Beyond MgB$_2$: high-temperature superconductivity in metallic covalently bonded C-B clathrates

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Abstract

The ambient-pressure dynamic stability of $XB_3C_3$ ($X = \text{Mg, Ca, Sr, Ba}$) compounds in the bipartite sodalite clathrate structure, one of which has been recently synthesized, is linked to the chemical pressure exerted by the metal cation, whose size can be tuned to stabilize the B-C framework. High-throughput density functional theory calculations on 105 analogous $Pm\bar{3}$ symmetry $XYB_6C_6$ binary-guest compounds find 22 that are dynamically stable at 1 atmosphere, expanding the number of potentially synthesizable phases by 19 (18 metals and 1 insulator). The density of states at the Fermi level and concomitant superconducting critical temperature, $T_c$, can be tuned by changing the average oxidation state of the metal atoms, with $T_c$ being highest for an average valence of $+1.5$. $K\text{PbB}_6C_6$, with an ambient-pressure Eliashberg $T_c$ of 88 K, is predicted to be the highest-$T_c$ compound. Density functional theory calculations suggest $K\text{PbB}_6C_6$ may be synthesized using high-pressure high-temperature techniques and quenched to ambient conditions.
Introduction

The advent of the high-pressure superconducting hydrides has renewed interest in conventional superconductors, demonstrating that their critical temperatures ($T_c$) may approach room temperature. The discovery of many of these compounds was theory driven, highlighting that first principles-based methods – consisting of crystal structure prediction (CSP) searches and electron-phonon coupling calculations – can identify promising superconducting materials for future syntheses. One of the structure types that has emerged to be conducive for superconductivity, initially pinpointed theoretically within binary hydrides of an electropositive metal, is the $XH_6$ superhydride in the $Im\bar{3}m$ structure. This structure type is based on a bcc packing of face-sharing $X@H_{24}$ truncated octahedra with six square and eight hexagonal faces, in which the hydrogenic lattice, isostructural with the sodalite-type clathrate, is stuffed with alkaline-earth or rare-earth metal atoms. Theory has identified many stable compounds possessing this motif – and recently a number of them have been synthesized under high pressure and their $T_c$s have been measured (e.g., CaH$_6$ [215 K at 172 GPa, 210 K at 160 GPa], YH$_6$ [220 K at 183 GPa, 224 K at 166 GPa], and (La/Y)H$_6$, with a transition ca. 237 K at 183 GPa tentatively attributed).

Achieving high-temperature superconductivity, even room-temperature superconductivity, is therefore no longer the ‘holy grail’. But, because none of the predicted or synthesized high-$T_c$ superhydrides are stable (or even metastably recoverable) at ambient pressure, the immediate challenge is to find light-element-based structural analogues or derivatives that could be metastable at 1 atm. One class of materials that are actively being considered can be constructed from the $XH_6$ superhydride lattices by replacing the framework hydrogen atoms by carbon and boron atoms (some examples are illustrated in Fig. 1). In these light-element hexahydride analogues the clathrate lattice is held together by strong covalent B-C bonds, which are metallized via electron transfer from an encapsulated metal atom with the appropriate valence. Vibrations of the covalently bonded metallic lattice induces electron-phonon coupling, resulting in superconductivity. Indeed, efficient electron-phonon coupling has been predicted for sp$^3$ carbon clathrate frameworks, which
represent a class of covalent metals similar to MgB$_2$.\cite{12,16}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Chemical pressure schemes of simple B-C clathrates in the bipartite sodalite $Pm\bar{3}n$ structure: (a) MgB$_3$C$_3$ (b) CaB$_3$C$_3$ (c) SrB$_3$C$_3$ and (d) BaB$_3$C$_3$ at ambient pressure. Chemical pressures are represented by atom-centered spherical harmonic functions in which the magnitude of the CP in a particular direction is represented by the size of the lobes and their color (white = positive and black = negative). The large negative pressures on the Mg atom demonstrate a poor fit inside the surrounding borocarbide cage, which improves (with a concomitant decrease in the negative CPs) as the size of the metal atoms increase from Ca to Sr to Ba. Metal atoms are denoted in purple, and B/C atoms emanate green/yellow stick bonds.}
\end{figure}

