First-principles prediction of phonon-mediated superconductivity in XBC (X=Mg, Ca, Sr, Ba)

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From first-principles calculations, we predict four new intercalated hexagonal XBC (X=Mg, Ca, Sr, Ba) compounds to be dynamically stable and phonon-mediated superconductors. These compounds form a LiBC like structure but are metallic. The calculated superconducting critical temperature, \( T_c \), of MgBC is 51 K. The strong attractive interaction between \( \sigma \)-bonding electrons and the \( \text{B} \text{1}_{g} \) phonon mode gives rise to a larger electron-phonon coupling constant (1.135) and hence high \( T_c \); notably, higher than that of MgB\(_2\). The other compounds have a low superconducting critical temperature (4-17 K) due to the interaction between \( \sigma \)-bonding electrons and low energy phonons (\( E_{2u} \) modes). Due to their energetic and dynamic stability, we envisage that these compounds can be synthesized experimentally.

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Hexagonal layered MgB\(_2\) is a well-known phonon-mediated superconductor with a \( T_c = 39 \) K [1]. In MgB\(_2\), the \( \sigma \)-band crosses the Fermi level and hybridization with other conduction electrons is weak. The high \( T_c \)-state of this material develops from the strong attractive interaction between the electrons of the \( \sigma \)-band and the \( E_{2u} \) mode of vibrations. Likely MgB\(_2\), materials intercalated with alkali (earth) metals show superconductivity with \( T_c \) much smaller than that of MgB\(_2\) [2–13]. Many studies have proposed possible ways to improve the transition temperature through carbon (or others) doping [14–16]. However, the \( T_c \) has not been found to improve significantly [14–19]. The \( T_c \) decreases on carbon substitution of B in MgB\(_2\) due to the introduction simultaneous disorder by carbon [16, 18, 20, 21]. Thus, it may be an alternative to examine the superconducting properties by synthesizing pure MgBC compounds.

From the first-principles investigations of LiBC with hole-doping, it was found to exhibit superconductivity below 100 K [22]. Unfortunately, experimentalists have not identified superconductivity in it due to induced structural distortions [23–27]. This is a similar effect to that of carbon doping in MgB\(_2\). Recently, LiB\(_{1+x}\)C\(_{1-x}\) materials have been predicted to be superconductors, like MgB\(_2\) [28]. Also on the basis of first-principles calculations, Gao et al. reported Li\(_b\)B\(_4\)C\(_2\) (also Li\(_2\)B\(_3\)C) to be MgB\(_2\) like superconductor with \( T_c \sim 53 \) K [27]. Since then, another phase, Li\(_b\)B\(_3\)C\(_3\), has been reported from ab initio studies to be a superconductor with a transition temperature of 16.8 K [29]. From the first-principles study of NaB\(_{1+x}\)C\(_{1-x}\), Miao et al. predicted that it would be more promising superconductor than LiB\(_{1-x}\)C\(_x\) [30]. Like LiBC, Ravindran et al. predicted that hole-doped MgB\(_2\)C\(_2\) is a potential superconducting material [31]. Since high-quality single crystals of LiBC have already been synthesized [16,17], it may be possible to synthesize XBC (X=Mg, Ca, Sr, Ba). In the present paper, we report, using the first-principles calculations, four new superconducting stoichiometric compounds (XBC (X=Mg, Ca, Sr, Ba)) that are dynamically stable and may be synthesized from constituent elemental solids. We find that strong electron-phonon interactions exist in all these materials. The MgBC structure has a predicted \( T_c (\sim 51 \) K) higher than that of MgB\(_2\); while SrBC and BaBC have a superconducting state below \( \sim 17 \) K (The CaBC structure has very small \( T_c (4 \) K)).

FIG. 1. The ground state crystal structure of XBC (X=Mg, Ca, Sr, Ba). The X, B, and C atoms are indicated by cyan, yellow, and red spheres, respectively.
FIG. 2. Electronic band structure of the four compounds: (a) MgBC, (b) CaBC, (c) SrBC, and (d) BaBC. The Fermi level is the zero of energy. The blue and red curves with symbols represent the energy bands that cross the Fermi level and form the Fermi surface. We have selected high-symmetry k-points in the Brillouin zone and the values of them in fractional coordinates are Γ(0,0,0), M (1/2,0,0), K (1/3,1/3,0), A (0,0,1/2), L (1/2,0,1/2), and H (1/3,1/3,1/2).

