$ clathrate (Fig. 3(c)) reveals that the valence band electrons near E_F are co-contributed by B, C, and Rb atoms. Notably, a high DOS at E_F implies a large population of electrons (or holes) near the Fermi surface that can participate in charge transport, which directly promotes Cooper pair formation and strengthens EPC interactions.

Further analysis of the band structures of the $Rb_2B_8C_4$ clathrate reveals that multi-band degeneracy and band crossings occur at high-symmetry point A and along the high-symmetry path of Z to R. This phenomenon indicates strong electron delocalization in these regions, which is beneficial for enhancing superconductivity by facilitating electron transport. Moreover, a flat band appears near the E_F along the Z to R path. The high density of states associated with the flat band promotes the formation of the Cooper pair and increases the superconducting transition temperature of the $Rb_2B_8C_4$ clathrate. The calculated T_c value of the $Rb_2B_8C_4$ clathrate is 34 K.

The Bader charge transfer before and after Rb doping of the B_8C_4 cage reveals that each Rb atom donates 0.8 electron to the B–C framework. Combined with the band structures of the $Rb_2B_8C_4$ clathrate, the electron donation from the metal Rb atom to the B–C framework is proposed to upshift the E_F . Consequently, the empty bands between the conduction and valence bands become more pronounced in the $Rb_2B_8C_4$ clathrate, and multi-band crossings emerge near the E_F , both of which may enhance the superconducting properties. This finding indicates that, in the host B_8C_4 cage, the mass of the doped atom is not the decisive factor in determining the EPC constant. Instead, the electronic contribution from the doped metal to the B–C network plays a more critical role in regulating EPC strength. This is likely the underlying reason why the Rb-doped B_8C_4 cage exhibits a higher T_c value than those doped with other metals. Fig. 4(a) shows the band structure of $Rb_2B_8C_4$ near the Fermi surface, where four half-filled bands cross the E_F . And as shown in Fig. 4(b), band 1 (red) and band 2 (green) form electron-like Fermi surfaces, while band 3 and band 4 form complex Fermi surfaces. Such complex Fermi surfaces may enhance the EPC strength by optimizing the multiband carrier concentration, thereby achieving a higher T_c value of 34 K.

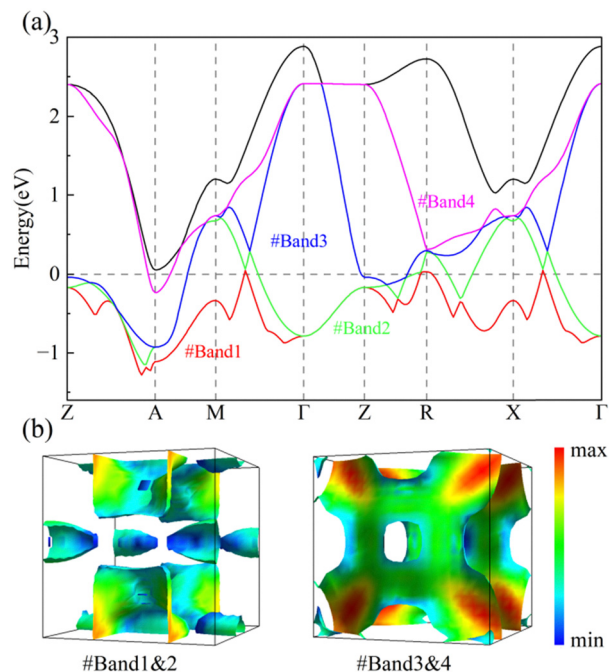


Fig. 4 Fermi surfaces (a) corresponding to the four bands crossing the E_F and (b) color-coded by the Fermi velocity of $\text{Rb}_2\text{B}_8\text{C}_4$.