Pure carbon clathrates have yet to be synthesized, and geometric constraints place strict limitations on the atoms that could potentially be stuffed into their cages.\cite{17,20} However, calculations have suggested that such materials can be stabilized by substituting some of the carbon atoms with boron and inserting small cations into the borocarbide framework.\cite{21} Boron and carbon are the lightest elements that can form strong covalent bonds, and materials based on these elements are known to be good candidates for phonon mediated superconductivity at atmospheric condi-
tions (e.g., MgB$_2$, $T_c = 39$ K$^{22}$) boron doped diamond $T_c = 4$ K for a doping level of 2.5%,$^{23}$ B-doped Q-carbon with a $T_c$ as high as $55$ K$^{24}$. $Pm3n$ SrB$_3$C$_3$ (Fig. 1(c)) is the first member of the family of borocarbide analogues of the clathrate hexahydrides to be predicted computationally via CSP techniques.$^{25}$ This compound, in the bipartite sodalite (Type-VII clathrate) structure, was computed to be thermodynamically stable between 50-200 GPa$^{25}$ with a predicted $T_c$ of 43 K at 1 atm (assuming $\mu^* = 0.1$).$^{26}$ Subsequently, SrB$_3$C$_3$ was synthesized at 57 GPa and quenched to ambient conditions in an inert atmosphere, and evidence for the superconducting transition was recently observed.$^{25,26}$ Not long after, an isotypic lanthanum phase, LaB$_3$C$_3$, was synthesized at milder pressure and quenched to ambient conditions, where its HSE06 bandgap was computed to be 1.3 eV.$^{27}$

The synthesis of these two metal borocarbides inspired numerous theoretical investigations of related materials. The superconducting mechanism in the hole-conductor $Pm\bar{3}n$ SrB$_3$C$_3$ was shown to result from the strong coupling between the $sp^3$ $\sigma$-bonding bands and boron-associated $E_g$ modes with a $T_c$ of 40 K, as estimated via solution of the Eliashberg equations.$^{28}$ In fact, the $T_c$ calculated for all of the $Pm\bar{3}n$ XB$_3$C$_3$ alkaline earth analogues ($X = Ca$, Sr, Ba) ranged from 40-50 K.$^{26,28-30}$ $Pm\bar{3}n$ ScB$_3$C$_3$ was dynamically unstable, however following the imaginary eigenvectors resulted in a non-centrosymmetric $Ama2$ structure with a spontaneous polarization that was large compared with other well known ferroelectric materials.$^{31}$ In the silicon analogues, $Pm\bar{3}n$ RbB$_3$Si$_3$ was thermodynamically stable with respect to the elemental phases between 7-35 GPa, and it remained metastable at 1 atm with an estimated $T_c$ of 14 K.$^{32}$ CSP coupled with high-throughput calculations have uncovered analogous clathrate cages, but with inequivalent C:B ratios, identifying $I4/mmm$ CaB$_2$C$_4$ and SrB$_4$C$_2$ stoichiometry structures as superconductors with $T_c$s of 2 and 19 K, respectively, while SrB$_2$C$_4$ and BaB$_2$C$_4$ were predicted to possess superior mechanical properties with Vickers Hardnesses, $H_v$s, of 44 and 41 GPa, respectively.$^{33}$ though they were not on the convex hull.$^{34}$ We note that metal-doped clathrates with pure carbon frameworks are also predicted to exhibit high-$T_c$ superconductivity,$^{15,16,34}$ however non-B-doped carbon clathrates have not been produced to date. We also note theoretical studies of the superconducting
and mechanical properties of sodalite-like BN frameworks\cite{25,26} and carbon-based materials\cite{24} as well as metal hexaborides with a wide variety of measured properties including superconductivity.\cite{37}

In this article we employ the Density Functional Theory-Chemical Pressure (DFT-CP) method to explain why certain metals in the $Pm\bar{3}n$ $XB_3C_3$ structure type are dynamically stable at ambient pressures, whereas others are not. Moreover, we expand the metal atoms that can be stuffed within the clathrate framework to include the lanthanides. Turning to systems with two metal atoms on adjacent sites, we find 22 that are metastable at atmospheric pressures. Our theoretical study suggests that a wide range of possible elemental occupations and stoichiometries could be stabilized in this family of structures, potentially as solid solutions. The valence of the metal atom is shown to be a key factor in determining the superconducting critical temperature, $T_c$, which we predict could surpass the boiling point of liquid nitrogen at 1 atm, in particular for KPbB$_6$C$_6$. Finally, we illustrate that both configurational and vibrational entropy contributions, typically not considered in first principles calculations, are important in stabilizing these phases at pressure-temperature conditions accessible within diamond anvil cells.