All calculations were performed using the plane wave pseudopotential approach and the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE-GGA) [32, 33] for the exchange correlation functional, as implemented in Quantum Espresso [34]. We use the ultrasoft pseudopotentials of Vanderbilt [35] and perform full structural relaxation. After optimizing the k-point mesh and cutoff energy, we selected a 12 × 12 × 4 k-point mesh for self-consistent field calculations, a 50 Ry cutoff energy for the wave functions, and a 400 Ry energy cutoff for the charge density. For the phonon calculations, we use a 662 grid of uniform q-points and the same k-point mesh as above [36]. We used a finer 18 × 18 × 6 k-point mesh for the calculation of the electron-phonon (e-ph) linewidth and e-ph coupling constants employing the optimized tetrahedron method in e-ph calculation [37]. We performed the phonon calculations using density functional perturbation theory (DFPT) of linear response [38]. For the electron-phonon coupling constant (EPC) calculations, we used the Migdal-Eliashberg formulism [39]. In this formulism, the Eliashberg spectral function is defined as [40, 41]

\[ \alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{qv} \delta(\omega - \omega_{qv}) \frac{\gamma_{qv}}{\hbar \omega_{qv}} \]

where \( N(E_F) \) is the density of states at the Fermi level.
FIG. 3. Calculated total density of states (DOS) of \( X_{BC} \) (\( X = \text{Mg, Ca, Sr, Ba} \)) within the energy range from \(-4\) to \(4\). The Fermi level is the zero of energy and indicated by the vertical dashed line.

and \( \gamma_{qv} \) is the electron-phonon linewidth for wave vectors \( q \) and \( v \). The EPC is determined by [40, 41]

\[
\gamma_{qv} = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega. \tag{2}
\]

Using the calculated EPC, the superconducting transition temperature is evaluated by the Allen-Dynes equation [40, 41]

\[
T_c = \frac{\omega_{ln}}{1.2} \exp \left[ \frac{(-1.04(1 + \lambda))}{\lambda(1 - 0.62\mu^* - \mu^*)} \right] \tag{3}
\]

where \( \mu^* \) stands for the Coulomb pseudopotential constant and its value ranges between 0.1 and 0.15 [42, 43]. \( \omega_{ln} \) stands for the logarithmic average frequency and is defined as [40, 41]

\[
\omega_{ln} = \exp \left[ \frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega) \right]. \tag{4}
\]

The crystal structure of \( X_{BC} \) (\( X = \text{Mg, Ca, Sr, Ba} \)) is similar to that of \( \text{MgB}_2 \). \( X \) atoms have no bonds with either \( B \) or \( C \). Boron and carbon are bonded together in a primitive fashion. Unlike \( \text{MgB}_2 \), the unit cell contains six equivalent atoms, two of each species. Figure 1 shows the hexagonal crystal structure of \( X_{BC} \) (\( X = \text{Mg, Ca, Sr, Ba} \)). Our theoretical value of the lattice parameters of \( \text{MgB}_2 \) is in a good agreement with the experimental value \((a = 3.086\,\text{Å} \text{ and } c/a = 1.42)\) [1], as listed in Table 1.

### Table I. Calculated fully relaxed lattice parameters of \( \text{MgB}_2 \) and \( X_{BC} \) of \((X = \text{Mg, Ca, Sr, Ba})

| Compounds | \( a(\text{Å}) \) | \( c/a \) |
|-----------|----------------|---------|
| \( \text{MgB}_2 \) | 3.081 | 1.145 |
| \( \text{MgBC} \) | 2.808 | 2.608 |
| \( \text{CaBC} \) | 2.951 | 2.745 |
| \( \text{SrBC} \) | 3.013 | 2.973 |
| \( \text{BaBC} \) | 3.084 | 3.190 |

The fully relaxed lattice constant along the \( a \)-axis is close to the value of \( \text{MgB}_2 \) while that along the \( c \)-axis of all compounds become around twice that of \( \text{MgB}_2 \) (see Table 1). We have found that all the studied compounds are energetically stable [44]. The electronic band structures of the four compounds are shown in figure 2. All the compounds possess metallic character. We see that two energy bands cross the Fermi level and form the Fermi surface for all materials. The symbols, \( \sigma \) and \( \pi \), indicate the type of bonding electrons belonging to the energy bands crossing the Fermi level. These bands are highly dispersive along all directions except \( L-H \). These bands are slightly flat along \( A-L \) above \( E_F \) and \( L-H \) below \( E_F \). The bands crossing the Fermi level are doubly degenerate along the \( \Gamma-A \) direction.