To further elucidate the superconducting mechanism of the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate, we calculate the projected phonon density of states (PhDOS), Eliashberg spectral function $\alpha^2F(\omega)$, and EPC integral $\lambda(\omega)$ of the $\text{Rb}_2\text{B}_8\text{C}_4$ compound under ambient pressure. The results are shown in Fig. 5. As shown in Fig. 5(a), three frequency regions make significant contributions to the EPC interactions in the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate, *i.e.* low-, intermediate-, and high-frequency regions. In the low-frequency region, the vibrational modes mainly originate from the metal atoms, while intermediate-frequency modes arise primarily from the coupled vibrations of non-metal (B and C) atoms, driven by B–C hybridization, and the high-frequency region is attributed primarily to strong covalent vibrations of C–C bonds. Combining the PhDOS in Fig. 5(a) and the atomic vibration modes (VM) in Fig. 5(b), it is observed that contributions from the Rb metal atom are concentrated exclusively in phonon modes below 200 cm^{-1} . In Fig. 5(b), yellow arrows indicate the vibration directions of the Rb atom, with their maximum contribution points marked by a red circle in Fig. 5(a). Within the low-frequency region, B and C atoms remain nearly stationary, while Rb atoms undergo large-amplitude vibrations along the *x*-axis, which confirms that low-frequency phonon modes are dominated by Rb atomic vibrations. In the intermediate-frequency region ($300\text{--}700\text{ cm}^{-1}$), vibrational modes of the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate are dominated by B and C atoms, with B atoms making a more prominent contribution. Red and blue arrows in Fig. 5(b) denote the vibration directions of B and C atoms, respectively. Their maximum contribution points are labeled by a green circle in Fig. 5(a), which clearly demonstrates that intermediate-frequency phonon modes originate primarily from the coupling between B–C bond bending vibrations (facilitated by B–C hybridization) and the

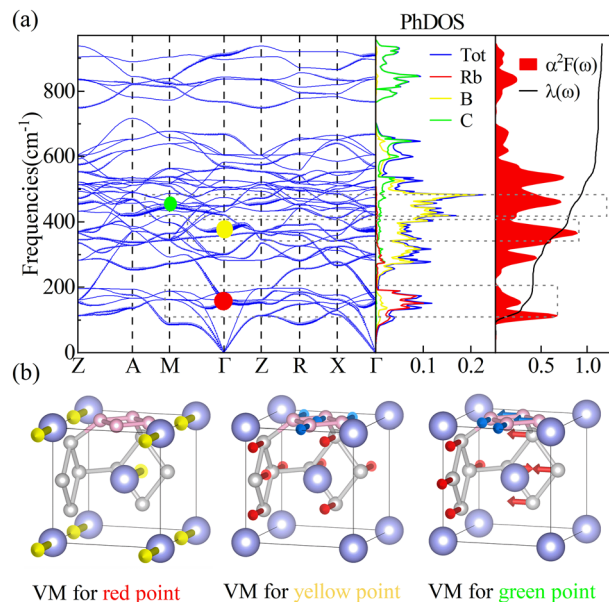


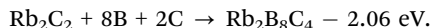
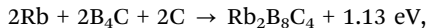
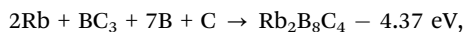
Fig. 5 (a) Calculated phonon spectrum, element-projected PhDOS, Eliashberg spectral function $\alpha^2F(\omega)$, and EPC integral $\lambda(\omega)$ of the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate. (b) Vibration mode (VM) diagrams corresponding to the red, green, and orange points.

overall lattice vibrations of the B_8C_4 framework. The PhDOS and EPC integral $\lambda(\omega)$ reveal that the intermediate-frequency region makes the most significant contribution to EPC interactions in the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate. Red and blue arrows indicate that the vibrational modes in this frequency range are dominated by B and C atoms. This observation confirms that the localized vibrational coupling of the strong covalent bonds formed by B–C hybridization enhances EPC interactions. The large bond dissociation energy of these strong covalent bonds leads to a sharp increase in the EPC integral $\lambda(\omega)$ parameter. Turning to the high-frequency region, it is evident that the vibrational contributions of B and C atoms are visibly diminished at frequencies above 900 cm^{-1} .