**Computational Methods**

Geometry optimizations and electronic structure calculations including band structures, the densities of states (DOS), electron localization functions (ELFs), and Bader charges were performed by using density functional theory (DFT) as implemented in the Vienna \textit{ab-initio} Simulation Package (VASP) version 5.4.1,\cite{38,39} with the gradient-corrected exchange and correlation functional of Perdew-Burke-Ernzerhof (PBE),\cite{40} and the projector augmented wave (PAW) method.\cite{41} The plane-wave basis set energy cutoff was 600 eV for the compounds containing lanthanide atoms, and 900 eV otherwise. The $k$-point meshes were generated using the $\Gamma$-centered Monkhorst-Pack scheme and the number of divisions along each reciprocal lattice vector were selected so that the product of this number with the real lattice constant was 50 Å in geometry optimizations and 70 Å
otherwise. Phonon calculations were carried out on a $2 \times 2 \times 2$ supercell containing 112 atoms\textsuperscript{42,43} using the VASP package coupled to the PHONOPY code.\textsuperscript{44} The electron-phonon coupling (EPC) calculations were carried out using the Quantum Espresso (QE) program,\textsuperscript{45} with further computational details provided in Section S1. The $T_c$s were estimated using the Allen-Dynes modified McMillan equation\textsuperscript{46} along with numerical solution of the Eliashberg equations\textsuperscript{47} with a renormalized Coulomb potential, $\mu^* = 0.1$. A DFT-Chemical Pressure Analysis,\textsuperscript{48} which visualizes the internal stresses inherent in a crystal structure as a consequence of steric constraints, was performed on select phases using the CPpackage\textsuperscript{2}\textsuperscript{49} as described fully in Section S8.

**Results and Discussion**

To examine the electronic properties of the borocarbide clathrates containing one or two electropositive elements, over a wide range of hole doping concentrations, we carried out Density Functional Theory (DFT) calculations using the Vienna \textit{ab initio} Simulation Package (VASP)\textsuperscript{38,39} (see Section S1 for the full computational details). Among the studied structures with a single element occupying the metal site only (simple clathrates) $Pm\overline{3}n \ X B_3 C_3 \ (X = \text{Sr, Ba, Y, and La})$ phases were dynamically stable at ambient pressure, in-line with the syntheses of the Sr and La analogues.\textsuperscript{25,27} Previous theoretical studies found the Sr, Ba and La containing compounds were local minima at ambient pressure,\textsuperscript{28,29} and a mere 1 GPa was sufficient to stabilize CaB$_3$C$_3$\textsuperscript{29} The stability pattern of these single-metal (simple) phases illustrates the importance of a good size match between the borocarbide cage and the metal atom within. To further explore this relationship, DFT-Chemical Pressure (DFT-CP) schemes,\textsuperscript{48} which show the internal tensions in a crystalline lattice due to atomic size effects, were calculated for the alkaline earth metal borocarbide series. Recently, we have employed this method to elucidate the relationship between the metal atom size and the dynamic stability of related systems, $Pm\overline{3}n \ XB_3 Si_3 \ (X = \text{Na, K, Rb, Cs})$\textsuperscript{42} and $Im\overline{3}m \ X H_6$\textsuperscript{20} and for those hydrides that did not correspond to local minima DFT-CP was used to understand their structural distortions and find ways in which they could be stabilized.
In the CP-schemes, shown for $XB_3C_3$ in Fig. 1, negative pressures, which are indicative of an atom too small for its coordination environment, are represented with black, and positive pressures – in white – indicate an atom too large for the cavity within which it resides. For the alkaline earth borocarbides, the metal atom is in all cases surrounded by negative CP, suggesting that the borocarbide cages are plenty large enough – and in some cases, too large – to comfortably fit the electropositive atoms. This feature is most prominent within $\text{MgB}_3\text{C}_3$, which is dynamically unstable at ambient-pressure. The size of the CP lobe grows smaller as the size of the alkaline earth metal increases, hinting at a progressively better fit going down the group, in-line with predictions of dynamic stability at 1 GPa for $\text{CaB}_3\text{C}_3$ and at ambient-pressure for both $\text{SrB}_3\text{C}_3$ and $\text{BaB}_3\text{C}_3$. This mirrors our findings for the $XB_3\text{Si}_3$ family, whose ambient-pressure dynamic stability was limited to the larger alkali metals Rb and Cs. The negative pressures on the metal atoms are balanced against positive pressures between the boron and carbon atoms, as the bipartite sodalite framework is drawn tight around them. The magnitudes of the positive pressures along the B-C contacts grow smaller when encapsulating larger metal atoms, reducing cramping in the borocarbide cage. Unlike in the superhydride analogues, the CP distributions around the boron and carbon atoms comprising the clathrate cage differ somewhat. The significant degree of electron transfer leads to the formation of anionic carbon and cationic boron held together by polar covalent bonds, increasing the effective sizes of the carbon atoms and decreasing those of boron. The differing CP distributions around boron and carbon atoms manifest as well in their vibrational properties, as we will soon see.