If we compare the band structure of \( \text{MgBC} \) and \( \text{CaBC} \), we see that the Fermi level in \( \text{CaBC} \) is shifted to higher energy than that of \( \text{MgBC} \). Therefore, this may lead to a reduction of \( T_c \) or eliminate the superconducting state of \( \text{CaBC} \). However, the shift in energy of \( \text{SrBC} \) and \( \text{BaBC} \) is small as compared to \( \text{CaBC} \).

Figure 3 shows the calculated total density of states of \( X_{BC} \) (\( X = \text{Mg, Ca, Sr, Ba} \)). The density of states at the Fermi level has increased significantly in all the studied compounds compared to \( \text{MgB}_2 \). In the case of \( \text{CaBC} \), the DOS at the Fermi level is similar to \( \text{MgBC} \) and notably lower than both of \( \text{SrBC} \) and \( \text{BaBC} \). As mentioned above, the DOS of \( \text{MgBC} \) at the Fermi level is much increased in comparison with that of \( \text{MgB}_2 \) for the electron injected by carbon [45]. Since the \( \sigma \)-band crosses the Fermi level, \( \sigma \)-bonding electrons can strongly attract certain modes of vibration, like the \( E_{2g} \) mode of \( \text{MgB}_2 \). Therefore, all compounds should be superconductors at a certain temperature. We will now investigate the electron-phonon coupling within Migdal-Eliashberg formulism.

The dynamical stability of a crystal is an important criterion in order to be able to synthesize it. Many researchers have reported the failure of synthesis of potentially promising materials due to dynamical instability [46]. The phonons determine the dynamical stability of a crystal; if any imaginary frequencies appears in the phonon band structure, the crystal structure is dynamically unstable. Recently, Kato \textit{et al.}
reported the possibility of MgB$_2$-like superconductivity in MgBY ($Y=$C, Be, Li) from electronic band structure analysis without considering the dynamical stability of these compounds [47]. They also predicted that MgBC might not be a two-band superconductor because the $\sigma$-band is completely filled. We note that the lattice constant of dynamically stable MgBC along the $c$-axis is twice as large as that of considered the one in their study [47], i.e., it has different atomic structure. The Fermi level in MgBC is raised to higher energy, even around the sigma anti-bonding states, compared to that of MgB$_2$. In this respect, MgBC is different in electronic structure to that of MgB$_2$.

Figure 4 shows the phonon dispersion relation and phonon density of states (DOS) of MgBC (upper panel) and CaBC (lower panel). We see that no imaginary frequency appears in the phonon band structure for both compounds. Therefore, hexagonal MgBC and CaBC are dynamically stable [48]. Low energy phonons mainly arise from Mg and Ca in MgBC, and CaBC respectively. Higher energy phonons arise from B and C in both compounds. In MgBC, the optical $\Gamma$-center modes are shifted to higher frequencies as compared to MgB$_2$. In contrast to MgB$_2$ (where the in-plane boron mode is $E_{2g}$), the B-C in-plane phonon at the
Γ-point is the $B_{1g}$ mode where electrons are strongly coupled, as indicated by the shaded area in figure 4. The shaded area corresponds to the highest peak region in the Eliashberg spectral function. The corresponding frequency of the $B_{1g}$ mode at the Γ-point is 495 cm$^{-1}$, which is much smaller than that of the value of 692 cm$^{-1}$ for MgB$_2$ [49].

For CaBC, low energy phonons of the $E_{2u}$ mode region arise from Ca atom and in this region, electrons are strongly coupled (maximum peak region in the Eliashberg spectral function). Higher energy phonons arising from B and C have very small contributions to electron-phonon interactions. Since the density of states (DOS) at the Fermi level of CaBC (see figure 3) is reduced as compared to MgBC, and the phonon frequency too (blue shaded region), σ-band electrons are not so strongly coupled with $E_{2u}$ modes of the phonons as like in MgB$_2$. Therefore, CaBC cannot be a MgB$_2$-like superconductor.