The EPC interaction was investigated by calculating the Eliashberg spectral function $\alpha^2F(\omega)$. The total EPC λ was obtained from the EPC integral in Fig. 5(a). Based on EPC constant λ and logarithmic average of phonon frequency ω_{log} , the T_c value of the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate under ambient pressure is further estimated using the McMillan equation. At ambient pressure, the $\text{Rb}_2\text{B}_8\text{C}_4$ clathrate exhibits an EPC λ of 1.19 and a T_c value of 34 K. The calculated PhDOS, $\alpha^2F(\omega)$, and EPC integrals $\lambda(\omega)$ for $\text{X}_2\text{B}_8\text{C}_4$ ($\text{X} = \text{Ca}, \text{Sr}, \text{Ba}, \text{and La}$) clathrates are presented in Fig. S12.⁵³ For these clathrates, the total λ values are 0.74 ($\text{Ca}_2\text{B}_8\text{C}_4$), 0.66 ($\text{Sr}_2\text{B}_8\text{C}_4$), 0.63 ($\text{Ba}_2\text{B}_8\text{C}_4$), 0.62 ($\text{La}_2\text{B}_8\text{C}_4$), and 0.56 ($\text{Ce}_2\text{B}_8\text{C}_4$), respectively. Based on the McMillan equation, the corresponding T_c values are 21 K, 17 K, 16 K, 13 K, and 10 K, respectively.

We ultimately explored the feasibility of experimentally synthesizing the $\text{Rb}_2\text{B}_8\text{C}_4$ superconductor. Several synthesis routes were designed, and the formation energy of $\text{Rb}_2\text{B}_8\text{C}_4$ under ambient pressure and the energy differences between

Rb₂B₈C₄ and its elemental phases (carbon, boron, and metallic Rb) were calculated using the PBE functional. The results are as follows:



The study confirms that for Rb₂B₈C₄, the enthalpy of formation for the elemental synthesis reaction $2\text{Rb} + 8\text{B} + 4\text{C} \rightarrow \text{Rb}_2\text{B}_8\text{C}_4$ is negative. Through calculation, the formation energy of Rb₂B₈C₄ is determined to be −0.224 eV per atom, thus demonstrating the viability of this prediction.

4 Conclusions

In summary, high-throughput structural searches are conducted to explore potential B–C clathrate superconductors under ambient pressure. Various X₂B₈C₄ B–C clathrates doped with metallic atoms, non-metallic atoms, and noble gas atoms are explored. Twenty-one distinct B–C clathrates with dynamical stabilities are uncovered at ambient pressure, among which six were confirmed to be potential superconductors. Our results reveal that the superconductivities of main-group and transition metal-doped B–C clathrates are modulated by two key factors: the magnitudes of charge transfers from the metal dopants to the B–C frameworks and the electronegativities of the guest metal atoms. The relatively high *T_c* of the Rb₂B₈C₄ (34 K) clathrate is attributed to the low electronegativity of the Rb atom and its large atomic radius, which induces structural compression of the B–C cages. This compression enhances EPC interactions and elevates the superconductivity of the Rb₂B₈C₄ clathrate. The simulated *T_c* values for other X₂B₈C₄ (X = Ca, Sr, Ba, La, and Ce) B–C clathrate superconductors are 21, 17, 16, 13, and 10 K, respectively. These findings expand the database of ambient-pressure superconductors and provide a feasible pathway for synthesis of high-quality B–C clathrate superconductors under mild conditions.

Conflicts of interest

There are no conflicts to declare.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6tc00100a>.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 12174352), the National Key Research and Development Program of China (Grant No. 2025YFA1411002), the Guangdong Basic and Applied Basic Research Foundation (Grant No. 2026A1515011030) and the Fundamental Research Funds for the Central Universities (Grant No. G1323525012).

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