Let us now turn to the borocarbides encapsulating two inequivalent metal atoms in adjacent cages (binary clathrates), with a focus on their stability patterns, electronic structure, and their propensity for superconductivity. Recently, Zhang and co-workers carried out cluster expansion calculations coupled with CSP to determine the lowest enthalpy geometries resulting from the reaction of $\text{SrB}_3\text{C}_3$ and $\text{RbB}_3\text{C}_3$ to form $\text{Rb}_x\text{Sr}_{1-x}\text{B}_3\text{C}_3$ with different metal ratios ($x = 0.125 - 0.5$), and considering different colorings. Relevant for our study, they found that a $Pm\overline{3}$ $\text{RbSrB}_6\text{C}_6$ compound, wherein the shortest metal-metal contacts were between Rb and Sr, possessed the most
negative enthalpies of formation (though for the CaYH\textsubscript{12} analogues, different colorings were preferred\cite{51,52}). Similarly, the most stable coloring for the Rb\textsubscript{0.4}Sr\textsubscript{0.6}B\textsubscript{3}C\textsubscript{3} stoichiometry corresponded to a homogeneous distribution of the two metal atoms.\cite{53}

With this in mind, we carried out high-throughput calculations on \textit{Pm\overline{3}} symmetry \textit{XY}B\textsubscript{6}C\textsubscript{6} borocarbides where the central metal atom in the structures shown in Fig. 1 was of one type, and those on the corners of another type. In total 105 compounds were relaxed at zero ambient pressure, and their dynamic stabilities were evaluated via phonon calculations. Of the considered phases, 22 different combinations including \textit{XY} = KCa, KSr, RbSr, CaBa, SrBa, KPb, SrPb, BaPb, CaY, SrY, BaY, SnY, PbY, KL\textsubscript{a}, RbLa, CsLa, CaLa, SrLa, BaLa, SnLa, PbLa, and YLa were found to be dynamically stable. In comparison, Zhang \textit{et al.} recently performed high-throughput calculations on 24 compounds in this structure type finding RbSr, KCa and KSr to be dynamically stable at ambient pressures,\cite{30} and Di Cataldo and co-workers considered all 12 combinations of an alkali metal and an alkaline-earth metal, concluding that RbSr, KCa and NaSr were dynamically stable at ambient pressure, whereas CsBa was dynamically stable above 10 GPa.\cite{29}

Therefore, in addition to the compounds identified as local minima by Zhang\cite{30} and Di Cataldo (excluding NaSr)\cite{29} and those that have been synthesized,\cite{25,27} we identified a number of hitherto unreported dynamically stable phases involving Sn, Pb, Y, La as well as combinations of two alkaline earth metals at ambient pressure, expanding the number of possibly synthesizable \textit{XY}B\textsubscript{6}C\textsubscript{6} phases by 19 (18 metals, and 1 insulator). The range of the B-C distances in the borocarbide cages, dictated by the ionic radii of the metal atoms within and their valence, turned out to be key for determining their dynamic stability. All of the structures that corresponded to local minima possessed B-C interatomic distances that fell between 1.68-1.81 Å, with the difference between them being smaller than 0.1 Å highlighting the importance of a good size-match for the metal ions with one another, as well as for the borocarbide cages encapsulating them.

The intercalant modifies the number of states that can participate in the superconducting mechanism and the B-C distances, which in turn influence the vibrational properties and the electron-phonon coupling (EPC). Previous theoretical studies have shown that the superconductivity in this
class of materials arises from motions associated with the clathrate framework, with the density of states (DOS) at the Fermi level, $E_F$, being a key descriptor for $T_c$. Assuming full electron transfer from the trivalent rare earths yields a formula of $X^{3+}[B_3C_3]^{3-}$, where the borocarbide cage is isoelectronic to diamond, resulting in an insulator. A maximal $T_c$ can be achieved by tuning the position of $E_F$ so it lies on one of the two peaks in the DOS plot below the gap in these electron-precise compounds (see Fig. 2). Pinning $E_F$ at the upper peak in the DOS, as in Sr$_{0.75}$La$_{0.25}$B$_3$C$_3$, yields a calculated $T_c$ of 59 K, while pinning it at the lower peak, as in Rb$_{0.4}$Sr$_{0.6}$B$_3$C$_3$, results in a $T_c$ of 83 K. The $T_c$s of ordered $XYB_6C_6$ alloys ($XY = \text{RbSr}, \text{KCa}$, and KSr, CsBa, NaSr), where $E_F$ lies close to the lower peak in the DOS, were predicted to fall between 72-82 K at or near ambient pressures.