The phonon energy of the blue shaded area at Γ-point is more reduced in SrBC and BaBC compared to CaBC, as shown in figure 5. Like CaBC, SrBC, and BaBC have $E_{2u}$ modes region where electrons are strongly coupled. However, unlike CaBC, the density of states of SrBC and BaBC at the Fermi level are notably higher. Therefore, electrons should be more strongly coupled than those in CaBC. For hexagonal SrBC and BaBC, we do not obtain any imaginary frequencies. Therefore, both structures are energetically [44] and dynamically stable [48]. The phonon density of states of MgBC exhibits three distinct peaks; in contrast MgB$_2$ has only one peak [18]. The first peak arises from the Mg of $E_{1u}$ mode and the second and third peaks arise from B and C. The second peak shows that B has a dominant contribution. The Eliashberg spectral function of MgBC also shows three peaks, in comparison with just one peak of MgB$_2$. The main peak around 694 cm$^{-1}$ arises from the predominant interaction between σ-band electrons and the $B_{1g}$ phonon mode. These three peaks in the Eliashberg spectral function are shifted to lower energy phonons ($E_{2u}$) in the case of the other remaining three compounds. For CaBC, the highest peak height is almost half of the highest peak height for MgBC, SrBC, and BaBC. From the Eliashberg spectral function, we can calculate the electron-phonon coupling constant, logarithmic average phonon frequency and hence the superconducting transition temperature using the Allen-Dynes equation [41]. Our calculated superconducting parameters of the four compounds are listed in Table 2. In the table, we have used the value of the Coulomb pseudopotential to be 0.1.

For MgB$_2$, our calculated electron-phonon coupling constant ($\lambda$) is 0.844, in a good agreement with the available results [27, 49] but slightly smaller than that of the value reported in Ref. [50]. This value is slightly larger than that of the obtained value by using Wannier interpolation method [51–53]. We find that the logarithmic average phonon frequency ($\omega_{ln}$) is 708 K, in a good agreement with available data [27, 49, 54–58]. We obtain $T_c=37$ K by using $\mu^*=0.1$, slightly smaller than that of the experimental value (39 K). We see that the maximum superconducting transition temperature is obtained for MgBC and minimum for CaBC. The electron-phonon coupling constant (1.135) of MgBC is a 26% larger than

![Graph showing Eliashberg spectral function and superconducting transition temperature as a function of $\mu^*$](image)

**FIG. 6.** Calculated Eliashberg spectral function $\alpha^2F(\omega)$ of MgB$_2$ and MgBC (upper panel), and of CaBC, SrBC, BaBC (middle panel). The lower panel shows calculated superconducting transition temperature as a function of $\mu^*$.

**TABLE II.** Calculated superconducting parameters of fully relaxed structures XBC of ($X=$Mg, Ca, Sr, Ba). We have used the value of $\mu^*$ to be 0.1 in Eqn. (3).

| Compounds | $\omega_{ln}$(K) | $\lambda$ | $T_c$(K) |
|-----------|------------------|----------|---------|
| MgBC      | 610.05           | 1.135    | 51      |
| CaBC      | 723.09           | 0.377    | 4       |
| SrBC      | 382.27           | 0.693    | 13      |
| BaBC      | 231.13           | 1.034    | 17      |
that obtained for MgB$_2$ (0.87-0.88) [27, 49, 50]. Thus, if we use the value of $\mu^*$ to be 0, we obtain $T_c=72$ K for MgBC. Even if we use the value of 0.15 for $\mu^*$, we still obtain a superconducting transition temperature above 40 K. Therefore, MgBC is a phonon-mediated superconductor with larger electron-phonon coupling constant and higher transition temperature than MgB$_2$. The larger electron-phonon coupling constant of MgBC arises from the strong coupling of three peaks in the phonon density of states, mainly due to the interaction between $\sigma$-band electrons with the B$_{1g}$ phonon mode. The others three compounds have a lower superconducting transition temperature compared to MgB$_2$.

In summary, we have predicted four new superconductors using the first-principles calculations. Hexagonal XBC ($X$=Mg, Ca, Sr, Ba) compounds are found to be phonon-mediated superconductors. Among these compounds, the calculated $T_c$ of MgBC is 51 K. The strong coupling between $\sigma$-bonding electrons and the B$_{1g}$ phonon mode gives rise to a larger electron-phonon coupling and hence high $T_c$. Thus, MgBC is a superconductor with $T_c$ higher than that of MgB$_2$. The other compounds have a low superconducting transition temperature due to the interaction between $\sigma$-bonding electrons and low energy phonons ($E_{2u}$ modes).

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