As described above, borocarbide cages stuffed with electropositive elements whose average valence is less than +3 are hole-doped metals. The band structure of this class of compounds exhibits rigid band behavior where the nature of the intercalant has a minimal effect on the shape of the bands, but can be used to precisely tune the placement of $E_F$. Remarkably, the resulting $T_c$ can be nearly doubled, for example, by replacing half of the alkaline earth atoms in SrB$_3$C$_3$ with Rb. That the band structure is mostly invariant to the identity of the intercalant is illustrated nicely for four representative compounds containing two metal atoms of different valences in Fig. 2. In all of the borocarbides considered, the states near $E_F$ were almost entirely due to the carbon-2p and boron-2p levels, with the former having a slightly larger contribution than the latter because of the enhanced electronegativity of carbon. The valence bands, on the other hand, are mostly of boron-2p and metal character. Around 1.15 and 2.00 eV below the top of the valence band in electron precise YLaB$_6$C$_6$ (Fig. S1) lie two peaks that could be accessed by $\sim$0.75 and 1.55 hole doping, respectively. The combination of a trivalent and a divalent metal atom (e.g. Sr$^{2+}$ and La$^{3+}$ with an average oxidation state of +2.5) moves $E_F$ down by about 1 eV, so it lies slightly above the first peak in the DOS (Fig. 2(a)). While the most common oxidation states of lead are +2 and +4, our calculations consistently show that lead adopts the former valence in the binary clathrates. Thus, the average oxidation state on the metal atoms is +2 in SrPbB$_6$C$_6$ and in KLaB$_6$C$_6$, so in both
the $E_F$s lie near the same position, falling within the pseudogap between the upper and lower DOS peaks (Fig. 2b,c)). Finally, KPbB$_6$C$_6$, with an average metal oxidation state of $+1.5$, possesses the highest DOS at $E_F$, which is pinned close to the top of the lower peak. These maxima in the DOS result from the presence of two nearly parallel flat bands exclusively of boron and carbon character that are found along the $X - M - (\frac{1}{3})\Gamma$ high symmetry lines and are separated by an energy gap of 0.5-0.7 eV. By choosing an appropriate combination of metal elements $E_F$ can be tuned to coincide with one of these two bands, thereby increasing the number of states that can participate in the superconducting mechanism and resulting in a “flat-band / steep-band” scenario proposed to be key for superconductivity in MgB$_2$, and others compounds. The DOS at $E_F$ is about the same for $Pm\bar{3} XYB_6C_6$ with $XY = SrLa$, SrPb and KLa suggesting their predicted $T_c$s will fall close to that of SrB$_3$C$_3$, whereas for KPbB$_6$C$_6$ it is nearly double, tantalizing with the potential of a higher $T_c$.

How do the identities of the metal atoms, their valences and the resulting DOS at $E_F$ influence the superconducting properties of the binary clathrates? To answer this question we used the Quantum Espresso (QE) program to obtain the Eliashberg spectral function, $\alpha^2 F(\omega)$, electron phonon coupling (EPC) constant, $\lambda$, and the logarithmic average frequency, $\omega_{\log}$ (Table S3), of the ambient-pressure dynamically stable compounds. The $T_c$s were estimated using the McMillan Allen-Dynes-modified (MAD) equation, with a renormalized Coulomb repulsion parameter, $\mu^*$, of 0.1, as well as via numerical solution of the (isotropic) Eliashberg equations, since this provides a more accurate estimate for strongly coupled systems whose $\lambda \geq 1.5$. The Eliashberg results are summarized in map form in Figure 3 where dynamically unstable combinations are marked with a cross and dynamically stable phases are colored according to their $T_c$. The values we obtained for SrB$_3$C$_3$ (39 K) and BaB$_3$C$_3$ (45 K) are comparable to previous estimates (40-45 K and 43-50 K respectively). Generally speaking, the phases with the lowest $T_c$s contained one divalent and one trivalent or one monovalent and one trivalent metal atom ($T_c = 30-43$ K), while superconductivity was predicted to persist to somewhat higher temperatures in borocarbide cages filled with divalent metal atoms ($T_c = 39-54$ K), and combinations of a monovalent and a divalent
atom remained superconducting until near the boiling point of liquid nitrogen ($T_c = 74-88$ K), perfectly correlating with the values of the DOS at $E_F$ calculated for the various metal combinations (Fig. 2).

Delving into the trends more deeply, for SrB$_3$C$_3$ and BaB$_3$C$_3$ as well as most of the phases where the average oxidation state of the metal atoms was +2 ($XY = CaBa, SrBa, KLa, RbLa,$ and CsLa), $\lambda$ was found to lie between 0.90-1.12 and $\omega_{\log}$ was between 501-588 K resulting in $T_c$s ranging from 36-48 K. The only exception consisted of two phases containing a Group 14 element, BaPb and SrPb, whose EPCs were 1.28 and 1.40, respectively. Though their $\omega_{\log}$ was
smaller, 400 K and 417 K, they still possessed a slightly higher $T_c$ (49 K for SrPb and 54 K for BaPb). The binary-metal borocarbides containing a divalent and a trivalent metal atom with an average oxidation state of +2.5 have not been studied before, however they represented the largest number of dynamically stable phases (Ca, Sr, Ba, Sn, and Pb in combination with La or Y). Their EPC ranged from 0.76-1.18 with the SnY and PbY combinations having the strongest coupling. Though some of these compounds possessed the highest $\omega_{\log}$ of any of the borocarbides considered (CaLa, SrLa and BaLa with values of 625-653 K) this increase was overshadowed by the smaller $\lambda$ resulting in a $T_c$ that did not surpass the one calculated for BaB$_3$C$_3$. Once again, the $T_c$ was higher for the four phases that contained a Group 14 element (SnY, PbY, SnLa and PbLa). In-
line with their increased DOS at $E_F$ the EPC of the KCa, KSr and RbSr containing compounds, whose average metal oxidation state is +1.5, were among the largest ($\lambda = 1.58, 1.61, 1.79$). Their calculated Eliashberg $T_c$s (75, 74, 77 K) were similar to previous estimates of Zhang et. al.$^{30}$ and Di Cataldo and co-workers.$^{29}$ However, KPbB$_6$C$_6$ possessed the largest coupling of any of the systems studied so far, $\lambda = 2.67$, and concomitantly the highest $T_c$ of 88 K. Notably, the EPC in this phase was nearly the same as the value calculated for the first high pressure superhydride to be predicted, $Im\bar{3}m$ CaH$_6$, with $\lambda = 2.69$ at 150 K resulting in a predicted Eliashberg $T_c$ of 235 K.$^{6}$

To analyze the phonon modes that are key for superconductivity, we plotted the phonon band structures, phonon (projected) densities of states, Eliashberg spectral functions and EPC integrals, $\lambda(\omega)$, of all of the identified superconducting phases (Fig. S6-10). A subset of these are plotted in Fig. 4: SrB$_3$C$_3$ and BaB$_3$C$_3$ were the simplest compounds considered, containing a single metal atom; $XY = SrPb$ and BaPb possessed the highest $T_c$s for combinations of metals whose oxidation state averaged +2; KSr, KCa, RbSr and KPb (with an average oxidation of +1.5) were characterized by $T_c$s approaching the boiling point of liquid nitrogen, and SnY had the highest $T_c$ for a +2.5 metal atom combination. For all of the phases considered the phonon spectra can be separated into two regions: the lower frequency modes (typically below 200 cm$^{-1}$ to 300 cm$^{-1}$) are mostly associated with the heavier electronegative atoms while the higher frequency modes can be attributed to boron and carbon atoms. The plots of $\lambda(\omega)$ showed that the higher frequency modes typically contributed to between $\sim$75-90% of the total EPC (Table S3). One notable exception was the highest $T_c$ compound we found, KPbB$_6$C$_6$ where the contribution of the lower and higher frequency modes towards the overall EPC was about the same. This will be discussed in detail below.

In $Im\bar{3}m$ CaH$_6$ the EPC was derived primarily from the $T_{2g}$ and $E_g$ modes at the Zone center, which corresponded to the in-plane breathing and rocking vibrations of the H$_4$ square faces.$^6$ To determine which modes contributed to the EPC in the borocarbide analogues, red circles representing the size of the contribution to $\lambda$ at a particular wavevector $q$ and frequency $\nu$ were overlaid on the phonon band spectra (Fig. S6-10, Fig. 4). For both SrB$_3$C$_3$ and BaB$_3$C$_3$(Fig. 4(a-b)) a mode at $\Gamma$ in which the boron atoms in the B$_2$C$_2$ square faces undergo a scissoring or B-C-B bending
motion (601 and 534 cm\(^{-1}\), respectively) exhibited the largest \(\lambda_{q\nu}\) of any of the modes, while the analogous C-B-C bend (807 and 723 cm\(^{-1}\)) barely contributed to the EPC. For the isotypic, but dynamically unstable, MgB\(_3\)C\(_3\) and CaB\(_3\)C\(_3\) phases the scissoring mode of the carbon atoms comprising the square faces also possessed a higher frequency than the boron scissoring motion. The lower frequencies for the boron scissoring motions are reflected in the larger negative CP lobes on the B atoms in Figure 1, compared to the smaller or absent negative CP lobes on the C atoms, as negative CP features are often aligned with softer phonon modes.\(^{27}\) Wang and co-workers also identified these doubly degenerate \(E_g\) modes, which couple with the C 2p states, as being the main contributors to the total \(\lambda\) in SrB\(_3\)C\(_3\) and BaB\(_3\)C\(_3\).\(^{28}\) For most of the binary-metal borocarbides this mode also possessed a large coupling strength, though in some cases, most notably KPbB\(_6\)C\(_6\), its contribution was negligible (Fig. 4(h) and Table S8).

In SrB\(_3\)C\(_3\) Wang et al. also identified a softening, or local decrease in frequency along an acoustic branch between \(\Gamma\) and \(M\) as being important in the EPC mechanism. In this mode the amplitude of the motion of the light elements was larger than that of the metal atoms despite the mode’s low frequency.\(^{28}\) In BaB\(_3\)C\(_3\), however, this mode did not soften nor did it contribute to the EPC, in line with the results of Wang et al. In binary clathrates, the set of low-lying optical phonons whose dispersion mimicked that of the acoustic modes could be associated with motions attributed to the lighter metal atoms. This is exemplified in Figure 4\(a\) with the modes below 100 cm\(^{-1}\) corresponding to Pb-based and the modes between 100-180 cm\(^{-1}\) corresponding to Sr-based motions. Certain combinations of metal atoms led to two sets of softened modes along the \(\Gamma - M\) branch, one corresponding to each metal atom as in SrPb and KSr, while in others only one of these modes displayed a local softening (BaPb), and yet in others, such as RbSr, no local softening was observed in this portion of the phonon band structure.

In addition to these previously discussed atomic motions that are important for the \(T_c\), our calculations identified a number of modes that have not yet been scrutinized. For the simple clathrates this includes the low-frequency optical mode, which softens around the midpoint of the \(\Gamma - X\), \(X - M\), \(M - \Gamma\), \(\Gamma - R\) and \(R - X\) path and, for BaB\(_3\)C\(_3\), a mode that softens substantially at the
$R$-point where it is doubly degenerate. Curiously, at the $R$-point this vibration in BaB$_3$C$_3$ results in a Jahn-Teller like distortion of the near-perfect square faces into rectangular units with two short, and two long B-C distances (Fig. S11). For many (but not all) of the binary clathrates with average +2 oxidation states, as well as some with an average oxidation state of +1.5, this mode is found to be highly softened at $R$ and a strong contributor to the EPC. A softening of the acoustic mode along some portion of the $X - M - \Gamma$ path was present in the KSr, KCa and KPb combinations, but not in RbSr. Finally, each of these four compounds, which had the largest DOS at $E_F$ and concomitantly the highest EPC, displayed softened modes along $\Gamma - R - X$, on either side of the $R$-point, and multiple soft modes at $R$, which were key for their very superb $T_c$.

The largest $\lambda_{q\nu}$ in the highest $T_c$ compound we found, KPb$_6$C$_6$, was a softened mode at 95 cm$^{-1}$ just off the $R$-point along the $\Gamma - X$ path, which could be described as a libration/wagging of the two boron and two carbon atoms on opposite corners of the square faces leading to the formation of a rectangle. Such motions are very similar to the Jahn-Teller-like distortions described above. Above it, near 121 cm$^{-1}$ lay a mode with a slightly smaller $\lambda_{q\nu}$ whose main contributions could be attributed to similar libration and wagging motions in the B-C network, and along the $\Gamma - R$ path the light elements afforded the main contributions to a mode with intermediate $\lambda_{q\nu}$. These three modes – at $R$, along $\Gamma - R$, and $R - X$ – were all associated with coupled square-to-rectangle and square-to-tetrahedral motions of vertex-sharing four-membered faces on perpendicular planes. Thus, even though the low-frequency modes below 300 cm$^{-1}$ contributed to $\sim 48\%$ of the total $\lambda$, they could be primarily characterized by the motions of the boron and carbon atoms, mirroring the findings for SrB$_3$C$_3$.$^{25,28}$

Given that SrB$_3$C$_3$.$^{25}$ and LaB$_3$C$_3$.$^{27}$ have been synthesized under pressure we wondered if some of the X$Y$B$_6$C$_6$ phases discussed above could be made using similar techniques and quenched metastably to ambient conditions? At zero pressure and temperature, the formation of ordered binary-metal borocarbides (from the elemental phases) is largely endothermic with computed $\Delta H_f > 150$ meV/atom.$^{29,30}$ However, high pressures and temperatures could be used to access ex-ergonic reaction pathways, for example the change in the free energy for the reaction Rb + SrB$_6$ +
Figure 4: Phonon dispersion curves, projected phonon density of states (PHDOS), Eliashberg spectral function scaled by the frequency \( (2\alpha^2 F/\omega) \), and the EPC integral \( (\lambda(\omega)) \) for a) Sr\(_3\)C\(_3\), b) Ba\(_3\)C\(_3\), c) SrPbB\(_6\)C\(_6\), d) BaPbB\(_6\)C\(_6\), e) KSrB\(_6\)C\(_6\), f) KCaB\(_6\)C\(_6\), g) RbSrB\(_6\)C\(_6\), h) KPbB\(_6\)C\(_6\), and i) SnYB\(_6\)C\(_6\) at ambient pressure. The radius of the bubble on the phonon dispersion curve is proportional to the electron-phonon coupling constant \( (\lambda_{q\nu}) \) for the mode \( \nu \) at wavevector \( q \).

\[ 6C \rightarrow \text{RbSrB}_6\text{C}_6 \] is negative above 3500 K and 50 GPa. Actually, the enthalpic instability of the binary-metal borocarbides could be expected: statistical analysis of the AFLOW data repository has shown that three or four component systems are typically only stabilized due to entropic factors that favor the formation of disordered systems. One famous example is high entropy solid solutions, which are synthesized at high-temperatures but do not phase segregate when the temperature is decreased. Assuming a large KPbB\(_6\)C\(_6\) supercell where there is no site preference for the two metal atoms, and using the Boltzmann formula (simplified via Stirling’s approximation)
we estimate the configurational entropy as \( S/k_B = \ln \frac{N!}{(N/2)!((N/2)!)^2} = \ln(1/2) \).\(^{59}\) This provides an upper bound to the stabilization that can be attained by randomly distributing the two metal atoms within the borocarbide cage. In a real system with some site preference the configurational entropy would be decreased; nonetheless we can use this value to estimate the conditions at which the configurational entropy would overcome the enthalpic penalty for the formation of KPbB\(_6\)C\(_6\) from the elements. As shown in Fig. S14, we find this transition to occur at 4000 K and 50 GPa (3500 K and 60 GPa), suggesting that KPbB\(_6\)C\(_6\) could potentially be made from the elements using laser heating within a diamond anvil cell, though other synthesis routes, not considered here, might also be viable. Including the vibrational contributions to the free energy at 60 GPa within the harmonic approximation decreases the synthesis temperature further to 2000 K.

Since \( sp^3 \) hybridized compounds containing boron and carbon, often in combination with a metal atom, are known to possess superior mechanical properties we used our machine learning approach,\(^{60}\) recently applied to related systems,\(^{61,62}\) to obtain the bulk and shear moduli combined with Teter’s formula to estimate \( H_v \) of the dynamically stable phases. As shown in Table S2, \( H_v \) falls between 20-26 GPa, in-line with previous results for SrB\(_3\)C\(_3\) based on calculated elastic properties,\(^{25}\) and comparable to measured values for tungsten carbide.\(^{63}\) As expected, both the moduli and the Vickers hardness decrease with increasing metallicity.

**Conclusion**

In summary, via DFT-chemical pressure (DFT-CP) calculations, we have shown that the size of the electropositive metal atom within the bipartite sodalite borocarbide clathrate cages, \( Pm\bar{3}n \) \( XB_3C_3 \), is key for their stabilization and dynamic stability at ambient pressure. The CP exerted by the larger metals on the cage within which they are confined elongates the B-C distances thereby minimizing the positive CP within the B-C network. Moving to borocarbide cages containing two different metals with the \( Pm\bar{3} \) \( XYB_6C_6 \) structure, from the 105 combinations considered, 22 were found to be dynamically stable. From these, 19 are newly identified, 18 of which are new
superconductors. The enclathrated metal atoms donate electrons to the borocarbide lattice and their average valence can be used to tune the number of occupied states at the Fermi level, $E_F$, so it falls on a peak in the density of states (DOS), thereby increasing the ambient-pressure $T_c$ from 30 K in SrLaB$_6$C$_6$ to 88 K in KPbB$_6$C$_6$. Both the configurational and vibrational energy are shown to stabilize KPbB$_6$C$_6$, suggesting it could potentially be synthesized at high temperatures above 60 GPa. Modes that are associated with distortions of the square faces in the borocarbide cages are important for the superconducting mechanism via electron-phonon coupling. We note in passing that our exploratory calculations on borocarbide cages stuffed with a single lanthanide element (Fig. S12-13) have uncovered a number of ambient-pressure metastable phases, suggesting that many more binary or even ternary metal combinations – some whose $T_c$s rival that of KPbB$_6$C$_6$ – could potentially be made. The compounds predicted here, in addition to the large number of possible elemental occupations and stoichiometries not yet studied, provide a pathway towards warm superconductivity in covalent materials stabilized at ambient pressure.

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publication website. It includes the computational details, electronic band structures and densities of states, Bader charges, structural parameters, Eliashberg spectral functions, phonon dispersion curves, EPC calculations and details of the chemical pressure calculations.

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